Green Energy and Technology

Mohammad Jawaid
Salit Mohd Sapuan
Othman Y. Alothman *Editors*

Green Biocomposites

Manufacturing and Properties

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To
Dr. Mohammad Jawaid
lovely
daughter
"Ayesha Jawaid"

Preface

The terms **green composites, biocomposites, ecocomposites** all broadly refer to materials that fabricate or developed by using natural fibres with synthetic matrix, natural fibres in biopolymers, synthetic fibres with biopolymers, etc. Green biocomposites attracted academicians, researchers and industries to develop green and sustainable products due to environmental awareness and strict government regulations. Green composites are eco-friendly and economical materials that can serve as an alternative to synthetic fibre reinforced polymer composites or plastic materials available in markets for different applications. Currently, green biocomposites are already available in markets for various applications such as automotive, construction, and buildings components.

The present book will cover the manufacturing and characterization technique of green biocomposites which will help researchers, scientists, and industries to understand the need of green biocomposites for utilization in development of different biodegradable and eco-friendly products. This book deals about the following topics: expert material selection for manufacturing of green biocomposites; challenges, potential, and barrier for development of sustainable biocomposites; lignin as additive for manufacturing of biocomposites; recent progress on rubber-based biocomposites; manufacturing of natural fibre/agrowaste-based biocomposites; tribological characteristics of green biocomposites; wood and non-wood particle-based green composites; woven natural fibre fabric reinforced biodegradable composites; kenaf biocomposites; impact of fibrillization on mechanical and thermal properties of doum fibre reinforced polymer composites; oil palm empty fruit bunch fibres and biopolymer composites; rattan fibre/natural rubber biocomposites, and natural fibre/synthetic fibre reinforced polymer hybrid composites.

We are highly thankful to all authors who contributed book chapters and provided their valuable ideas and knowledge in this edited book. We attempt to gather all the scattered information of authors from diverse fields around the world

(Malaysia, Jordan, USA, Turkey, Italy, UK, Singapore, Oman, India, Morocco, Eritrea, Korea, and Pakistan) in the areas of green composites and biocomposites and finally complete this venture in a fruitful way. We greatly appreciate contributor's commitment for their support to compile our ideas in reality.

We are highly thankful to Springer UK team for their generous cooperation at every stage of the book production.

Serdang, Malaysia	Mohammad Jawaid
Serdang, Malaysia	Salit Mohd Sapuan
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Expert Material Selection for Manufacturing of Green Bio Composites

B.A. Ahmed Ali, Salit Mohd Sapuan, Mohammad Jawaid and M.L. Sanyang

Abstract The innovation in material science reveals more materials day by day and the material database grows exponentially. The conventional material selection systems fail to handle this large material database. The explosion all over the world is increasingly using the computing power to solve complex problems. Accordingly, it is applied in the field of engineering to obtain an optimum solution. The Expert System is a computer application that emulates the decision-making ability of a human expert for a specific task. This chapter presents a brief perception of implementing the expert systems for material selection of green bio composites. Due to the increasing ecological problem the synthetic materials are being reduced in the manufacturing industry and replaced by so called "bio composite" materials. The bio composites have different fibre orientations, matrices and constitutions would result in diverse characteristics in physical, mechanical, thermal and environmental properties. These dissimilar attributes of bio composites would increase the challenges for the material selection process. Hence, few case studies with automotive interior components are discussed for better understanding and to show the implementation of the expert system for the material selection of green bio composites. The result shows that these expert system has dramatically advanced the material selection to enforce green technology and sustainability in manufacturing and design.

Keywords Material selection · Expert system · Bio composites · Automotive · Manufacturing · Sustainability

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1 Bio Composite Materials

The earlier practice in the system of material selection is generally based on the experience of design engineers and the materials available readily for the common use. As the engineers hardly be prepared to take risks with new materials and systems. But, due to extensive research and development in the field of material science, many new materials are emerging. The term innovation plays a giant role in materials and gave birth to new reinforced composite materials with higher performance, weight reduction and at lower cost (Rao 2008). Carbon reinforced composite materials and synthetic hybrid composite materials plays a big role in the market. Later, the concern of environmental awareness and sustainability fabricated the biodegradable composites and natural fiber composites (Milanese et al. 2011). The 100 % renewable biopolymers are typically called as green bio composites.

Lucintel (2011) estimates the natural fiber composite market is expected to reach US$ 3.8 billion this year. Natural fiber composites penetrate almost in all the market segment and have significant potential in automotive, aerospace, marine, construction, wind energy and consumer goods. Recently, great revolution is taking place in the automotive industry, initially the metal components are replaced with plastics. Secondly the plastics are substituted with eco-friendly bio composite materials to protect the global environmental consciousness (Stewart 2010; Park and Dang 2011; Mohanty et al. 2005; Shen et al. 2010).

As, these non-eco-friendly synthetic polymers are hazardous and have aggressive effects on the human health. For better understanding, the polymers mainly used in the automobile parts and the environmental factors associated with the polymers are shown in Table 1. The hazard level and biodegradability are mapped with (1–7) scale.

Hence, green bio composite is a dire need for the globe to guarantees a better solution for the environmental awareness issues. The usage of bio composites in the automobile application would results in lower weight of components and thereby improves the fuel efficiency and also reduces emissions. At the end of cycle these bio composites results in added energy and carbon credits.

Many researchers complement their substantial work to improve the properties of the natural fibres, like kenaf (Sapuan et al. 2013; El-Shekeil et al. 2012; Aji et al. 2009), banana pseudo stem (Zainudin and Sapuan 2009), Sugar palm (Leman 2009;

Table 1 Environmental factors of plastic polymer materials used in automotive (Grassie and Scott 1988; Lithner et al. 2011; Stephane and Sylvie 2013)

No.	Material name	Abbreviation	Hazard level (lower-the-better)	Biodegradability (higher-the-better)
1	Polypropylene	PP	II	3
2	Poly-vinyl chloride	PVC	V	1
3	Polyethylene	PE	III	2
4	Acrylonitrile-butadiene styrene	ABS	V	1
5	Polystyrene	PS	III	2

Bachtiar 2008; Ishak et al. 2011), sugarcane bagasse (Wirawan et al. 2011). Moreover, the natural fibres are motivated by potential advantages of lower price in raw materials, lesser density and ecological advantages of using these green resources which are biodegradable and renewable (Milanese et al. 2011). Table 2 shows the database collection of natural fibre composite materials.

2 Expert System in Material Selection

The practise of using printed handbooks and datasheets in the manufacturing design process with a limited choice of materials are considered as outdated technology (Djassemi 2009; Sapuan 2001). Utilisation of Computer technology in the field of material selection has gained widespread attention in recent decades

Table 2 Database collection of natural fibre composite materials

No.	Natural fiber composites	Density (kg/m^3)	Tensile strength (MPa)	Young's modulus (GPa)
NF1	Kenaf 40 % + PP	1072.00	42.00	6.80
NF2	Hemp 40 % + PP	1076.00	52.00	6.50
NF3	Sisal 40 % + PP	1044.00	34.00	5.50
NF4	Jute 40 % + PP	1036.00	28.00	3.70
NF5	Banana stem 40 % + PLA	712.00	32.00	3.12
NF6	Coir 40 % + PP	1023.00	10.00	1.30
NF7	Pineapple 40 % + PS	1526.00	38.40	1.97
NF8	Bamboo 40 % + HDPE	940.00	21.21	2.75
NF9	Banana stem 40 % + PP	712.00	39.00	1.05
NF10	GreenGran NF30	1000.00	41.00	3.90
NF11	EFB 40 % + PP	875.00	18.00	0.90
NF13	Flax 36 % + Vinylester	1250.00	91.20	9.76
NF14	Kenaf 30 % + PP	1027.00	27.00	5.80
NF15	Banana stem 30 % + PLA	712.00	35.00	3.03
NF16	Flax 36 % + PE	1250.00	71.60	8.35
NF17	Kenaf 30 % + PLA	1550.00	130.50	14.40
NF18	Pineapple 30 % + PS	1526.00	52.90	2.29
NF19	Bamboo 30 % + HDP	940.00	25.47	2.67
NF20	Banana stem 30 % + PP	712.00	45.25	0.98
NF22	Flax 36 % + Epoxy	1250.00	88.30	10.89
NF23	GreenGran NF50	1080.00	55.00	6.90
NF24	EFB 30 % + polyurethane	1000.00	17.00	0.50
NF25	Kenaf 50 % + PP	1120.00	35.00	7.50

(Mumtaz et al. 2013). As the computer is mentioned for its fast processing, huge volume of data storage and result accuracy, this computational power was applied for the selection system.

The optimal selection of bio composites involves diversified choice of materials with various influencing criteria in the selection process, thus making the selection process more complicated. In order to safeguard from deciding inappropriate materials, the expert system software tools can help us in the appropriate materials selection. From literature, it comes to our understanding the application of expert or knowledge system can be applied particularly in the fields of training and decision making (Mockler et al. 2000)

The three main components of expert system is shown in Fig. 1.

- The Knowledge base: It contains real facts and heuristic rules (expert-level) for solving given domain problems. The knowledge engineers are responsible to introduce the rules to the domain expert system.
- The Inference engine: It serves as a middleware and provides a link between the knowledge base and the user interface. The inference engine chooses the applicable rules in order to reach the recommend solutions and organize procedure for knowledge base.
- The User interface: It allows the expert system user to input the parameters for problem consideration. The manipulation of the system was monitored by the user through this interface. The system output was displayed in user view by this interface screen.

The expert system uses a database management system (DBMS) as a centralized storage medium. DBMS is the software that authorizes to manage data efficiently, and the application program provides facility to access the stored data (Laudon and Laudon 2002).

3 Material Selection Software

The conventional method of materials selection is substituted with sophisticated software tools by fast changing technology. Many commercial software systems and decision making tools have been supporting the materials selection in the field

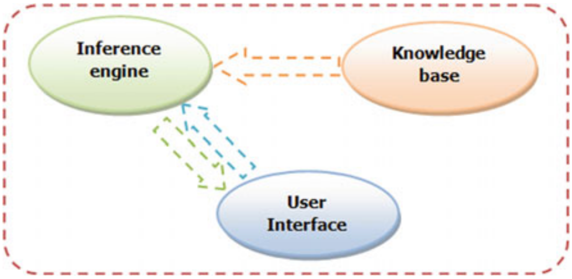

Fig. 1 Three main components of expert system

of manufacturing. Ashby (2005) enables the material selection with the best graph method initially for metals, later developed Cambridge Material Selector (CMS) software, the selector software widely in use for all the material family with the database. It is mostly like material screening software and not a material evaluation tool. Sapuan and Abdalla (1998) developed a system for material selection of pedal box system based on rule-based reasoning for polymer-based composites in particular for the usage of automotive components. The software package uses the Knowledge Engineering Environment (KEE) as a tool kit.

Analytical Hierarchy Process (AHP) is a commercial material selection software tool developed by Saaty and Vargas. The concept of AHP generally consists of three basic levels, namely decomposition, comparative judgement and the synthesis of priority (Saaty and Vargas 2012). The decision of optimal material is based on the pair wise comparison of the candidate materials by applying the rating scale. The judgments are based on the authors' experience, knowledge through journals and handbooks (Hambali et al. 2010). Table 3 shows the fundamental rating scale of Saaty.

Earlier research works concluded their judgement of optimum material selection with few numbers of alternate materials and apply the traditionally analytical calculations rather than computational software tools (Jahan et al. 2010). Some studies also show that existing expert material selection system selects the materials with the screening or ranking orders (Lan et al. 2011), which deals with human assumption. Furthermore, some existing research work used commercial software tools for material selection process and focused on synthetic fiber composites with few candidate materials (Hambali et al. 2010).

Table 3 The fundamental rating scale (Saaty and Vargas 2012)

Intensity of importance	Definition	Explanation
1	Equal importance	Two activities contribute equally to the objective
2	Weak	
3	Moderate importance	Experience and judgement slightly favour one activity over another
4	Moderate plus	
5	Strong importance	Experience and judgement strongly favour one activity over another
6	Strong plus	
7	Very strong or demonstrated importance	An activity is favoured very strongly over another; its dominance demonstrated in practice
8	Very, very strong	
9	Extreme importance	The evidence favouring one activity over another is of the highest possible order of affirmation
Reciprocals of above	If activity *i* has one of the above nonzero numbers assigned to it when compared with activity *j*, then *j* has the reciprocal value when compared with *i*	

4 Open Source Material Selection Software

Most of the material selection software available in the market are commercial software. With the expectation of developing an open source free software for material selection, this challenge was taken. The software programming language JAVA™ NetBean was used to develop the application of expert system for material selection. The Java was preferred as it is an open source software, platform independent and is having the ability to move easily from one platform to another. Java programming is well known as “write once and use anywhere, anytime” and works on a distributed environment. Java is the most widely used for web based application development and easy to deploy as hypertext transport protocol (http) for World Wide Web (www) usage.

The system was designed by identifying the components. The Java based expert system block diagram for material selection was shown Fig. 2.

In general, the expert system has four modules. For user-friendly access of the expert system different interface screens was designed. The modules are as below:

1. Knowledge-base of material
2. Selection of case study
3. Selection module
4. Process module

The interface screen model of the expert system is shown in Fig. 3.

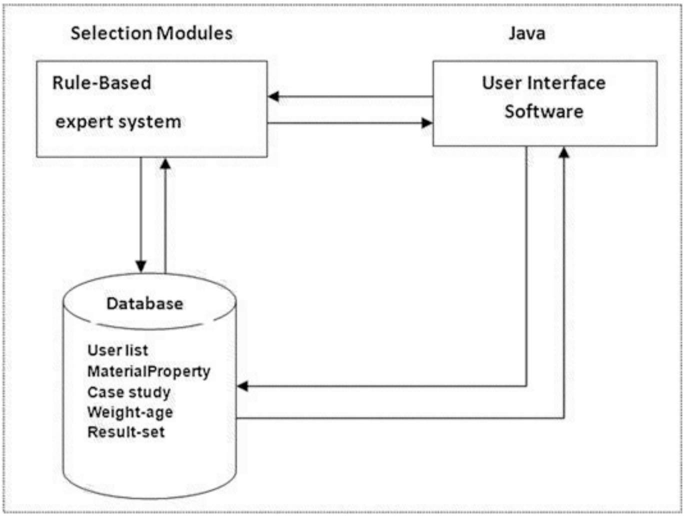

Fig. 2 The Java based expert system block diagram for material selection

5 Case Study with Automotive Components

The performance of the expert system can be illustrated by a case study for better understanding and to know about the feasibility of the material selection methods. Three different automotive interior components are selected as case study for this research purpose. The performance of the expert system was explained with these case studies. The selected components as case study are as follows:

1. Door panel
2. Dashboard
3. Rear panel

The expert system interface screens are designed with user friendly access. Initially, the database of the expert system to be updated with the record of candidate materials. The knowledge-base of natural fiber composites are gathered from previous research works and literature studies. Initially a record set of 70 candidate materials are uploaded in the database. New material can be easy added to the database through the "update" option available in the expert system.

The next interface screen shows case study selection module. The screen displays the provision to add the data to the case study. The user can select a particular automotive component as case study from the available list. The range of data can be entered and saved to the system by pressing the save button. Three case study can be added to the system; in future the system can be customised to accommodate more case studies.

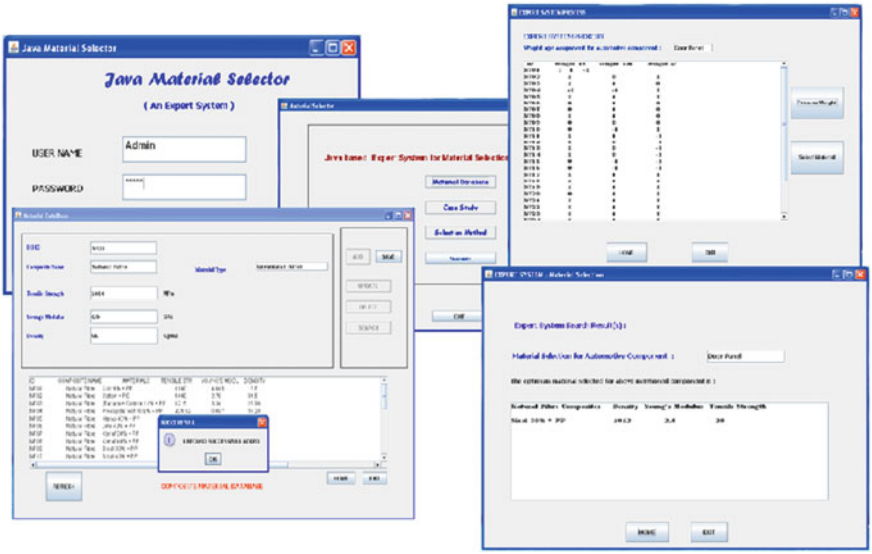

Fig. 3 The interface screen model of the expert system

The selection module consists of rule base search engine for the expert system. Initially three material properties i.e. density, tensile strength and young's modulus were taken into consideration. To frame the rule base logic, each material properties are assigned with weightage. The weightage assignment for material properties (attributes) are based on the product design specification (PDS) of each automotive interior component. The PDS range values were extracted from renowned automotive industry product data sheet of Borealis group (Borealis 2011) as stated in Table 4.

5.1 Weighted Range Method (WRM)

In the material selections, the technique of weighted range method was implemented to enhance the performance of the search engine. This proposed method is based on the assigned range value of weightage from product design specification of the candidate materials. The weightage range value are described by the following steps:

(i) For easy computing, the attributes of candidate materials are represented by the set of decision matrix.

$$\begin{aligned} \mathrm{A}_{ij} \text{ where } i &= 1, 2, 3 \ldots m \\ j &= 1, 2, 3 \ldots n \end{aligned}$$

(ii) The criteria and alternatives for the decision matrix are determined. Let C be the set of criteria denoted as C_j where j = 1, 2, 3 … n. The candidate materials of natural fibre composites are the alternatives. Let A be the set of alternatives denoted as X_i where i = 1, 2, 3 … m.
Then the representation of normal decision matrix as in Table 5.

(iii) To determine the weighting factor (α) the rule is formulated for each candidate material (X) with respect to the PDS value. Then each material property (C) was defined as:

- For each candidate material selected (X_j) say the property of material (C_i) falls within the limit of PDS range then the value of weight zero (0) was assigned to Aij

Table 4 PDS for automotive door panel

Material properties	Composite value range
Tensile strength (MPa)	22–28
Young's modulus (GPa)	1.7–3.0
Density (kg/m^3)	980–1050

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Table 5 Decision matrix

Alternatives (X_i)	Criteria (C_j)			
	C_1	C_2	⋯	C_n
X_1	A_{11}	A_{12}	⋯	A_{1n}
X_2	A_{21}	A_{22}	⋯	A_{2n}
⋮	⋮	⋮	⋮	⋮
X_m	A_{m1}	A_{m2}	⋯	A_{mn}

$$\alpha(Aij) = 0,\ i = 1, 2, 3\ldots n,\ j = 1, 2, 3$$

- For each candidate material selected (X_j) say the property of material (C_i) is above the limit of PDS range then the value of weight positive one (1) was assigned to A*ij*

$$\alpha(Aij) = 1,\ i = 1, 2, 3\ldots n,\ j = 1, 2, 3$$

- For each candidate material selected (X_j) say the property of material (C_i) falls below the limit of PDS range then the value of weight negative one (−1) was assigned to A*ij*

$$\alpha(Aij) = -1,\ i = 1, 2, 3\ldots n,\ j = 1, 2, 3$$

The relationally represented of the above rule can be written as:

$$\begin{aligned}
&weight\_TS_i = TS_{\min} \le X_{i1} \le TS_{\max} = 0;\ \ X_{i1} \ge TS_{\max} = 1\ ;\ X_{i1} \le TS_{\min} = -1\\
&weight\_YM_i = YM_{\min} \le X_{i2} \le YM_{\max} = 0;\ \ X_{i2} \ge YM_{\max} = 1\ ;\ X_{i2} \le YM_{\min} = -1\\
&weight\_D_i = D_{\min} \le X_{i3} \le D_{\max} = 0;\ \ X_{i3} \ge D_{\max} = 1\ ;\ X_{i3} \le D_{\min} = -1\\
&where\ \ i = 1, 2, 3\ldots n\quad and\quad TS = \text{Tensile strength},\\
&YM = \text{Young's modulus},\ D = \text{Density}
\end{aligned}$$

From Table 4 the PDS range value for the automotive interior component i.e. door panel can be substituted as:

$$\begin{aligned}
&D_{\min} = 980 \text{ and } D_{\max} = 1050\\
&TS_{\min} = 22 \text{ and } TS_{\max} = 28\\
&YM_{\min} = 1.7 \text{ and } YM_{\max} = 3.0
\end{aligned}$$

The alternative representation of applying the expert rule for the candidate material in the material selection process can also be stated as:

```
FOR(M = 0; M <= number of rows; M++)
IF minimum Tensile strength 22 (MPa)
```

AND minimum Young's modulus 1.7 (GPa)
AND maximum Density 1050 (kg/m^3*)*
THEN select optimum bio composite material.

The result array after the assignment of WRM weightage to each attribute of candidate material can be segregated into three set of results. Based on the preferred criteria the result can be processed. The final result can be defined as three precisions according to the above case:

1. Result with high degree of fulfilment, best weightage of all alternative materials from all three criteria with exact match. i.e. selects zero weightage for all three materials is defined as High_ precision selection
2. Result with medium degree of fulfilment, weightage of all alternative materials from any two sets of criteria match. i.e. selects any two zero weightage from all three materials is defined as Medium_precision selection
3. Result with low degree of fulfilment, from weightage of all alternative materials selects any one of criteria match. i.e. selects one zero weightage from all three materials is defined as Low_precision selection

The representation of above precision sorting with syntax approach can be written as:

```
LOOP ( index initialization ;  index  < = weightage_array.length() ; index ++)
{
    IF (( weight_TS == 0 && weight_YM ==0 && weight_D==0))
        THEN  high_ precision[i]=index;
    ELSE IF (( weight_TS == 0 && weight_YM==0) || (weight_YM == 0 && weight_D==0) ||
             (weight_TS == 0 && weight_D==0))
        THEN medium_ precision [i] = index;
    ELSE IF (weight_TS == 0 || weight_YM==0 || weight_D==0)
        THEN low_ precision [i] = index;
}
```

After executing the above WRM approach, the Java based expert system selects the optimal material from the set of bio composite alternative materials for the case study of automotive interior door panel. The result set of bio composite materials that satisfies medium precision criteria can be calculated and shown in Table 6.

Table 6 Material selection based on medium precision

ID	Natural fibre composite	Weight_TS	Weight_YM	Weight_D
NF18	Jute 40 % + PP	0	1	0
NF19	Kenaf 30 % + PP	0	1	0
NF28	Vetiver grass 20 % + PP	0	−1	0

To further narrow down the selection, the high precision can be applied. The high precision will give the exact selection result from available bio composite materials. The result set of materials that satisfies high precision criteria selection based on the proposed Java based WRM material selection expert system to determining the optimum bio composites for automotive interior door panel was Sisal 30 % + PP with density of 1012 kg/m^3 (physical property) and the Young's modulus 2.8 GPa and tensile strength 28 MPa (mechanical property). Thus, the above selected biodegradability high precision natural fiber composite material with high sustainability can be recommended to the automotive manufacturer to enforce green technology.

6 Conclusions

The developed version of expert system serves diversified material selection. Initially focused for few bio composite material selections as implementation with three properties. As the database of bio composite grows the new materials can be easily updated to the expert system and can be customised for addition properties of like impact strength etc., Moreover, in future the system has the potential to be modify with other selection alternatives for entire material family. By implementing two tiers of search engine, the time required for material selection is also shortened. The proposed logic with WRM method is easy and offers multiple result criteria. The high, medium and low precision selection offers multiple choice of selection. Among high cost commercial material selection software, the proposed expert system stands as free software with GNU licence. As the Java software is platform independent and easy to be deployed in web server application and access through World Wide Web (www) this expert material selection system can be one stop application for material selection.

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Sustainable Biocomposites: Challenges, Potential and Barriers for Development

Faris M. AL-Oqla and Mohammad A. Omari

Abstract Since natural fibers have many advantages, modern societies start switching for new green materials including natural fibers to contribute meeting the demand of weight reduction, environmental issues as well as customer satisfaction attributes. However, fully replacement of green bio-composites has many challenges. Inadequate availability of data regarding the performance of bio-composites due to the large variety of their constituents is the most challenging barrier in this field. A gap in the way of assessing bio-composites relative to comprehensive desired criteria for various industrial applications have been revealed. Therefore, processing consideration and proper selection of the composite constituents and their characteristics should be extensively investigated in order to achieve good part design with bio-composites. Moreover, high coefficients of safety factors are still required in such green products. Inconsistency of natural fibers properties as a major drawback as well as others that limit their applications in bio-composites are comprehensively discussed here.

Keywords Bio-composites · Composites drawbacks · Bio-composites limitations · Green products

1 Introduction

Recently, green composites became one of the most significant research themes worldwide. Its significance revealed due to several reasons such as: the high performance in mechanical properties, many processing advantages, low cost and light weight, availability and renewable, cheap, environmentally friendly, recyclability and degradability features (AL-Oqla et al. 2014a; Faruk et al. 2012a). Enhancing the natural fiber polymers will form a new class of materials that have a good

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potential in future as a substitute for rare wood based materials in many structural applications (Sapuan et al. 2013; AL-Oqla and Sapuan 2014b; AL-Oqla et al. 2015c). Different cells of hard plant fibers are bonded together by natural substance called lignin, acting as cementing materials. The composites- mainly consist of cellulose fibrils embedded in lignin matrix- exhibits high electrical resistance. Combining this composite into low modulus polymer matrix, will produce materials with better properties appropriate for various applications (AL-Oqla et al. 2016; Bendahou et al. 2008; AL-Oqla and Sapuan 2014c; Dittenber and GangaRao 2011). Moreover, electrical properties for the natural fibers polymers such as volume resistivity, dielectric strength are hot areas of research since the significance of these properties in use (Bora et al. 1993; George et al. 2013; AL-Oqla et al. 2015c).

1.1 Green Bio-Composites

Keywords such as “biodegradable”, “biocomposite”, “sustainable”, “biocompatible”, “green”, “bio-based”, “renewable”, “environmentally friendly”, “eco-friendly”, and “biopolymers” are common sight in the packaging-related literature. This explicitly demonstrated the growing awareness and concern of people regarding environmental issues driven by non-biodegradable and non-renewable plastics as well as the rapid depleting fossil fuel reserves. Generally, the term bio-composites covers composite materials made from the combination of;

1. natural fiber reinforced petroleum derived polymers which are non-biodegradable,
2. biopolymers reinforced by natural fibers, or
3. biopolymers reinforced synthetic fibers (i.e. glass, carbon etc.)

Bio-composite materials on the other hand, defined as: composite materials in which at least one of the constituents is derived from natural resources (AL-Oqla et al. 2014b). This includes composite materials made from the combination of: natural fiber reinforced petroleum derived polymers which are non-biodegradable, and biopolymers reinforced synthetic fibers such as glass and carbon, these two categories are not fully environmentally friendly (Mohanty et al. 2002). The third category which is, biopolymers reinforced by natural fibers which commonly termed as “green bio-composites” are more environmentally friendly (John and Thomas 2008). The term biodegradable bio-composites are those in which the polymeric matrix is biodegradable. It includes two different families: bio-based and petroleum-based. Biodegradable polymers are different than biopolymers in raw material. Biodegradable polymers can be created from bio-based or petroleum-based and can be classified as green polymeric matrices. In addition, bio-based bio-composites or sometimes called fully biodegradable green composite are terms used when both the fiber and matrix are from renewable resources. These bio-composites have less environmental impact.

1.2 Driving Factors for Bio-Composites

With the growth of environmentally conscious society, materials producers start concentrate on products which are "environmentally friendly". Such products (environmentally friendly and sustainability) can only be realized by considering the entire life cycle of the product; from the raw material extraction to the disposal, those materials generally poses no harmful impacts on the environment during their life cycle. Moreover, modern industries have been challenged with continuous pressure from the government, consumers and media; fascinating the industry to develop more sustainable products. The plastic industry usually responds to these new stringent environmental protection laws and has launch innovating sustainable packaging as bioplastics products. It was reported that the bioplastic market was estimated to reach a value of $3.94 billion soon (Ibrahim et al. 2014). The growing growth in the commercialization of biodegradable starch-based packaging materials is mainly affected by several factors. Some of those factors are (1) greater environmental awareness, (2) petrochemical resources shrinkage (3) government laws and company policies, and (4) suitable technology.

2 Bio-Composites in Macroscale

In these materials, natural fibers (such as sisal, hemp, kenaf, coir, jute, flax, date palm etc.) are used as reinforcing material (fillers) for polymer-based matrices. In light of the governmental emphasis on the new environmental regulations as well as sustainability concepts, ecological, social, and economical awareness, (Kalia 2011b; Faruk et al. 2012b); the optimal utilization of natural resources was highlighted. Utilizing natural fibers in particular, would decrease waste disposal problems, and reduce environmental pollution. Natural fiber composites (NFCs) as environmentally attractive materials have been proven and emerged as an alternative to the glass-reinforced or carbon reinforced polymer composites. The properties and performance of engineering products made from NFCs depend upon the properties of their individual components as well as their compatibility and interfacial (polymer/filler) features. Natural fibers have been utilized in such composites in various sizes ranged from micrometer to several centimeters. Various bio-fiber characteristics are illustrated in Table 1 (Khalid Rehman Hakeem et al. 2014).

Many examines have addressed the capabilities of bio-fibers as reinforced fillers in polymeric matrices. Most of the studies have focused on the mechanical properties, modifications to improve compatibility, manufacturing processes as well as other technical issues. The studded aspects of such composites included fibers treatments, crystallinity, fiber modification, weathering resistance, durability, and thermal stability (Alves et al. 2010; Mir et al. 2010; Sarikanat 2010). In addition, a gap in the way of assessing NFCs relative to comprehensive desired criteria for

Table 1 Physical characteristics of bio-fibers

Agricultural biomass	Fibre length (mm)	Fibre diameter (mm)	Thickness of single cell wall (microm)	Width of lumen (microm)
Oil palm	0.6–1.4	8.0–25.0	–	6.9–9.8
Coconut coir	0.3–1.0	12.0–14.0	0.06–8.0	–
Banana	0.1–4.2	12.0–30.0	1.2–1.5	13.4–22.4
Pineapple leaves	3.0–9.0	5.9–80.0	1.8–8.3	2.4–3
Jute	0.8–6.0	5.0–30.0	5.2–11.3	3.4–7.6
Sisal	0.8–8.0	7.0–47.0	8.0–25.0	8.0–12.0
Flax	10.0–65.0	5.0–38.0	10.0–20.0	–
Cotton	15.0–56.0	10.0–45.0	3.6–3.8	15.7–16.4
Ramie	30.0–60.4	7.0–80.0	2.8–3	12.8–13.0
Kenaf (bast)	1.4–11.0	4.0–36.0	1.6–12.6	5.4–11.1
Kenaf (core)	0.4–1.1	0.27–37.0	0.5–11.5	14.8–22.7
Bagasse	0.7–2.8	10.0–40.0	1.4–9.4	1.0–19.1
Bamboo	2.0–3.0	14.0–17.8	3.0–9.0	3.8–8.6
Rice	0.4–1.2	8.0–15.5	2.0–5.6	1.1–8.7
Corn	0.4–1.4	12.1–26.7	2.4–6.5	2.4–20.1

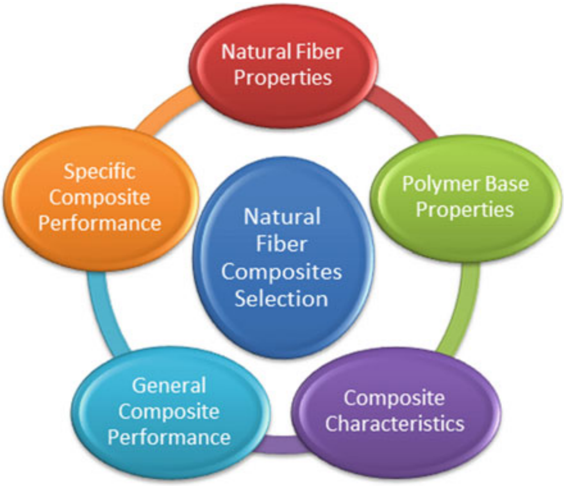


Fig. 1 Levels of factors affect green composites

various industrial applications have been developed (AL-Oqla and Sapuan 2014c). In such assessment framework, criteria that affect the NFCs and their products were categorized and classified into levels, where principal criteria were suggested, collected and arranged according to each level. Moreover, several comparisons between bio-fibers were successfully conducted to demonstrate their own beneficial characteristics. Figure. 1 demonstrates the proposed levels (AL-Oqla and Sapuan 2014c),

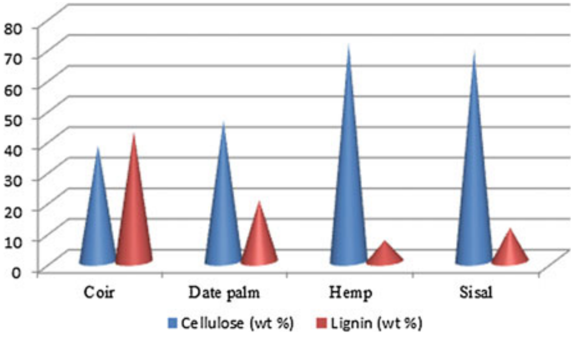


Fig. 2 Comparison regarding cellulose and lignin contents of bio-fibers

whereas Fig. 2 illustrates one of such comparisons regarding cellulose and lignin contents of some bio-fibers (AL-Oqla and Sapuan 2014c).

3 Nanocomposites

Nanocomposites are mainly innovative materials in which at least one filler length is in the nano-meter scale. In regard to the filler geometry, nanocomposites can be sorted into three principal categories 1—Fumed silica dioxide and nano metallic powder are identified by having: length, width and thickness, all in the nano-scale. 2—Carbon nanotube got two dimensions in the nano-meter. 3—Expanded layered graphite platelets and clay have only single dimension in the nano-meter range (Cheng et al. 2010). Physical and thermal properties of composites reinforced with nanoparticles filler are superior to those filled with micron-sized particle of the same filler (Alamri and Low 2012). Moreover, some exclusive properties, which traditional micro-particles cannot attain, make nanocomposites be prominent and draw attention. Greater stiffness, strength and glass transition temperature are resulted from the considerable surface area developed when nano-particles are randomly distributed in the matrix (Benhamou et al. 2014). Carbon nanotubes, though, still cannot be formed in mass production context due to the complex manufacturing process. Thus, work is intended to bridge the gap in price and property by offering substitute nano materials like nano clay and exfoliated graphite platelets reinforced composites. These materials are plentiful in nature and have excellent mechanical and physical properties. Nanocomposites become attractive due to the tremendous interaction between nano-metric particles and the polymeric matrix within the structure, for example, an interphase of 1 nm thickness occupies about 30 % of the entire volume in case of nanocomposites where as it gets to 0.3 % of the total volume of polymer in case of micro-filled composites. The great surface area (interfaces) within the nanocomposites promotes adhesion energy, increasing molecular bonding, and this increase in chemical bonding enhances the polymer crosslinking resulting in improvements in mechanical properties (Ye et al. 2007).

3.1 Nanofibers from Natural Fibers

Nanofibers are fibers that have diameter equal to or less than 100 nm. One chief characteristic of nanofibers is the massive availability of surface area per unit mass. The high surface area of nanofibers offers a remarkable capacity for the attachment or release of absorbed molecules, functional groups, catalytic moieties, ions and nanometer scale particles of many kinds. On the contrary, a small participation made by the interphase provides diverse potential of performance tailoring and is capable of influence the properties of the matrices to a much higher extent under rather low particle content (Ye et al. 2007).

3.2 Nanoclay

Due to the tiny size and depth of the platelets, only one gram of clay layer includes over a million units of platelet (Majeed et al. 2013). There is a considerable progress in mechanical and physical properties of clay reinforced composites at a very low silicate loading (4 wt%). The field of polymer/ nanoclay composites has gained attention due to the fact that it is feasible to melt-mix resin with silica layers, and no need to use organic solvents. Polymer- silicate nanocomposites could have three types of morphological structures (Alexandre and Dubois 2000). A phase divided composite is obtained when matrix is incapable of intercalate between the silicate layers as shown in Fig. 3a. In intercalated formation, more than one matrix

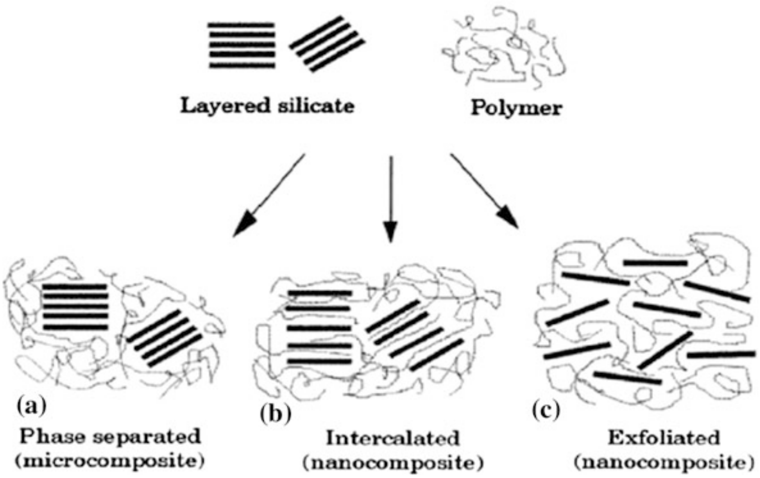


Fig. 3 SEM images of **a** intercalated, **b** expanded, and **c** sonicated (exfoliated) silicate nanocomposites (Alexandre and Dubois 2000)

molecules are intercalated between clay layers as shown in Fig. 3b but the layers remain parallel. In fully exfoliated structures, the silica platelets are no longer close to each other and the nano-metric layers are fully distributed in the matrix Fig. 3c.

Natural graphite is a black carbon stone, hardest material exists in nature. Its elastic stiffness is about 1000 MPa. The basic element of graphite is the graphene, in which a huge number of benzene rings are reduced to form a firm planar layer. The interlayer spacing is around 3.35 Angstrom and the force between the layers is Van der Waals type (Matsumoto et al. 2012).

3.3 Polymeric Based Nanocomposites/Applications

Polymeric based composites have been employed particularly in blast/ impact loading. Applications involve marine structures; mostly, lightweight glass/carbon polymeric-based composites, and modern concepts for the mitigation of blast/shock/impact effects (Cheng et al. 2010). Sandwich composites utilizing balsa wood and foam cores are currently being attributed in several navy applications such as in surface ship deck structures, and radar pole. Numerous new and promising cores have been explored in sandwich structures. Different types of cores have been used including Tycor; is an engineered three-dimensional fiber reinforced damage soft core for sandwich structures and has the potential to improve ballistic impact resistance.

Mechanical properties of polymer-based nanocomposites have been widely investigated where improved properties such as stiffness, strength, impact-toughness, gas permeability, vibration damping, and flame retardancy have been all reported. Key factors like filler loading, degree of filler dispersion (exfoliation), and type of interfacial linking can strongly modify the properties of bulk polymers (Hassan et al. 2011). To prepare a nanocomposite, small filler content is normally preferred due to their infinitesimal volume and huge interfacial area produced. Polymer-filled nanocomposites can be manufactured through melt processing or in situ polymerization. For the melt processing, pre-melt polymer is used for making the nanocomposite, whereas in the in situ polymerization the nanoparticles are diffused in monomers and then polymerization process of monomers continues to nanocomposite creation.

Ideal dispersion of filler inside the matrix is aimed to improve the bulk-material mechanical properties, while clustering can have improvements in electrical properties and decline in mechanical performance on the other side (Hassan et al. 2011). Synthesizing a totally agglomerated-free nanocomposite is hard, filler/ matrix interaction taking place at the interface needs to be controlled. Numerous studies have shown impressive advance in stiffness of nanocomposites with addition of nano-particles (Kalia et al. 2011). Again, total dispersion (exfoliation) and optimal filler orientation are difficult to reach. For example, the polymer chain ideally expands in between nanoparticles, increasing the inter-particle spacing which causes spatial adequacy toward complete exfoliation.

4 Barriers for the Development of Green Bio-Composites

Inconsistency of natural fibers properties is the main drawback that limits their applications in the composite industry (AL-Oqla et al. 2015a). Their properties mostly vary from one harvesting season to another or even from one plant to another (AL-Oqla et al. 2015b). Variations in physical properties affect in variation in mechanical properties as well when compare with synthetic fibers. Mixing batches of fibers from various harvest or parts of a single plant leads to resolve this problem (Koronis et al. 2013; AL-Oqla et al. 2014c). In fact, the properties of natural fibers may vary according to (1) rain and soil environments of the plant (2) maturity of the plant (3) part of the plant where the fibers are extracted from, and (4) harvest and treating method of the fiber (AL-Oqla et al. 2015e; AL-Oqla and Sapuan 2014a; Arbelaiz et al. 2005; Mohanty et al. 2002). A comparison between various specific strengths for different natural fiber types are illustrated in Fig. 4 (AL-Oqla et al. 2015b), and different natural fiber types are illustrated regarding their specific moduli in Fig. 5 (AL-Oqla et al. 2015b).

Another drawback of natural fibers is high moisture sensitivity which places a big challenge to use them for packaging applications and during shipment and long-term storage (AL-Oqla et al. 2014c). The hydrophilic nature of natural fibers leads to their low microbial resistance and susceptibility to rotting (Mohanty et al. 2002). Natural fibers absorb water from the surrounding environment. This causes

Fig. 4 Comparison of different natural fiber types regarding specific strength

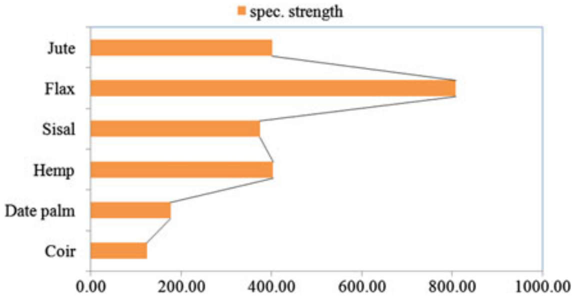
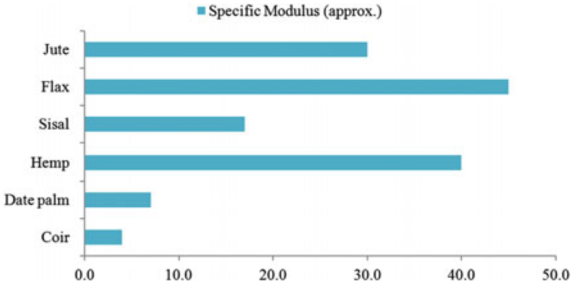


Fig. 5 Comparison of different natural fiber types regarding specific modulus



fibers to swell and have unstable dimensions, and changes the mechanical and physical properties of the composite. However, surface treatment can be useful in decreasing water sensitivity of natural fibers (Satyanarayana et al. 2009; Jawaid and Abdul Khalil 2011). Average values of moisture contents for various natural fibers are illustrated in Fig. 6 (AL-Oqla et al. 2014c).

Poor compatibility between polymeric matrices (since they are (non-polar) in nature and natural fibers (polar) causes poor fiber-matrix adhesion) is another drawback of the green composites (AL-Oqla et al. 2015a, d; AL-Oqla and Sapuan 2015; Azwa et al. 2013). Poor bonding will significantly affect the mechanical properties of the natural fiber reinforced polymer composites. In order to increase the adhesion between the fibers and thermoplastic matrix, chemical "coupling" agents can be used (AL-Oqla et al. 2015e; AL-Oqla and Sapuan 2014a; Aridi et al. 2016). Another technology been used is surface modifications on natural fibers to improve their adhesion with different matrices (Faruk et al. 2012a).

Moreover, low thermal stability of natural fibers is another disadvantage as they can only withstand temperatures up to 200 °C. More temperature will cause to degrade and shrink the fibers (Mohanty et al. 2002). This leads to change natural fiber physical and/or chemical structures due to depolymerization, hydrolysis, oxidation, dehydration, decarboxylation and recrystallization (Thakur et al. 2012; Yao et al. 2008). This in turn increases processing time to improve fibers properties. Thermal characteristics of raw, ripe, and matured betel nut husk (BNH) fiber are demonstrated in Figs. 7 and 8. They show the Thermogravimetric analysis (TGA) results of the weight loss and the temperature at 5 % weight loss for the fibers obtained at a heating rate of 10 °C/min and the initial degradation temperature was measured by the temperature at 5 % degradation (Yusriah et al. 2014).

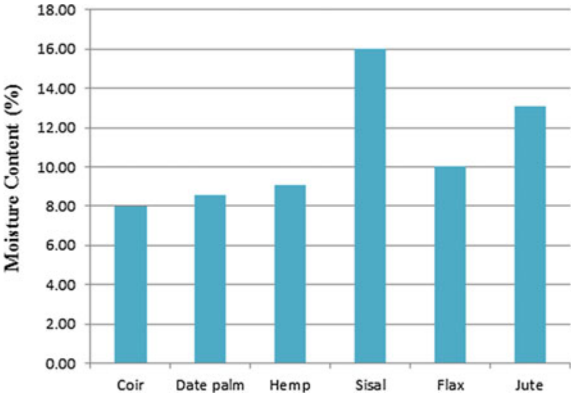


Fig. 6 Average values of moisture contents for various natural fibers

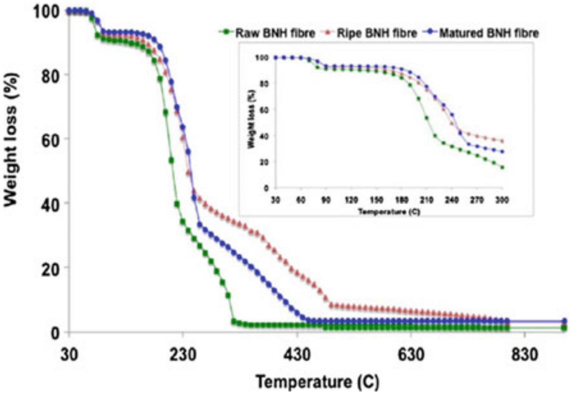


Fig. 7 Thermogravimetric analysis of raw, ripe and matured BNH fiber

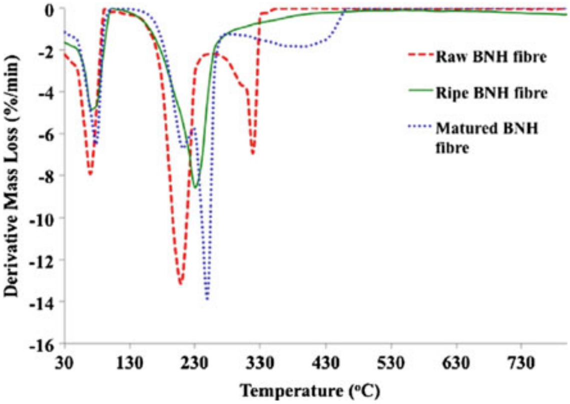


Fig. 8 DTG curves of BNH fibers

5 Material Selection for Bio-Composites and Its Importance

Material selection is the procedure of selecting specific material properties from a cluster of defined nominees after the physical design structures has been determined (Dweiri and Al-Oqla 2006). Or the identification of materials after appropriate manufacturing processes, which will hold the dimensions, shapes, and properties desired for the product to perform its required function at the lowest cost.

Material selection for a specific purpose is an important task since materials play significant role during the whole product design process (Dalalah et al. 2010; Dweiri and Al-Oqla 2006). It requires interdisciplinary efforts with experts from diverse backgrounds, depending on the product field of application (Jahan et al. 2010; AL-Oqla and Hayajneh 2007; Al-Oqla and Omar 2012; Al-Oqla and Omar 2015; AL-Oqla et al. 2015d). Materials selection process is considered as the main step of engineering design (Ashby and Johnson 2013). Materials are responsible for function, shape and interaction with other components of the product, also they effect on customer selection decision (Rashedi et al. 2012; AL-Oqla et al. 2015c; AL-Oqla et al. 2016).

6 Consequences of Improper Material Selection Decision

Wrong materials selection for engineering applications has many consequences; waste of money and time on the redesigning or fabrication of the designed parts (Jahan et al. 2010). Also leads to failure or undesired outcomes of products. Incorrect selection of materials leads to pre-mature failure of the product in the field of application. This will directly affect the productivity, performance of products and reputation of the company (Jabbour et al. 2013; Al-Widyan and Al-Oqla 2011, 2014; Al-Oqla and Omar 2012). Many factors affect material selection for a particular application (AL-Oqla and Sapuan 2014c; Ashby and Johnson 2013). In past years, material and design engineers typically select materials using trial and error method or based on previous experiences. Huge number of industrial materials and too many parameters will increase the complexity of the material selection task. Moreover, rapid growth of 'new materials' (i.e. natural fibers and bio-based polymers) which are alternatives to traditional materials, makes selection combination is really difficult process (Al-Oqla and Sapuan 2015; AL-Oqla et al. 2015e). Hence, systematic material selection procedure should be adopted to assist in evaluating and selecting the best materials for a precise product component (AL-Oqla et al. 2016).

7 Bio-Based Materials Usage

Over the last couple of decades, a growing number of new car models encouraged by government regulations, in both Europe and North America, have featured green materials in their components. Bio-materials have been playing a major role in many industries:

1. Parts (replacing glass fibers with plant fibers) which is started in the early 1990s in different components (Ashori and Nourbakhsh 2010).
2. Food industry (bottles, containers, cups, disposable tableware, and packaging) (Majeed et al. 2013).
3. Medical applications (disposable equipment and tools designed for easy breakdown) (AL-Oqla et al. 2015c).
4. Automobiles components (door panels, package trays, seat backs, trunk liners… etc.) (AL-Oqla and Sapuan 2014c; Friedrich and Almajid 2013).

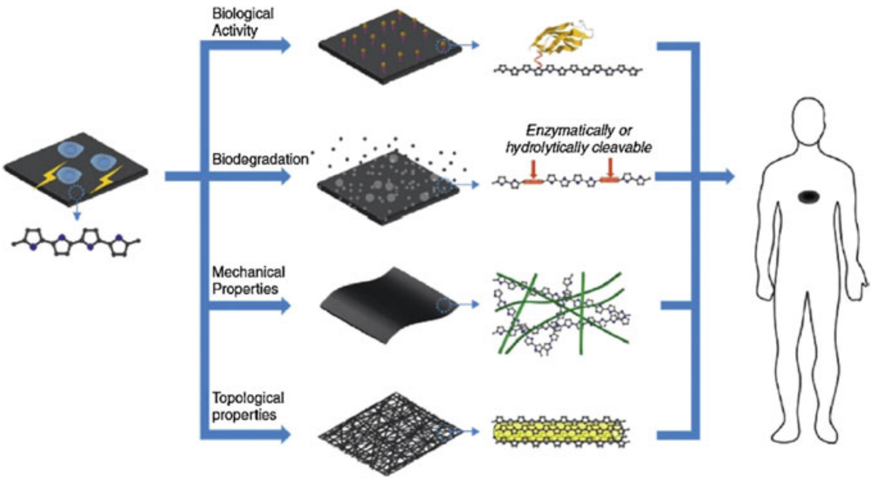


Fig. 9 Some aspects considered for biomimetic conductive polymeric materials

Moreover, bio-materials have been utilized in applications as a replacement for synthetic fiber composites as diverse as toys, marine railings, cases for electronic devices such as laptops and mobile phones, packaging, and funeral articles (Ho et al. 2012). In sports, surfboards incorporating bio-composites are presented. Recently, the production of natural fiber surfboard provides possibilities for better mechanical performance plus economic viability. Several researches on the other hand, have studied the suitability of the natural fibers as fillers for conductive polymers. The effects of several factors like fiber content, fiber length, temperature, fiber type, humidity and water absorption, and their chemical treatments have been investigated to enhance their favorite electrical characteristics. Such characteristics include DC conductivity, relaxation phenomenon, dielectric constant, electric charging phenomenon, surface current curves, capacitance, electrical resistivity, dielectric loss, volume and surface conductivities, dissipation and loss factors and so on. It was appeared that these bio-composites exhibit better electrical and thermal characteristics and may have potential applications as novel functional materials in textile and biological areas. On the other hand, various textile fibers and fabrics such as polyester, cotton, viscose rayon and wool, are now developed with conducting polymers for modern applications like electro-magnetic interference, conductive fabrics, super-capacitor, heating devices, shielding and antimicro-bial fabrics (Babu et al. 2013; Najar et al. 2007; Hardy et al. 2013). A schematic diagram of the reflected aspects for designing biomimetic conducting polymer-based materials is shown in Fig. 9 (AL-Oqla et al. 2015c).

Moreover, in the past fifteen years, bio-composites have been adopted by the European automotive industry. Nowadays, biomaterials have been gaining power in the United States. These materials are classified according to their physical and mechanical properties and each group occupied specific area in automotive components; Flax, sisal, and hemp are good in floor panel's seatback linings and door interiors. Coconut fiber and bio-based foams are used in seat bases, back pillows, and head restraints. Cotton and other natural fibers use in interior components. Abaca fiber used to create under-floor body panels. Natural latex uses to improve the safety of interior components by making the surfaces softer (Holbery and Houston 2006). Many automobile manufacturers as Audi, Honda, BMW, Chrysler, Fiat, General Motors, Mazda, Opel, Renault, Ford, Mercedes Benz, Peugeot, Toyota, Volkswagen, and Volvo start using bio-based materials from local sources (Ashori and Nourbakhsh 2010). Recently, Several attempts to use natural fiber composites in structural applications: an area which has earlier been the reserve of synthetic fibers like glass and aramid (Prajer and Ansell 2014). Combination of natural fibers with nano-materials to develop structural components that could possibly be used in automotive components is also an area of research.

- **Announced Usage**

Toyota manufacturer is the only company which stated that it plans to replace 20 % of the plastics used in its vehicles with bio-based plastics in their current productions. Ford on the other hand, has modified its specifications requirements to include a minimum amount of bio-based content in seat foams without specify numeric value. Generally, main sources of biomaterials are soybean, castor bean, corn, and sugar cane. Table 2 below shows a good comparison significantly- not only in the type of material used and its application, but also in terms of the renewably-sourced content in the material.

Table 2 The portion of renewably-sourced content in some automotive component

Bio-based content of some automotive components	Feedstock	Material	Application	Bio-based content (%)
BMW 7-series	Sisal	Acrylic polymer	Interior door panel	70
Chrysler sebring	Kenaf, hemp	Polypropylene	Interior door panel	50
Ford fiesta and focus	Kenaf	Polypropylene	Interior door panel	50
Ford fusion and lincoln MKZ	Soy	Polyurethane	Seating headrests	13–16
Multiple fiat vehicles	Castor	Zytel	Fuel lines	60
Nissan leaf	Corn	Sorona	Floor mats	20–37
Toyota camry	Castor	Zytel	Radiator end tank	40

8 Future Developments

Developments and new trends for bi-composites have occurred as a result of the enhancement of fiber selection as well as polymer-fiber evaluation methodologies. This in fact encourages all of treatment and interfacial engineering in addition to composite processing. Hence, it is necessary to found practical motivations relative to environmental performance considering bio-materials. This in order would allow designers to make informed judgments without conducting exhaustive experimental work as well as waste time and efforts. Such proposed methods may include elaborating more desired characteristics of bio-composites' constituents that designers have to take into consideration for sustainable designs to enhance achieving better performance for the future.

9 Conclusions

Bio-composite materials have been adopted in various applications. However, their implementations as alternatives for conventional materials are relatively slow. This is due to the fact that bio-composites have several limitations and barriers for development comparable to traditional materials. The inherent characteristics of their constituents are one of these limitations. In additions, the improper compatibilities between the fillers and matrices make the performance uncontrollable and difficult to be predicted. Therefore, keen selections for the constituents have to be properly studied and established. Moreover, proper theories and methodologies have to be examined in order to expand the usage of bio-composites into wider industrial applications. Recent methodologies for enhancing better performance in green composites have also to be supported to expand the development of such type of materials.

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Natural Fiber-Based Biocomposites

Longhe Zhang, Jing Zhong and Xiaofeng Ren

Abstract Due to the depletion of fossil resources such as crude oil, coal and natural gas, the impact of energy crisis is becoming more severe as seen from the intense fluctuation of the crude oil price. The growing public concern of using petroleum-based synthetic polymers has stimulated the interest in biodegradable materials from the renewable resources. Recent years have seen a remarkable progress in the development of biocomposites. There is abundant literature concerning the physical properties, manufacturing, applications, and many other aspects of biocomposite research. In this chapter, biodegradable polymers and fillers are introduced in details. A brief overview of some key elements in biocomposites research is given, including surface modification of natural fibers; classification of biocomposites and their general properties; manufacturing of the biocomposites; and applications of the biocomposites.

Keywords Natural fiber · Composites · Biopolymer · Adhesion · Surface modification · Coupling agent

In the beginning of human history, people evolved and differed from the other animals with the milestone that they learned to use tools to make living easier. The oldest materials the ancestors used are wood, stone and shells, then in the recent five thousand years people learned how to make ceramic containers and refine iron, bronze and other metals from the ores. All these materials already exist in the nature and people only need to learn how to extract them. In the recent one century, a revolution in the materials development has occurred along with the emerging of synthetic 'polymer'. The modern concept 'polymer' is defined by Hermann

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Staudinger in 1920 as a large molecule consisting of repeating units bonded covalently. The properties of polymeric materials can be tailored by the type of monomers, architecture, fillers, etc.

Despite the profound influence of polymers in the modern society, there is a growing concern of using synthetic polymers. Due to the decreasing amount of fossil resources such as crude oil, coal and natural gas, the concern of energy crisis is becoming strong which can be seen from the intense fluctuation of the crude oil price. It is known that the most commonly used plastics including polyethylene (PE), polyvinyl chloride (PVC) and polypropylene (PP) are all synthesized from crude oil. So the consumption of hundreds of millions tons of polymer will generate huge stress on the energy for a long haul. The other issue induced by the wide usage of polymers is the "white pollution", because most of the plastics have high resistance to degrade and hence they can be accumulated in the environment and creating pollution.

The above mentioned two issues stimulate the interest in biodegradable materials from the renewable resources. Biodegradable materials include biodegradable polymers and biodegradable fillers. In this chapter, biodegradable polymers, fillers and biocomposites will be introduced and discussed.

1 Biopolymers

The biodegradable polymers from renewable resources are also called biopolymers. This concept is introduced in 1980s. Based on the resource, biopolymers can be divided into several classes.

1.1 Natural Biopolymers

1.1.1 Protein

Proteins are heteropolymers with different kinds of aminoacid units which are connected by the peptide linkage, the primary structure of protein is shown in Fig. 1. Chemical structure of proteins varies with different resources. They usually form into primary, secondary, tertiary and quaternary four-level structure, as shown in Fig. 2.

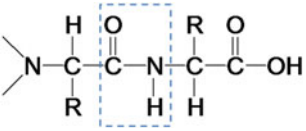


Fig. 1 Primary structure of protein

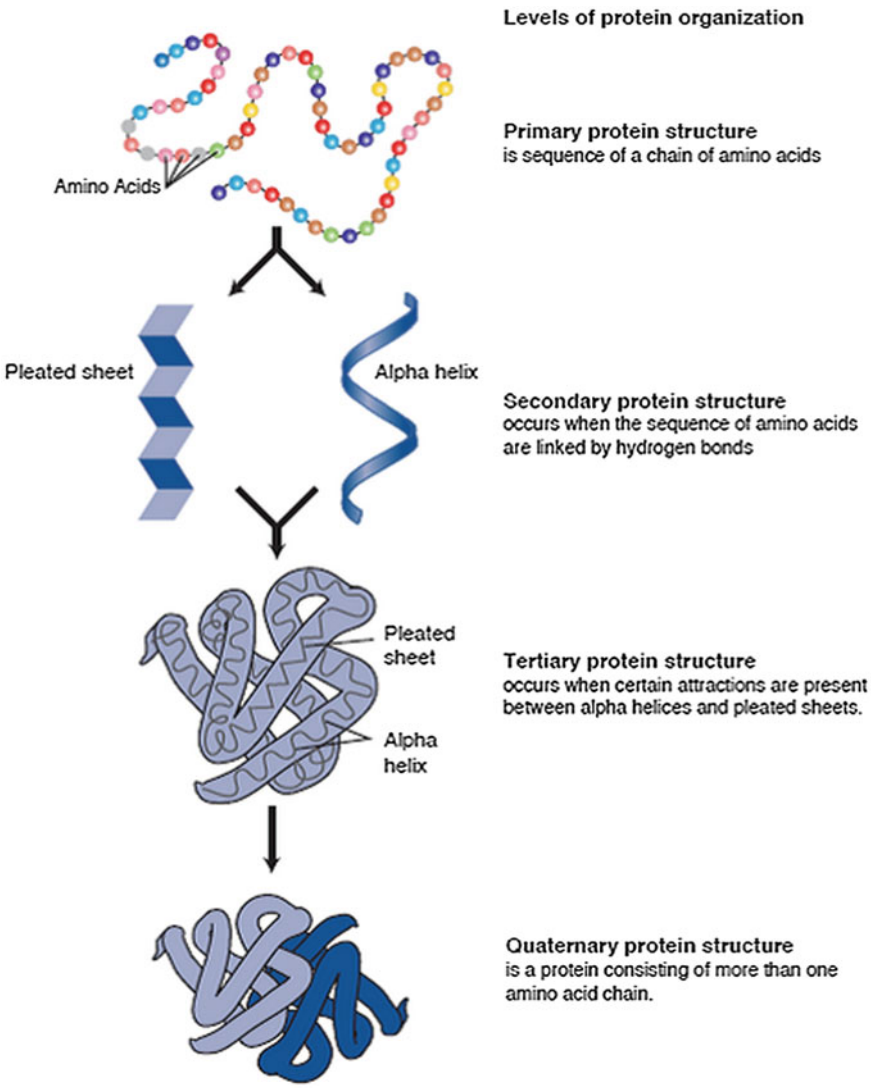


Fig. 2 Four-level structure of protein (Courtesy: National Human Genome Research Institute. https://www.genome.gov)

Collagen is a kind of protein derived from the animal. It is a biobased elastomer which is usually found in the animal tissues. The components of collagen contain glycine, proline, and hydroxyproline with flexibility more related to the glycine content (Gelse et al. 2003). The three components of collagen are shown in Fig. 3. The strength of the collagen is highly related to the hydrogen bond between

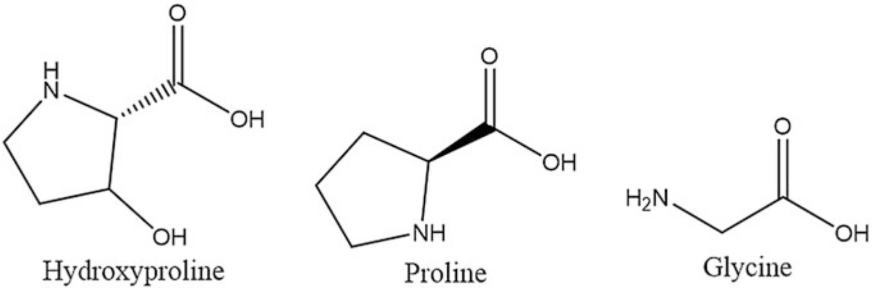


Fig. 3 Components of collagen

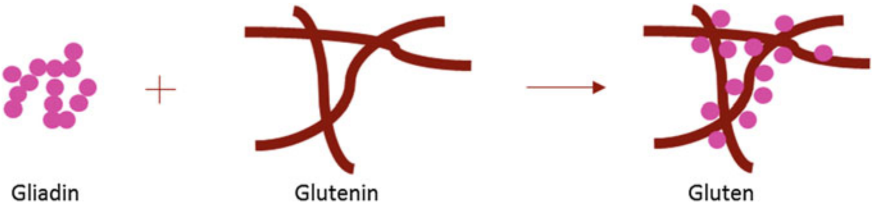


Fig. 4 Structure of gluten

hydroxyprolines. The collagen is mostly used in the medical application, no commercial application is reported in the area of replacing traditional elastomer.

Compared with collagen, wheat gluten and soy protein are more familiar which are vegetable proteins (Ren and Soucek 2014). Wheat gluten is consisted by gliadin and glutenin. Gliadin is a low molecular weight aminoacid with disulphide bond while glutenin is with much higher molecular weight. Gluten can be made into bio-films with presence of plasticizer such as water and glycerol. The property of gluten will change above a temperature of 60 °C due to the occurrence of crosslinking reaction (Vroman and Tighzert 2009) (Fig. 4).

Soybean is one of the major crops in the world. In 2012, the production of soybean worldwide is 240 million tons/year. In US, the production is 84 million tons/year (Ren et al. 2016; Li et al. 2015a, b; Ren and Li 2013). In the dried soybean, the soy protein content can be as high as 36 %, it can be isolated and make into plastic. The earliest application of soybean protein was reported in automotive using soybean meal and phenol formaldehyde (Sue et al. 1997). The objective of using soybean protein is to reduce cost in the beginning. Nowadays, the environmental and energy concern stimulates the interest in soy protein plastic. Similar to gluten, plasticizer is necessary in soy protein plastic. Without any plasticizer, the shear modulus of soy protein plastic is 1.76 GPa (Wang et al. 1996). With different preparation conditions and plasticizer, the tensile strength is in the range of 10–40 MPa and the elongation at break is about 1.3–4.8 % (Paetau et al. 1994). The elongation will increase and Young's modulus will decrease with increasing the plasticizer content. Soy protein has been studied widely, however, the price and performance of soy protein plastic inhibits the wide use in commodities.

1.1.2 Starch

Starch is a kind of polysaccharide, it is one of the most abundant natural polymer in the world and it exists in many plants such as rice, wheat, tuber crops, etc. Based on the structure it can be classified to amylose (poly-α-1,4-D-glucopyranoside) and amylopectine (poly-α-1,4-D-glucopyranoside and α-1,6-D-glucopyranoside), as shown in Fig. 5.

The mechanical properties vary with different ratio between amylose and amylopectine. At a higher content of amylose, the strength and elongation at break are higher. Several commercialized starch based resins are available and they are shown in Table 1.

1.1.3 Soybean Oil Based Plastic

Soybean oil content in the dried soybean is about 20 %. The basic structure of soybean oil is triglyceride, it usually contains 16 % saturated fat, 23 % monounsaturated fat and 58 % unsaturated fat (Poth 2001). The double bound in the unsaturated fat can be converted to epoxy bond by reaction with peroxide, and this soybean oil is called expoxidezed soybean oil (ESO) (Soucek and Ren 2015; Xu

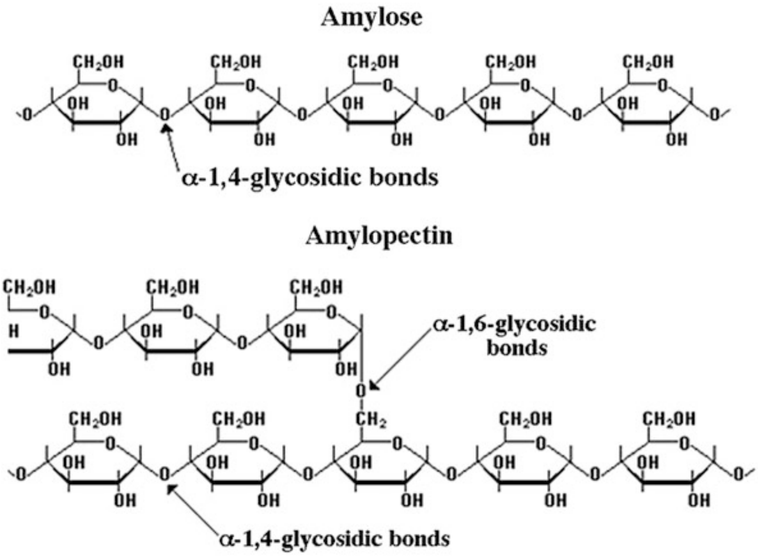


Fig. 5 Structures of starch

Table 1 Commercialized starch based resins

Trademark	Description	Company
Perfectafilm™	Modified starch	Avebe
Mater-Bi®	Blends of starch and biodegradable polymer, such as PCL	Novamont
TRELLIS EARTH disposables	High starch content bioplastic material	Trellis bioplastics
BIOPLAST®	PLA/starch	Biotec
Plantic™	Amylose starch/PVOH	Plantic technology
TRBF90	PLA, starch, PBAT	Torise biomaterial
Solanyl BP	Reclaimed potato starch	Solanyl biopolymers
VEGEMAT®	Fibers/starch/protein/lipids/additives	Vegeplast

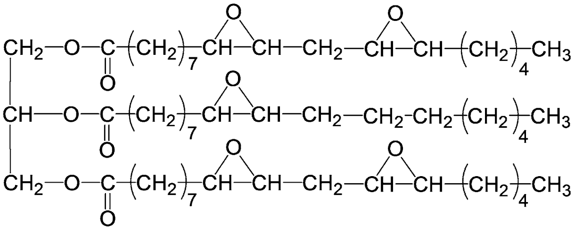


Fig. 6 Chemical structure epoxidized soybean oil

Table 2 Commercilized soybean oil based products

Trademark	Company	Description
Impact Gel™	Impact Gel® Corporation	Use of epoxidized soy oil to produce an impact gel for a variety of bedding applications
MASEO	Dixie Chemical Company, Inc	Maleinated acrylated epoxidized soybean oil
INFIGREEN® Recycled Polyols	Emery Oleochemicals	Used in foam seats of the Jeep Grand Cherokee and Dodge Durango
BetaFoam™ Renue	Dow Automotive Systems	New cavity-sealing foam made with 25 % renewable soy oil

et al. 2004). An example of ESO is shown in Fig. 6. ESO is not polymer, but it can be crosslinked with curing agent and become a new polymer. The curing agent can be triethylene glycol diamine (TGD) and triethylenetriamine (TETA) and Diethylenetriamine (DETA) (Liu et al. 2002, 2005). Recently, the United Soybean Board supported a series of study in the soybean oil based polymers, and some of them are commercialized as shown in Table 2.

1.2 Microbial Biopolymers

Unlike the chemically synthesized polymers, some of the biopolymer can be synthesized by microorganisms from different sugar resources. In some of the microorganisms, the yield can be as high as 80 % of the weight of the bacterial cell (Lenz 2005). The most representative microbial biopolymer is Polyhydroxyalkanoates (PHA). The chemical structural of PHA is shown in Fig. 7. The properties vary from ductile to brittle with different length of R (Chandra and Rustgi 1998). PHAs are fully degradable by the breakage of the ester from the end of the chain (Stevens 2003). Polyhydroxybutyrate (PHB) is a kind of PHA with R group being methyl. It has high crystallinity of above 50 % with a melting temperature about 180 °C. The virgin material is brittle and the glass transition temperature is 50 °C (Savenkova et al. 2000). In order to overcome the shortcoming such as brittleness and easy degradation, plasticizer is usually used, and the most common one is citrate ester. Other ways besides microorganism synthesis can be used to produce PHB, for example, ring opening of β-butyrolactone (Juzwa and Jedlinski 2006). The benefit of polymerization reaction method over microbial production is that the stereoregularity can be ajusted. Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) is a copolymer of hydroxybutyrate and hydroxyvalerate. It was obtained in 1983 by Imperial Chemical Industries (ICI) with a trade name of Biopol. The structure is shown in Fig. 8. PHBV can be fermented by bacterial from the culture medium with propionic acid (Sheu et al. 2009). As a high crystallinity, the melting point of PHBV is 108 °C, and the melting temperature is changed with content of hydroxyvalerate unit. With a higher content of hydroxyvalerate unit, the melting temperature is higher and with a higher content of hydroxyvalerate, the impact strength will increase (Hsieh et al. 2009). The glass transition temperature of PHBV is between −5 and 20 °C (Hori et al. 1993). The pure PHBV is brittle and the elongation at break is less than 15 %. All the PHAs can be completely biodegradable in soil, salt water, home composting and industrial composting environments.

Fig. 7 Chemical structure of PHB

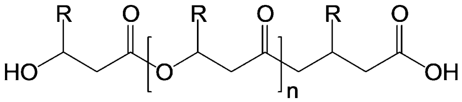
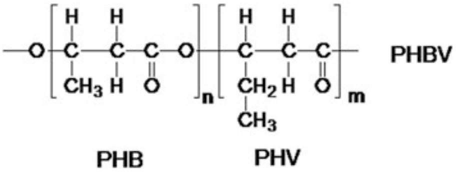


Fig. 8 Chemical structure of PHBV



1.3 Synthesized Biopolymers

Most of the commercialized biopolymers are all chemically synthesized polymers. More than 90 % of the synthesized biopolymers are polyesters because they contain the easily hydrolysable ester bonds. Biodegradable polyester consists of aliphatic polyesters and aromatic polyesters.

Polylactide (PLA) is a group of biopolymers by polymerization of lactic acid. Lactic acid can be obtained using anaerobic fermentation by lactobacillus. Due to the chirality of lactic acid, lactic acid has two structures. Consequently, PLA has three different stereostructure: poly(L-lactide) (PLLA), poly(D-lactide) (PDLA) and pol(DL-lactide). PLLA and PDLA are both semi-crystalline polymers. The melting temperature of PLLA is about 170–180 °C, and the glass transition temperature is 60–65 °C. The crystallinity is about 37 %. PLLA has a high tensile stress of 45–66 MPa, but the elongation at break is only 3–100 % (Nampoothiri et al. 2010; Gross and Karla 2002; Xu and Guo 2010). Dupont patented the first commercialized PLA in 1954 (Nampoothiri et al. 2010). Nowadays, the whole capacity of PLA production in the world is more than 150,000 metric tons per year. It is possible to synthesis PLA via polycondensation reaction. However, the molecular weight for PDLA cannot increase above 3000 and for PLLA it cannot increase above 6500. The most common production method used in the industry is ring-opening polymerization of lactide. Lactide is a cyclic lactic acid dimer which is between the condensation between –OH and –COOH of the L-lactic acid, D-lactic monomers or their mixtures, the three lactides are shown in Fig. 9. Then the L-lactide, D-lactide and DL-lactide are polymerized into higher molecular weight PLA with catalyst. The most common catalyst used in industry is stannous octoate, while in the lab, demonstraions tin chloride is often used (Nampoothiri et al. 2010).

The commercialized PLA are listed in Table 3. The PLA ranks #1 in consumption of biopolymer market. However, due to the limitation of application, several companies ceased their production of PLA, for example, Mitsui Chem., Shimadzu and Dainippon Ink Chem. in Japan, Treofan in Netherlands and Chronopol in USA. Now, the production of PLA is shifting from American and Europe to Asian, it is believed that by 2020, the production of PLA will increase to 720,000 tons and half of that is from Asian.

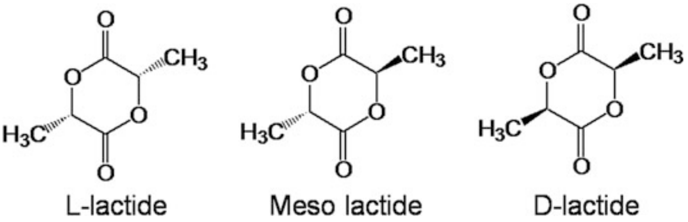


Fig. 9 Three different lactides

Table 3 Commercialized PLA products in the world

Trademark	Company	Country
NatrueWorks Ingeo®	Cargill Dow	USA (PLLA PDLA PDLLA)
Resomer®	Evonic	Gernamy (PLLA, PDLLA)
L series, D series	Corbion	Netherland (PLLA, PDLA)
Futerro®	Futerro	Belgium (PDLLA)
Lacea®	Mitsui Chem	Japan (PLGA)
TERRAMAC	UNITIK	Japan
ECODEAR™	Toray	Japan
REVODE	Hisun	China

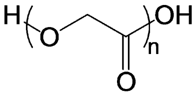


Fig. 10 Chemical structure of PGA

Table 4 Commercialized PGA in the world

Trademark	Company	Country
Surgicryl®	SMI	Belgium
Kuredus®	KUREHA CORPORATION	Japan
Kureha®	Kureha America	USA
Bondek®	Teleflex	USA
Polymtec®	Polymtec	China

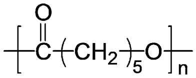


Fig. 11 Chemical structure of PCL

Poly(glycolic acid) (PGA) is also a linear aliphatic biopolymer which is produced by ring opening polymerization of cyclic glycolide. The first commercial trademark of PGA is Dexon by American Cyanamid Corporation in 1962. The chemical structure of PGA is shown in Fig. 10.

It is a semi-crystalline polymer with crystallinity of 45–55 %. The melting temperature is about 220–225 °C and glass transition temperature about 35–40 °C (Nair and Laurencin 2007). There are several commercialized products as shown in Table 4.

Polycaprolactone (PCL) is usually obtained by ring opening polymerization of ε-caprolactone using catalyst such as stannous octoate, the chemical structure is shown in Fig. 11.

PCL is a semi-crystalline polymer with a melting temperature of 60–65 °C and glass transition temperature of −60 °C. The yielding stress is about 23 MPa and elongation at break can be as high as 700 % (Vroman and Tighzert 2009). The commercialized PCL products are listed in Table 5.

Table 5 Commercialized PCL products in the world

Trademark	Company	Country
Capa™	Perstorp	Sweden
PLACCEL	Daicel Corporation	Japan
Ecovio®	BASF	Germany
Tone®	Union Carbide	USA
Esun®	Shenzhen Esun	China

Table 6 Commercialized PBS products

Trademark	Company	Country
GS PLA®	Mitsubith Chemical	Japan
Bionolle™	Showa	Japan
Ecoflex®	BASF	Germany
Hexing PBS	Anqing Hexing Chemical	China
Enpol®	Ire Chemical	Korea
PBS	Xinfu Pharmaceutical	China

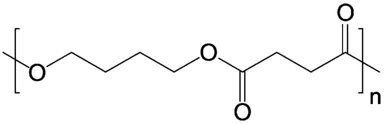


Fig. 12 Chemical structure of PBS

Poly(butylene succinate) (PBS) is also a aliphatic polyester by polymerization between succinic acid and 1,4-butanediol. The oligomer is first obtained by the polymerization is esterification of succinic acid and 1,4-butanedio first and then higher molecular weight PBS is synthesized via polycondensation (Xu and Guo 2010). PBS is a semi-crystalline polymer with melting temperature about 110 °C, the crystallinity is about 35–40 % (Yoo and Im 1999). The yield stress is 30–35 MPa and Young's modulus is about 300–500 MPa, the elongation at break is about 300 % (Xu and Guo 2010). The glass transition temperature is between −45 and −10 °C. The processability is better than PLA and PGA. The commercialized PBS products are listed in Table 6.

Besides aliphatic polyesters, commercialized biodegradable aromatic polyesters are also synthesized with terephatalic acid. The most widely used one is Ecoflex® from BASF and Origo-Bi® from Novamont. Eastman had a similar product with brand name of Easter Bio®, but it was sold to Novamont. It is reported that, the mechanical properties and degradation rate is changed with different content of terephtalic acid (Witt et al. 2001) (Fig. 12).

Some of the synthesized polyamides are also reported biodegradable if they contain amide bond as peptide bond. However, due to the semi-crystalline structure, the degradation is much lower than polypeptides (Paredes et al. 1998). Bayer commercialized a polyamide with trade name of BAK®, but they ceased the production in 2001. Polyester based polyurethane is also reported biodegradable, and the polyester part can be PCL, PLA and PGA (Nakajima-Kambe et al. 1999; Hassan et al. 2006; Li et al. 2015a, b).

Nowadays, investments in biopolymers are increasing. In Europe, several legislations have been approved in order to expand the usage of biodegradable polymers. In England, the PLA plastic bags are widely used in the market, and more than 20 billion bags are used yearly. Based on the investigation of Grapentine, 41 % of US customers and 59 % of European customers would like to use biodegradable packaging materials. 77 % of European customers would like to pay 5 cents and 74 % American customers can pay 10 cents more. However, the prices of the biopolymers are still unaffordable by now. For example, PLA is 50–200 % more expensive than the traditional polymers like PE, PP.

2 Natural Fillers

Fillers are always used in the traditional polymers to modify the properties of polymer and also lower the cost of the final polymeric products. The traditional fillers include silica, calcium carbonate, clay, glass fiber, graphite, carbon black, carbon nanotubes, carbon fiber, graphene, etc. Nowadays, from the prospective of sustainable development, the interest has been increasing using the natural fibers to replace the traditional fillers due to their biodegradable nature, low cost, light weight and high specific strength. Natural fibers can be derived from animal and plant. Animal fibers such as silk, feather and wool are proteins while the plant fibers are combination of cellulose, hemicellulose, lignin, and so on. The plant fibers spread widely on the earth, based on the origin of the fibers, they can be classified into leaf fiber, stem fiber, stem fiber, fruit fiber, seed fiber, grass fiber, bark fiber and so on (John and Thomas 2008). The plant fibers can be called wood fiber. The compositions of different wood fibers are listed in Table 7. It can be seen that the first three highest content components are cellulose, hemicellulose and lignin, which accounts for 90 % of the dried weight of wood fibers. Small amount of pectin, wax and protein also exist in the fibers. The modulus, density and specific strength are shown in Table 8. The specific strength of some wood fibers can be compared to the glass fiber and some are even higher.

A new class of composites contains naturel fibers and biodegradable polymers are becoming attractive. They are called green composites. The green composites are wholly degradable and can be used as sustainable materials in some specific areas even to replace some of the traditional polymer composites (Qiu et al. 2011, 2012a, b). Sometimes, the wood fibers are applied just to bring a wood-like appearance and in some cases, the wood fibers are needed in the biopolymer to improve specific properties. A number of research have been carried out in the green composites, some of them are summarized in Table 9. Green composites can be prepared using solution mixing, extrusion, compression molding and hand lay-up, some of the examples are also shown in Table 9. The most prevailing preparation method is melt mixing due to the low cost, convenience and

Table 7 Composition of different wood fibers (Bledzki et al. 1996; Hon 1992; Ugbolue 1983; Mukherjee 1986; Mohanty et al. 2002)

Fiber type	Cellulose	Lignin	Hemicellulose	Pectin	Wax	Micro-fibrillar angle (°)
Hemp	70.2–74.4	2.7–5.7	17.9–22.4	0.9	0.8	6.2
Flax	71	2.2	18.6–20.6	2.3	1.7	10
Kenaf	31–39	15–19	21.5	–	–	–
Cotton	82.7	–	5.7	–	0.6	–
Jute	61–71.5	12–13	13.6–20.4	0.2	0.5	8.0
Sisal	67–78	8.0–11.0	10–14.2	10	2	20
PALF	70–82	5–12	–	–	14	11.8
Sweet sorghum	50	15	23	–	–	–
Ramie	68.6–76.2	0.6–0.7	13.1–16.7	1.9	0.3	7.5
Henequen	77.6	13.1	4–8	–	–	–
Fruit Coir	36–43	41–45	0.15–0.25	3–4	–	41–45

Table 8 Mechanical properties of different natural fibers and traditional fibers (Bledzki et al. 1996, 2009; Ugbolue 1983; Mohanty et al. 2000, 2002; Bledzki and Jaszkiewicz 2010; Bisanda and Ansell 1992; Bledzki and Gassan 1999)

Fiber type	Modulus (GPa)	Density (g/cm^3)	Specific strength (modulus/density)
E-Glass	70–73	2.5–2.55	27.5–29.2
Jute	13–26.5	1.35–1.46	8.9–19.6
Flax	27.6–70	1.4–1.5	19.7–50
Hemp	70	1.48	47.3
Cotton	5.5–12.6	1.5–1.6	3.4–8.4
Ramie	61.4–128	1.45	42.3–88.3
Coir	4–6	1.15	3.48–5.2
Sisal	9.4–38	1.33–1.45	6.5–28.6

environment friendliness. Among all the biodegradable polymers, PLA is the most widely used one, so most of the green composites are choosing PLA as the matrix. Some of the studies on PLA/natural fiber composites and their mechanical properties are summarized in Table 10, and a fiber concentration of 30 wt% is selected to compare with each other.

At the present moment, the green composites are not qualified using in the structural applications to replace the traditional composites due to the poor mechanical properties. Therefore, they are limited in the area where does not require very high loading resistance in the construction, such as furniture, interior decoration and automotive panels (Hollaway 2010; Dittenber and GangaRao 2012; Araujo et al. 2008). The shortcomings of incorporation of natural fibers in polymer are obvious, for example, high moisture absorption, low flame resistance, narrow processing window and incompatibility with polymer (Azwa et al. 2013; Ren et al.

Table 9 Processing method of different green composites

Matrix	Fiber	Processing method
PLA (Huda et al. 2008)	Kenaf	Compression molding
PBS (Liu et al. 2009)	Jute	HAAKE Mixer
Soybean oil resin (Hong and Wool 2005)	Keratin feather	Compression molding
Wheat flour-based plastic (Dobircau et al. 2009)	Cotton	Extrusion
PLA, PBS, PHB, PBAT, starch thermoplastic (Bodros et al. 2007)	Flax	Film stacking
Starch (Lawton et al. 2004)	Cellulose	Kitchen mixer and baking
Polyurethane (Bakare et al. 2010)	Sisal	Closed mould
PLA/P(3HB-co-4HB) (Musiol et al. 2015)	Jute	Injection molding
Starch (Romhany et al. 2003)	Flax	Hot presssing
Wood flour (Cunha et al. 2001)	Starch cellulose acetate	Compounding
PLA (Yu et al. 2010)	Ramie	Two-roll milling
PLA (Tokoro et al. 2008)	Bamboo	Extrusion
PLA (Zhong et al. 2010, 2011)	Sweet Sorghum	HAAKE mixer
PHB (Wong et al. 2002)	Flax	Solution mixing
Polyester (Gowda et al. 1999)	Jute	Hand lay-up

Table 10 Mechanical properties of PLA/natural fiber composites

Composites	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength (kJ/m^2)
PLA/30 wt% kenaf (Srebrenkoska et al. 2009)	28.3	2.87	47	2.1	54.3
PLA/30 wt% ramie (Yu et al. 2009)	52		105		
PLA/30 wt% jute (Yu et al. 2009)	49		101		
PLA/30 wt% cellulose (Bledzki et al. 2009)	92	8	152	7.9	
PLA/30 wt% newspaper fiber (Huda et al. 2006)	68	5.3	106	5.4	
PLA/30 wt% cellulose fiber (Huda et al. 2005)	73	6.7	83	6.2	
PLA/10 wt% wheat straw/10 wt% corn stover/10 wt% soy stalks (Sanchez-Garcia and Lagaron 2010)	55	5.6	80	6.9	
PLA/30 wt% cordelia rayon (Bax and Muessig 2008)	58	4.9			72
PLA/30 wt% wood flour (Petinakis et al. 2009)	55				36

2012a, b). A lot of studies have made in order to overcome these drawbacks, which will be discussed in the following sections.

3 Nature Fiber and Biopolymer Based Biocomposites

Recent years have seen a remarkable progress in the development of biocomposites. There is abundant literature concerning the physical properties, manufacturing, applications, and many other aspects of biocomposite research. In this section, we intend to give brief overview of some key elements in biocomposites research, including (a) surface modification of natural fibers; (b) classification of biocomposites and their general properties; (c) manufacturing of the biocomposites; and (d) applications of the biocomposites.

3.1 Surface Modification

The mechanical performance of polymer composites mainly depends on a few key factors, including the physical properties of the individual components (i.e. the matrix and reinforcing fibers), the interaction between the fiber and the matrix, and the orientation of the reinforcing fibers. The highly polar and hydrophilic nature of the fiber surface makes them difficult to bond with commonly-used nonpolar matrix, e.g. polyolefin. Consequently, the weak fiber-matrix interface is not effective for stress transfer, leading to poor mechanical properties of the biocomposites (Ren et al. 2012a, b, 2013). Besides the weak interface, natural fibers tend to aggregate and cannot disperse well in relatively nonpolar matrix in the manufacturing process. Clearly, without uniform distribution of the fiber within the matrix, the composite cannot achieve optimized performance. In addition, the hydrophilic surface may easily absorb moistures and cause the weakening of the composites. Hence, surface treatment of the natural fibers is critical to improve the mechanical performance of the biocomposites, since the treatments can strengthen the fiber-matrix interface and reduce the moisture sensitivity (Qiu et al. 2012a, b).

Currently, a wide range of surface treatment methods have been investigated, which fall into three major categories, namely chemical treatment, physical/physic-chemical treatment, and biological treatment. Since there are few reported related to the surface modification of animal fibers, herein we will focus on the progress of cellulosic fibers.

3.1.1 Chemical Treatments

Alkaline Treatment

Alkaline treatment, i.e. mercerization, is one of the most efficient chemical treatment methods that are now widely used for surface modification of natural fiber. The main function of alkaline treatment lies in following two aspects. First, alkaline treatment breaks down the fiber bundles into small and shorter fibers due to the disruption of hydrogen bonding between the fibers (Li et al. 2007; Mishra et al. 2002; Fuqua et al. 2012). Meanwhile, it induces a significant microstructure change in cellulose crystalline (Van de Weyenberg et al. 2006). To realize alkaline treatment, typically fibers are immersed in sodium hydroxide solution with a determined time period and temperature. During this process, Na^+ penetrates into the cellulose crystals, causing the swelling of the fiber. Part of the hydroxyl groups on the surface of the fibers will be ionized into alkoxides, which further expanding the molecular dimensions. Hydroxyl groups are recovered by the subsequent water wash. This process leads to the generation of a more thermodynamically stable cellulose crystalline compared to an untreated sample. Second, it partially removes the non-cellulosic components, such as hemicellulose, lignin, or wax, from the surface layer of the fiber. The removal of artificial impurities, if present, is also achieved during the treatment. The effect of alkaline treatment on the microstructure of fibers could be illustrated as shown in Fig. 13 (Mwaikambo and Ansell 2002).

Based on these reasons, alkaline treatment enhances the surface roughness and area of the natural fibers and thereby improves the fiber-matrix interfacial adhesion due to improved mechanical interlocking with the matrix. At the same time, more cellulose is exposed on the fiber surface after the treatment, providing more reaction

$$\text{Cell-OH} + \text{NaOH} \rightarrow \text{Cell}{-}\text{O}^{-}\text{Na}^{+} + \text{H}_2\text{O} + \text{surface impurities.}$$

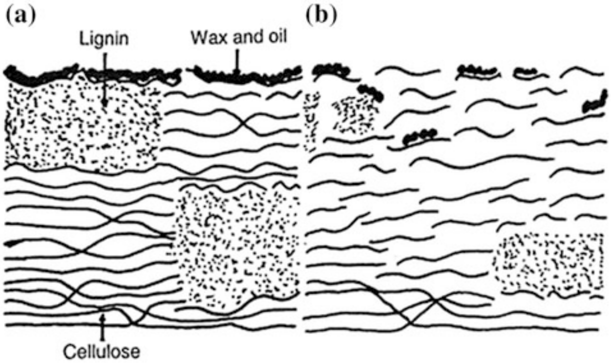


Fig. 13 Schematic illustration of the microstructure of cellulosic fiber **a** before treatment and **b** after alkaline treatment. (Reproduced with permission from Mwaikambo and Ansell 2002)

sites for further modification (Bogoeva-Gaceva et al. 2007; Valadez-Gonzalez et al. 1999a, b). However, it should be noted that alkaline treatment results in an increase of amorphous cellulose at the cost of crystalline cellulose (Agrawal et al. 2000).

As one of the most used process for natural fiber modification, numerous studies have been done to understand the effect of different alkaline treatment conditions on the natural fibers and the properties of the resulting biocomposites. Generally, alkaline treatment has been demonstrated to improve the mechanical properties of the fiber reinforced biocomposites. Recent progress has been summarized in a few review articles (Fuqua et al. 2012; Gurunathan et al. 2015; Faruk et al. 2012; Mohanty et al. 2001).

Silane

Organosilanes have been used as coupling agents for glass fiber modification to improve the adhesion between the glass fiber and polymer matrix (Li et al. 2007). To be an effective coupling agent for composites, an organosilane should bear functional groups that can form chemical bonds with both phases, i.e. the polymer matrix and reinforcing fibers. For example, the type of the functionality reactive to the matrix could be vinyl group if unsaturated polyester is chosen (Park and Jin 2001; Hu et al. 2009). On the other hand, in contrast to the case of glass fiber where siloxane alkoxy groups can react with the silanol groups on glass fiber, trace amount of water are required to generate silanol groups so that the condensation reaction between silanol groups and the hydroxyl groups on the cellulose could occur (Belgacem and Gandini 2008). A schematic illustration of the reactions in silane treatment process is shown in Fig. 14. The alkoxysilanes first undergo hydrolysis and then condensation to form chemical bonds with the cellulose surface. With appropriate design of the functional group, cellulose and the polymer matrix could be chemically linked by the silane treatment, which significantly increases the fiber-matrix adhesion.

It should be noted that silane treatment can be improved if performed after an alkaline treatment, since an alkaline treatment increases the reactive sites and clean the surface of the fibers. The effect of the type and concentration of silane, the time and temperature of the reaction, and moisture content, were studied (Zimniewska et al. 2011). When applied to fabricate biocomposites, the fiber-matrix interaction from silane treated fibers is much stronger than that from alkaline treated fibers, and therefore the resulting biocomposites show stronger tensile strength (Valadez-Gonzalez et al. 1999a, b; Yu et al. 2010; Gwon et al. 2010).

Esterification

Due to the wide availability of hydroxyl groups on the surface of natural fibers, esterification has been developed as another surface modification method. Different than silane treatment that forms covalent bonds between the fiber and matrix, most,

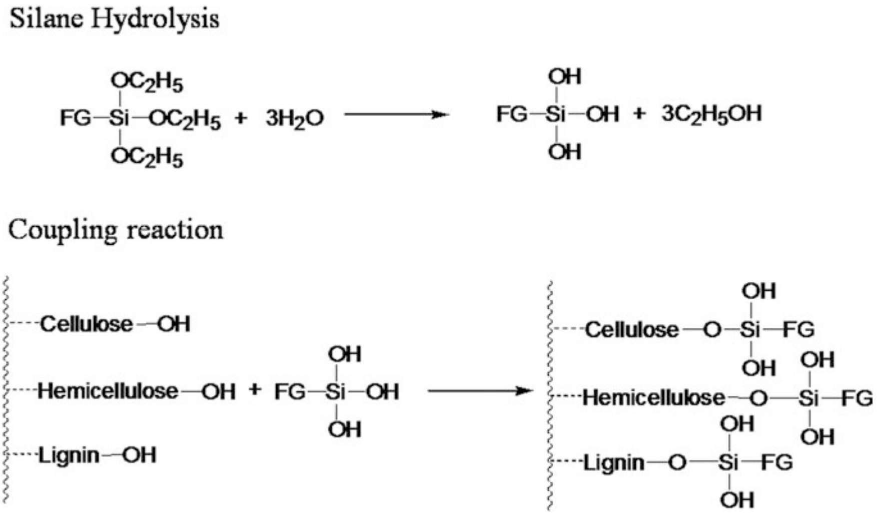


Fig. 14 Reactions in silane treatment. FG refers to the desired functional groups selected for the polymer matrix. (Reproduced with permission from Fuqua et al. 2012)

if not all, esterification treatments only aims to functionalize the cellulose surface. During the esterification, the hydrophilic hydroxyl groups are transformed to more hydrophobic ester bonds, which increase the hydrophobicity of the fibers and thereby the fiber-matrix compatibility.

Among different esterification methods, acetylation is most used and has been employed in industrial scale a few decades ago. Various compounds could be used to achieve acetylation, e.g. acid chloride, acetic anhydride, and acetic acid (Fuqua et al. 2012; Zhang et al. 2015). In a typical procedure, natural fibers are first soaked in acetic acid solution and subsequently reacted with acetic anhydride at higher temperature, due to the fact that neither acetic acid nor acetic anhydride reacts sufficiently with the cellulose when they are used separately (Gurunathan et al. 2015; Manikandan Nair et al. 2001). Studies reveals that the acetylating agents are more likely to react with the hydroxyl groups on the amorphous constituents such as lignin and hemicelluloses instead of those on high crystalline celluloses, since it is relatively difficult to reach the hydroxyl groups in the closely packed region via diffusion (Rowell 1992). Nevertheless, acetylation was found to improve the moisture resistance, dimensional stability and environmental stability (Mohanty et al. 2001; Rowell 1992; Manikandan Nair et al. 1996). Biocomposites based on acetylated natural fibers are reported to exhibit enhanced mechanical properties due to the improved fiber-matrix interface (Tserki et al. 2005). However, it was also observed that excess acetylation causes the degradation of the cellulose (Bledzki et al. 2008).

Besides acetylation, esterification of cellulose can be achieved through a few other routes. Maleic anhydride has been used to modify a wide variety of natural fibers, e.g. banana, hemp, and sisal (Mishra et al. 2000). Benzoylation treatment has been performed using benzoyl chloride for sisal fibers (Manikandan Nair et al. 1996), bamboo fiber (Kushwaha and Kumar 2010), Cannabis indica fiber (Singha and Rana 2012), and flax fibers (Wang et al. 2007). Consistent with acetylation, maleation and benzoylation increased the hydrophobicity of cellulose surface and hence lead to reduced water absorption, improved compatibility with polymer matrix, and enhanced mechanical performance of the composites.

Maleated Polymer as Coupling Agent

Besides reacting with cellulose, maleic anhydride is more often used to prepare maleated polymers that can be used as coupling agents between cellulose fiber and polymer matrix, since the maleic anhydride group can react with the hydroxyl group on the cellulose surface to form chemical bonds and the polymer can be chosen to match the type of the matrix. In this way, high compatibility can be achieved between the fiber and the matrix once the processing conditions are properly employed. Particularly, maleated polypropylene (MAPP) has been most widely used probably due to the importance of PP matrix and the commercially availability of MAPP (Mohanty et al. 2001). To prepare maleated polypropylene, peroxide reagent is used to initiate free radicals on the PP backbone. The formed free radicals subsequently react with maleic anhydride to obtain MAPP, as shown in Fig. 15 (Park et al. 2006). The maleic anhydride groups on MAPP can further react with OH groups on cellulose (Fig. 16). Once cellulose is modified with MAPP, the surface energy of the cellulose will be greatly reduced, improving the interfacial adhesion between the fiber and matrix. It is believed that molecular weight and anhydride content of MAPP will affect the interphase between MAPP and the polymer matrix, which subsequently has an effect on the compatibility of the fiber and matrix (Sanadi et al. 1995). When PP is used as matrix, cocrystallization between the PP and MAPP occurs to further improve the compatibility (Bullions et al. 2004; Trejo-O'reilly et al. 2000). Although the interphase formed

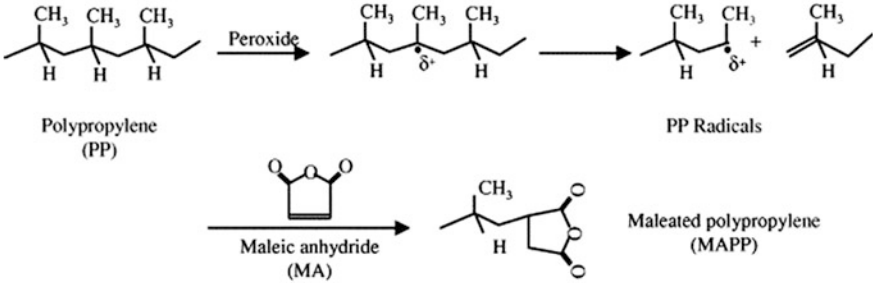


Fig. 15 Preparation of maleated polypropylene. (Reproduced with permission from Park et al. 2006)

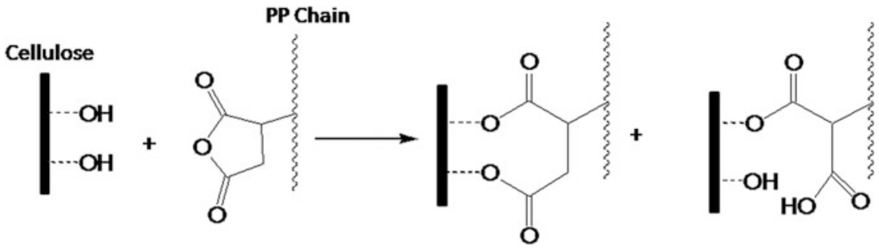


Fig. 16 Reaction between maleated polypropylene and cellulose

between MAPP and the polymer matrix has not fully understand, MAPP has been regarded as one of the most effective surface treatment for PP-matrix composites. For example, it was shown that the jute fiber composites with MAPP coupling agents has twice the mechanical strength compared to the composites based on silane treatment (Bera et al. 2010). There are a large number of studies about biocomposites based on MAPP coupling agent and PP matrix, which have been summarized by a recent review (Faruk et al. 2012). Besides PP, maleic anhydride has been applied to many other polymer matrix, e.g. poly(lactic acid) or polystyrene (Fuqua et al. 2012).

Polymer Grafting

Surface modification of natural fibers by graft copolymerization is currently one of the hottest topics in polymer materials. By introducing polymer chains onto the fiber surface, people can take advantage of the abundant knowledge from polymer science to modify the natural fibers. This essentially opens the door to unlimited possibilities of natural fiber polymer composites. As shown in Fig. 17, by grafting polymer chains onto cellulose, it is possible to control the physical properties, surface characteristics, biological properties, and environmental responsiveness of these cellulose-based biocomposites. This applies to any natural fiber based biocomposites, though cellulose is dominantly being modified.

Graft copolymerization can be done via many types of polymerizations, such as conventional or controlled free radical polymerization, ionic polymerization, ring opening polymerization. Despite of their precise control on the polymerization process, cationic or anionic polymerization is not frequently used for natural fiber modification because of their demanding experimental conditions and it might be challenging to avoid the side reactions on natural fibers in these polymerizations (Roy et al. 2009). Cellulose grafting via ring opening polymerization (ROP) can be easy to achieve since the hydroxyl groups on the natural fiber surface could act as initiators for the polymerization. More interestingly, popular cyclic monomers for ROP, such as lactones or lactides, lead to biodegradable polymers, including poly (ε-aprolactone) and poly-L-lactide. Homogeneous and heterogeneous grafting copolymerization for cellulose by ROP was recently reviewed (Carlmark et al.

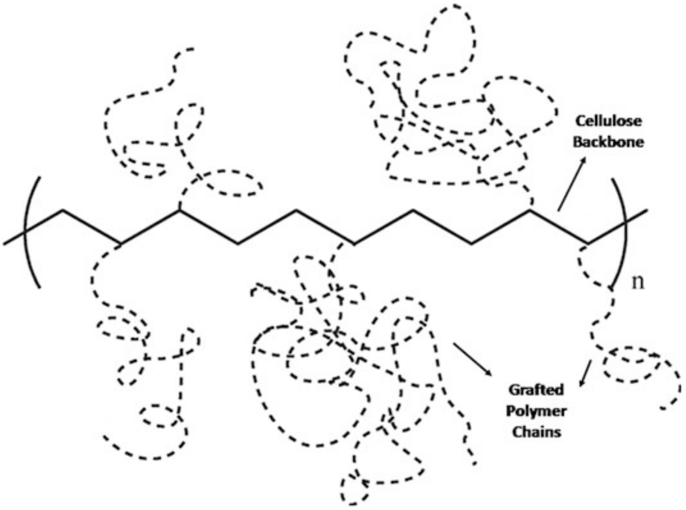


Fig. 17 A schematic representation of cellulose-graft-copolymer. (Adapted with permission from Roy et al. 2009)

2012). Compared to ionic polymerization and ROP, free radical polymerizations have been receiving a lot more efforts (Roy et al. 2009; Kang et al. 2015; Joubert et al. 2014; Malmstrom and Carlmark 2012). Free radicals can be generated by a wide variety of approaches, including ultraviolet, high energy radiation, plasma, redox systems, etc. This provides great flexibility for the reaction design. It should be noted that significant amount of the recent progresses on this aspect focuses on the application of controlled free radical polymerization for polymer grafting. Reversible deactivation radical polymerization (RDRP) techniques, including but not limit to atom transfer radical polymerization (ATRP) (Matyjaszewski 2012), reversible addition-fragmentation chain transfer polymerization (RAFT) (Zhang et al. 2014a, b, 2015), or nitroxide-mediated polymerization (NMP) (Nicolas et al. 2013), have been extensively applied to this area. To further understand the recent progress in this field, the readers are referred to an excellent source for polymer grafted cellulose (Thakur 2015).

Other Chemical Treatments

Bleaching is a commonly used technique to reduce the color and enhance the whiteness of treated fibers. Bleaching agents, such as sodium chlorite ($NaClO_2$), sodium hypochlorite (NaClO), or hydrogen peroxide (H_2O_2), degrade lignin by reacting lignin's hydroxyl group. As the color of cellulose fiber is mainly from the conjugation structure inside, delignification caused by bleaching can effectively improve the whiteness of the fibers (Fuqua et al. 2012). On the other hand, delignication and dewaxing in the bleaching process also increase the surface roughness of the fibers and thereby increases the fiber-matrix adhesion (Li et al. 2007; Rayung et al. 2014; Mishra et al. 2002).

Due to the presence of hydroxyl groups, there are many other possible ways to modify the cellulose surface, such as isocyanate-hydroxyl reaction (Mansour et al. 1994), etherification (Hon and Ou 1989; Mansour et al. 1994), or triazine (Bledzki et al. 1996). All these modifications have been demonstrated to improve the mechanical properties of biocomposites. The underlying mechanism is similar to silane coupling agent or other surface functionalization, i.e. greatly increase the hydrophobicity of the otherwise highly polar surface of natural fibers, which improve the interfacial adhesion between the fiber and polymer matrix.

3.1.2 Physical or Physico-Chemical Treatment

There are many types of physical or physico-chemical treatments to modify the surface of the natural fibers. Compared to chemical treatments, most of the physical or physic-chemical treatments do not lead to severe change in the bulk properties but mainly in the surface composition of the fibers. Common physical treatments include mechanical treatment, heat treatment, steam explosion, etc. Common physic-chemical treatments include plasma discharge, corona, laser, γ-ray, UV irradiation, etc. Some of these techniques are briefly summarized as follows.

1. Simple mechanical treatment, including calendaring, stretching, and rolling (Fuqua et al. 2012; Bledzki and Gassan 1999). These methods are capable to separate fiber bundles and increase the fiber surface area, so that the fiber-matrix adhesion is enhanced. However, they may also cause the damage to the fiber, such as reducing the fiber aspect ratio.
2. Heat treatment of fibers refers to heating the fibers at relatively high temperature, close or slightly below the glass transition of lignin, at which the fibers may start to degrade (Satyanarayana et al. 2009). Non-cellulose components degrade from the fiber bundles and therefore the fiber bundles separate into single fibers. Under such conditions, the physical and chemical properties of the fibers are subject to severe change according to the temperature and time of the treatment. It was reported that heat-treated sisal fibers (150 °C and 4 h) improve the mechanical properties of the sisal-epoxy composites due to the increased crystallinity of the fiber (Rong et al. 2001). It was believed that the molecular structure of the sisal fibers can be reorganized to improve the crystallinity at high temperature.
3. Steam explosion is another method to separate fiber bundles into single fibers. It is a process of first heating the fibers at high temperature and high pressure and then mechanically disrupting the fibers by violent discharge, (“explosion”) into a collecting container (Ramos 2003). Steam explosion are capable to fractionate cellulosic fibers into three main components, i.e. cellulose, hemicellulose, and lignin, with high yields. The treated fibers exhibit higher surface area and higher

crystallinity, which improves the physical properties of the treated fibers and the composites. More detailed discussion about this promising technique can be found in literature (Ramos 2003; Satyanarayana 2004).

4. Electric discharge techniques (Corona, plasma, or ionized air) and irradiation techniques (laser, γ-ray, UV irradiation) have attracted significant interest due to their low environmental impact for modifying the natural fiber surface. The progress of these techniques has been well reviewed by Gandini and coworkers (Belgacem and Gandini 2005, 2008).

3.1.3 Biological Treatment

Compared to other surface treatment techniques, the utilization of biological agents such as enzyme and fungi are getting more attention due to their “greener” process (Fuqua et al. 2012, Gulati and Sain 2006; Kharazipour et al. 1997; Lee et al. 2011). Particularly, the investigation and application of enzyme treatment has been rapidly increasing, since it offers a few advantages over conventional chemical treatments explained as follows. First, it is a milder, environmental-friendly, and low-energy process without solvents. The enzymatic systems could be recycled when necessary (George et al. 2014). Second, it allows the improvement of fiber surface cleanliness and fiber bundle separation. Enzyme treatment could selectively remove pectic and hemicellulosic components in cellulose fiber. Since pectin binds the fiber together, its degradation will cause an improved separation between the fibers. Tibolla and co-workers prepared cellulose nanofibers from banana peel by both chemical treatment and enzyme treatment (Tibolla et al. 2014). In their procedure, the chemical treatment process includes alkaline treatment, bleaching and acid hydrolysis while enzyme treatment includes alkaline treatment and hydrolysis by xylanase, a type of hydrolytic enzyme. Although both methods provided isolated cellulose nanofibers, it was found that enzymatic hydrolysis is less effective in removing the lignin components compared to bleaching and acid hydrolysis and therefore less pure nanofiber suspensions, as shown in Fig. 18. In other studies, it was found that enzyme treatment may lead to a much quicker growth of molds on the treated fibers (Nykter et al. 2008).

3.2 Biocomposites

Biocomposites can be produced using different combination of polymer matrix and natural fibers. For a biocomposite, while the natural fibers determine the stiffness and strength, polymer matrix dominates most of other properties, namely the appearance, environmental resistance, ductility, etc. The polymer matrix used for biocomposites can be simply divided into two groups, i.e. non-biodegradable petroleum-based matrix, and bio-derived or biodegradable polymer matrix. In this

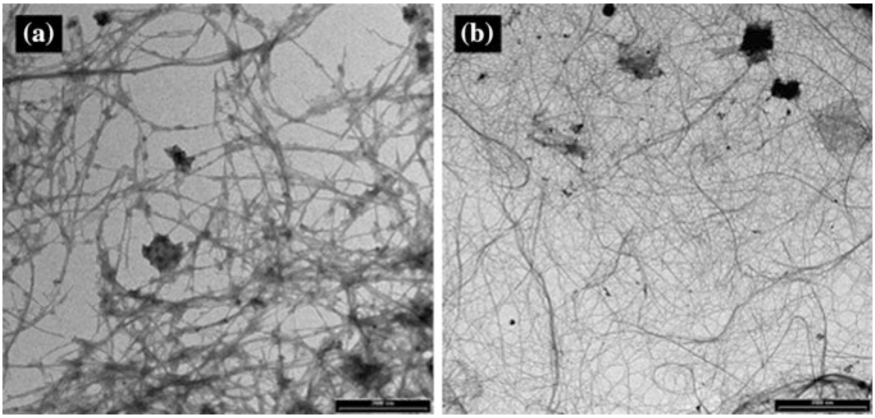


Fig. 18 TEM images of cellulose nanofibers produced from banana peel through **a** chemical treatment, i.e. alkaline treatment, bleaching and acid hydrolysis; and **b** enzyme treatment including alkaline treatment and enzyme hydrolysis. *Scale bar* 2000 nm. (Reproduced with permission from Tibolla et al. 2014)

section, a brief overview of various biocomposites and their manufacturing will be included.

3.2.1 Thermal Stability of Natural Fibers

Compared to glass fibers, a serious drawback of natural fibers is their low thermal stability, which limits the processing conditions of natural fiber biocomposites. It was reported that for lignocellulosic fibers, cellulose starts to degrade as early as 160 and 210 °C in a thermo-oxidative environment and inert environment, respectively; hemicellulose decomposes at the temperature around 160–170 °C while lignin at 220–250 °C (Monteiro et al. 2012; Nguyen et al. 1981a, b; Saheb and Jog 1999). Thermal stability of biocomposites based on a wide variety of natural fibers has been summarized recently (Monteiro et al. 2012). Yao and coworkers studied the thermal decomposition behavior of ten types of commonly used natural fibers, as shown in Fig. 19 (Yao et al. 2008).

Due to the relatively low thermal stability of the natural fibers, the manufacturing process of biocomposites should not exceed the decomposition temperature of the fibers. For thermosets-based biocomposite, the curing temperature should not cause degradation of the fibers while for thermoplastics-based biocomposite, the processing temperature should not exceed the decomposition temperature. Therefore, polyolefins, e.g. polypropylene and polyethylene are ideal since they can be processed at temperature lower than 200 °C. Thermoplastics such as polyamides may be difficult to process with natural fibers since temperature higher than 250 °C is required (Bledzki et al. 2008). Degradation of natural fibers, if occurred during the manufacturing process, will result in (a) inferior mechanical performance due to

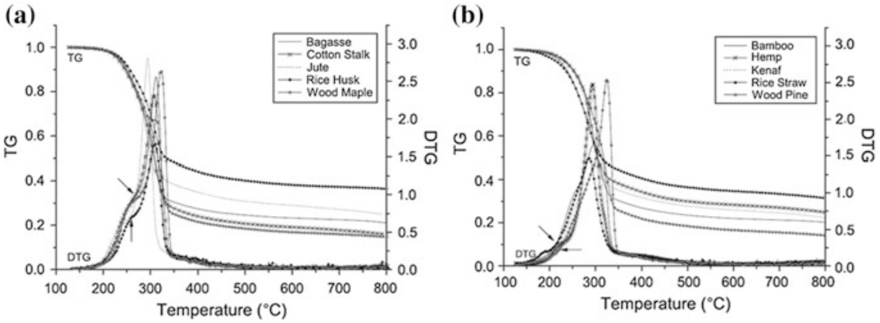


Fig. 19 Thermogravimetric decomposition profile of ten types of natural fibers with a heating rate of 2 °C/min. TGA profiles **a** with clear and **b** without clear hemicellulose shoulders. *TG* Thermogravimetric residual weight. *DTG* Derivative of TG. (Adapted with permission from Yao et al. 2008)

weaker fiber-matrix interface; (b) porous products due to the volatile decomposed compounds; (c) discoloration of the products (Saheb and Jog 1999).

Different strategies have been proposed to improve the manufacturing process of the biocomposites. Mohanty et al. (2009) employed inorganic salts to depress the melting point of polyamides so that the polyamides can be processed at suitable temperatures that would not degrade natural fibers. It is noticed that hydrolysis of the natural fiber or even hydrophilic matrix could easily occur during processing and therefore drying the natural fibers and hydrophilic matrix is critical to maintain the structural integrity of these components. Surface treatments also improve the thermal stability of the natural fibers. The thermal stability of natural fibers is reported to be enhanced by grafting acrylonitrile, enzymatic treatment, plasma treatment, or γ irradiation (Rahman et al. 2015).

3.2.2 Petroleum-Based Polymer Matrix

Although biodegradable matrices ideal towards environmental sustainability, they are usually not an economic solution. Actually, cellulose fibers have been used to reinforce thermoset matrix in automotive industry as early as 1920s, but later they were less competitive compared to synthetic fibers in terms of performance, production, and price (Bledzki et al. 2015). Due to the dominant consumption of the petroleum-based polymers in the global market, utilization of these polymers as matrices would be more commercial viable and realistic for current stage.

Thermoplastic Polymer Matrix

The most commonly used thermoplastic polymers matrices for biocomposites are probably polypropylene and polyethylene, both of which are polyolefins. There are mainly two issues about polyolefin-based biocomposites. First, natural fibers and polyolefin matrix are highly incompatible due to the highly hydrophilic/polar surface of natural fibers and the nonpolar nature of polyolefins. Coupling agents are necessary to strengthen the interface between the nonpolar polyolefin matrix and natural fibers. Second, biocomposites show poor dimensional stability due to moisture sensitivity from the fibers. This issue could also be addressed by coupling agents or other surface treatments (Wanjale and Jog 2011).

As effective compatibilizers, maleated polyolefins can directly be applied in the composite fabrication process. Very recently, Bledzki and coworkers have compared biocomposites using polypropylene and four natural fibers, namely softwood, abaca, jute and kenaf fibers (Nguyen et al. 1981a, b). The matrix/fiber ratio and the manufacturing methods are kept the same to better evaluate the effect of different natural fibers. TP Licocene PPMA 6452, a type of Maleated PP wax, was used as compatibilizer. The fiber-matrix interfaces of all the fabricated biocomposites were evaluated by scanning electron microscopy (SEM) and it was found that all the biocomposites exhibited very good interface due to the presence of compatibilizer. The stress-strain curves of the biocomposites are shown in Fig. 20. After incorporating natural fibers, the composites are stiffer but less stretchy compared to pure PP. This approach demonstrates that different fibers will alter the properties of the fabricated biocomposites. The literature on polyolefin-based biocomposites has been recently summarized by a few review articles (Faruk 2012; Wanjale and Jog 2011; Saheb and Jog 1999; Pickering et al. 2015).

As mentioned above, thermal stability of natural fibers is a critical factor when choosing the manufacturing/processing conditions of biocomposites. Critical review written by Fuqua (Fuqua et al. 2012) and Faruk et al. (2012) describes the appropriate processing conditions for different case scenarios of biocomposite.

When short fiber/filler and thermoplastics are used to fabricate biocomposites, compounding has to be performed first to ensure a good dispersion of fiber/filler in

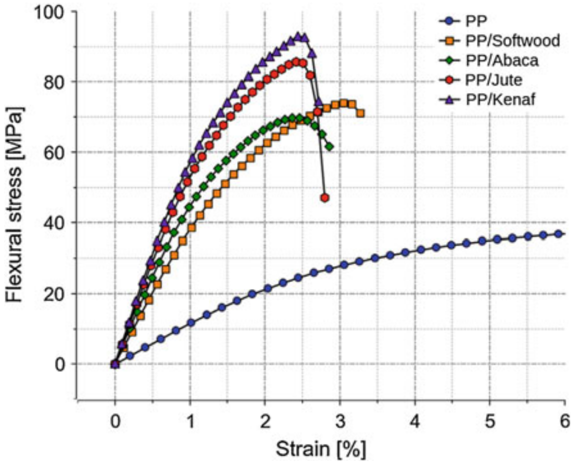


Fig. 20 Stress-strain curves of pure PP and PP composites using softwood, abaca, jute and kenaf. (Reproduced with permission from Bledzki et al. 2015)

thermoplastic matrices. Twin screw extruder is the most efficient method for compounding since it generates very strong shear force to promote dispersion and also allows continuous output of the composite products (Yang et al. 2006; Zhou et al. 2010). However, the shear force could be so strong to reduce the short fiber length (Joseph 1999). Despite its milder shearing, single screw extruder fails to disperse the fiber/filler as well as twin screw extruder (Rahman et al. 2009; Islam et al. 2010). When desired dispersion is realized, the mixture could be processed into final shape by conventional processing methods, e.g. extrusion, compression molding or injection molding.

Unlike short fibers, it is very difficult to achieve uniform fiber dispersion while maintain the fiber length after processing when continuous long fibers and thermoplastics are processed, To optimize the properties of the composites, special manufacturing methods have been used, such as film stacking or suspension impregnation. In film stacking, mats of natural fibers and films of the thermoplastics are stacked layer-by-layer, which is subjected to compression molding to promote the impregnation (Pervaiz and Sain 2003). Suspension impregnation is essentially solution blending of the fiber and the matrix to prepare matrix-coated fibers. The modified fibers can be further compression molded into a composite with desired shape (Shanks et al. 2004).

Thermoset Polymer Matrix

Thermoset resins have been long used to produce high stiffness composites. Many types of thermosetting resins could be used to prepare biocomposites, such as phenolic resin, epoxy, polyurethane, polyester, or vinyl ester (Fuqua et al. 2012; Thakur and Thakur 2014; Faruk et al. 2012). Although the thermoset-based biocomposites will be very difficult to recycle compared to thermoplastics-based biocomposites, they provided many advantages in the manufacturing process:

(a) Before curing, most of the thermosetting systems are low molecular weight monomers or oligomers in the liquid form and they are capable to cure under certain conditions, such as heat, UV or moisture. Therefore, thermosets can be easily processed before curing and they will keep the shape of the mold in which the curing process occurs.
(b) The temperature required for curing is usually much lower than the processing temperature for thermoplastics. This can effectively avoid the thermal degradation issue of natural fibers at high temperature. Mechanical degradation could also be avoided since high pressure is not required.
(c) It is much easier to achieve high loading and well dispersion of the fibers compared to thermoplastics-based biocomposites.

Specifically, resin transfer molding (RTM), vacuum-assisted resin transfer molding (VARTM), compression molding, pultrusion, and other approaches have been used to manufacture thermosets-based biocomposites (Fuqua et al. 2012).

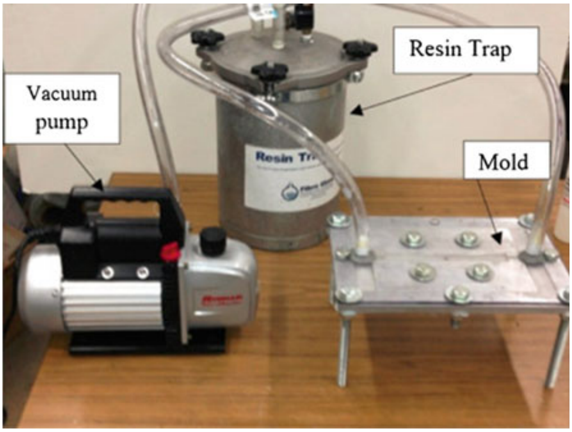


Fig. 21 A processing facility to perform VATRM for biocomposite fabrication. (Reproduced with permission from Barari et al. 2016)

RTM, a closed mold process in which composites are formed between two mold parts, has been used in many studies (Oksman 2001; Rouison et al. 2006). A positive pressure is used for resin injection in RTM process, while in VARTM process a negative pressure generated by vacuum is used to pull the resin into the mold cavity (Barari et al. 2016). A VARTM facility consisting of a RTM mold, a vacuum pump, and a resin trap is shown in Fig. 21. Compared to RTM, the application of vacuum in VARTM effectively reduces the voids in the final composites. However, VARTM is not suitable for high fiber loading process and therefore RTM is more effective for most of the biocomposites manufacturing (Fuqua et al. 2012). Compression molding process is a simple process but can be used to process very high fiber loading composites. Pultrusion is a continuous extrusion process to fabricate composites with a pre-selected cross-section profile. For pultrusion process, care must be taken to make sure the fibers are not mechanically degraded due to the high shear condition.

3.2.3 Biodegradable Polymer

Biodegradable polymers have seen significant development during the last few decades due to the ecological concern and the depletion of petroleum resources. According to Gurunathan and coworkers, biodegradable polymers can be divided into two categories based on the synthesis, namely natural-derived polymers and synthetic polymers, as illustrated in Fig. 22 (Gurunathan et al. 2015). Specifically, natural-derived polymers include agro-polymers, e.g. polysaccharides and proteins, and microbial polymers, e.g. polyhydroxyalkanoates. Depending on the source of monomers, synthetic biodegradable polymers can be classified into bio-based polymers based on bio-derived monomers, and petrochemical polymers based on normal petroleum-based monomers. When these biodegradable polymers are used together with natural fibers, “green composites” can be produced with 100 %

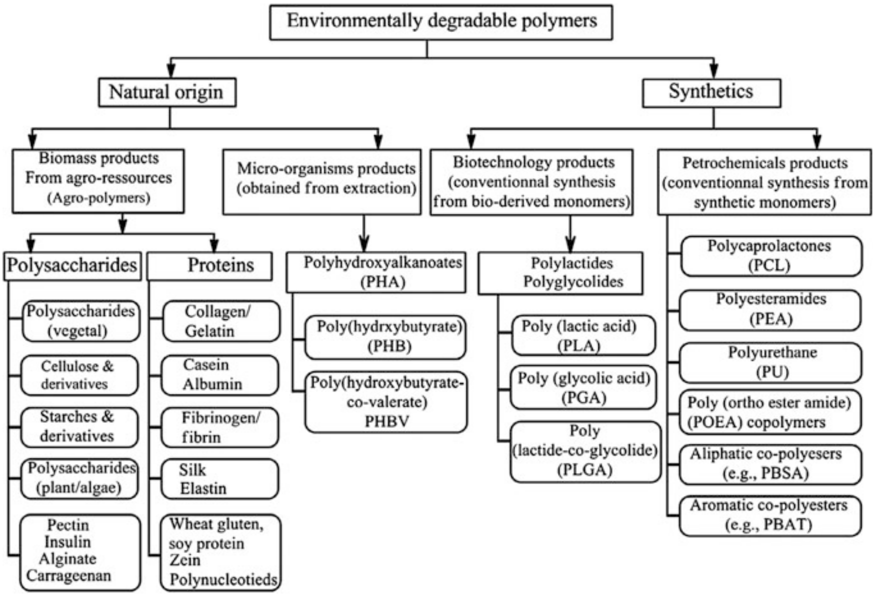


Fig. 22 Classification of biodegradable polymers based on synthetic methods. (Reproduced with permission from Gurunathan et al. 2015)

biodegradability. Biocomposites based on these biodegradable polymers have been the subject of a great number of studies, with, probably, poly(lactic acid) (PLA) and starch as the most promising candidates for matrices.

The degradation behavior of PLA via three mechanisms has been summarized (Averous 2008). PLA could be thermally decomposed at 230 °C. When water is present, hydrolysis of the ester bonds will occur and could be accelerated with thermal or microbial degradation process, if applicable. Biodegradability of PLA, the key property of this class of polymer, has been extensively studied. As illustrated in Fig. 23, PLA degrades via hydrolytic mechanism in the initial stage, in which the decomposition of ester groups causes a decrease in molecular weight. This stage may be accelerated by higher temperature or acidic/basic environment. In the second stage, PLA oligomers can be degraded by micro-organisms. This stage, i.e. biotic degradation, produces carbon dioxide, as indicated by the right axis of the figure (Hartmann 1998). Some of the studies on PLA/natural fiber composites and their mechanical properties are summarized in Table 10. Fiber concentration of 30 wt% is selected to compare with each other.

Starch is another promising candidate for the development of novel biocomposites due to its low price, wide availability, biodegradability, and renewability (Lenz 2005). However, biocomposites based on starch may suffer poor mechanical performance due to the moisture absorption and low processability of starch. Very recently, biocomposites composed of an amylopectin-rich starch and cellulose nanofiber with excellent moisture resistance and mechanical properties have been

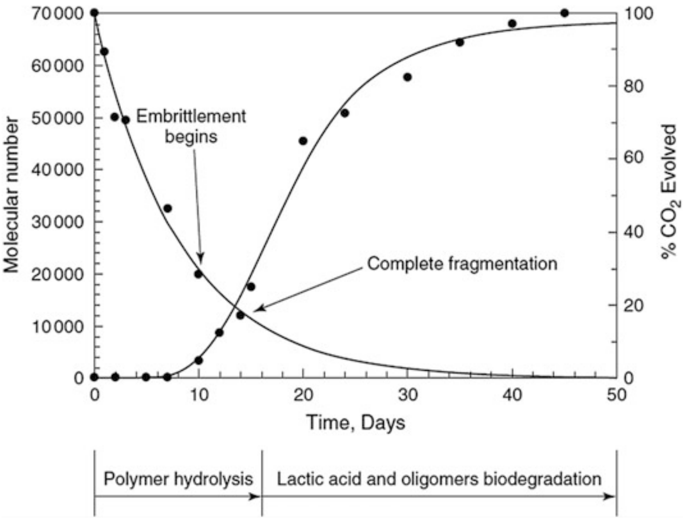


Fig. 23 Abiotic and biotic degradation of PLA. (Reproduced with permission from Hartmann 1998)

reported (Prakobna et al. 2015). Nanofibers with core-shell structure were prepared, with cellulose fiber as the core and starch as the shell. This modified nanofibers improves their distribution in the matrix compared to a simple solution blending of fiber and starch matrix. Biocomposites using core-shell nanofibers showed reduced moisture sorption due to fewer moisture sorption sites. Therefore, due to the better interfacial adhesion and moisture resistance, these biocomposites exhibits excellent mechanical properties under high humidity, as shown in Fig. 24. On the other hand, biocomposites fabricated by simple mixing method show deteriorated performance.

Except PLA (Mukherjee and Kao 2011) or starch (Xie et al. 2013) that have been mentioned above, other biodegradable polymers are also being investigated in a great number of studies, including polyhydroxyalkanoate (Roy and Visakh 2015) and soy-based polymers (Reddy 2015).

3.3 Applications

Due to their advantages of sustainability, light-weight, high specific strength, low costs, and other advantages, biocomposites have been extensively investigated to develop a wide range of applications. However, the poor durability, moisture sensitivity and low thermal stability of natural fibers may hinder the usage of biocomposites when structural properties or exterior environmental stability are required. Design and manufacturing of biocomposites are still being researched to optimize their performance in various applications.

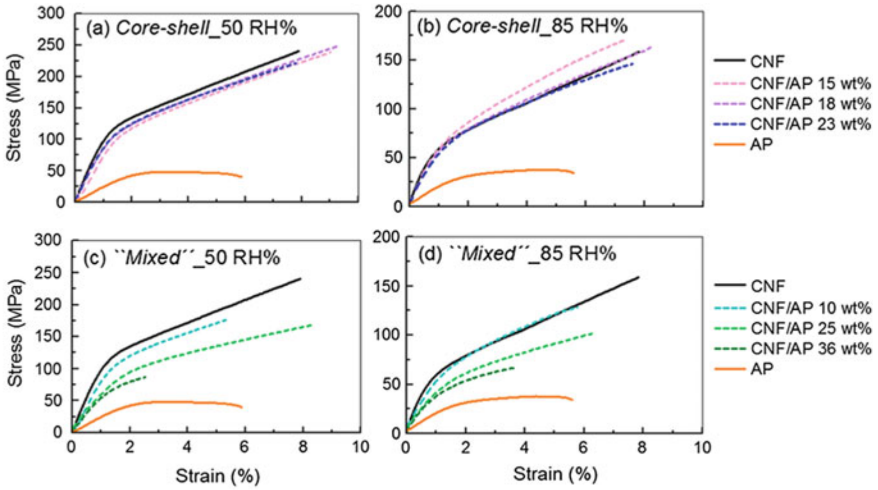


Fig. 24 Stress-strain curves of biocomposites based on starch and cellulose nanofibers under different humidity. *RH* Relative humidity. (Reproduced with permission from Prakobna et al. 2015)

3.3.1 Automotive

In recent years, the automotive industry is seeking more sustainable and recyclable materials for vehicle production. Requested by European Commission, 85 and 95 % of the weight of a vehicle has to be recyclable by 2005 and 2015, respectively. Therefore, the lightweight and sustainability of biocomposites make them very interesting to automotive industry.

Attempts have been made to replace glass fiber by natural fibers in plastic composites used in automobiles (Alves et al. 2011). Particularly, for interior components that do not require high strength and excellent durability, lightweight and cost-effective natural fibers are ideal alternatives to expensive armaid, carbon, or glass fibers. Soy-based seat foams have been used in Toyota Matrix and RAV4. Sugar cane derived bioplastics was used in the luggage compartment in Toyota CT 200. Flax/sisal reinforced polyurethanes were used in door trim panels in Audi A2 (Koronis et al. 2013). There are much less examples of biocomposites used as external parts due to their limited weatherability. Abaca fibers reinforced polypropylene used as the spare tire well covers of Mercedez-Benz A-Class coupe vehicles (Brosius 2006). Some of the biocomposites being produced in automotive industry have been summarized by Bledzki and coworkers, as shown in Table 11 (Bledzki et al. 2006).

Table 11 Commercial application of biocomposites in automobiles (Adapted with permission from Bledzki et al. 2006)

Fiber	Matrix	Commercial products
Wood fiber	Acryl resin	IP in Opel Astra, Zafira, Volvo V40 DP in Opel Astra, Zafira
Needle feed wood fiber mat	Acryl resin	IP in DC A-Class, New Compact Car Mitsubishi Colt, Smart 44 DP in New Compact Car Mitsubishi Colt, Opel Astra, DC DP, C219
Flax/Hemp/Sisal fiber mat	Polyurethane	DP in DC S/E class
Bast Fiber mat	Epoxy Resin	DP in BMW 5 series
Bast/polypropylene fiber	Polypropylene	DP in DC W251
Wood Flour	Polypropylene	DP in Fiat Punto, Bravo, Alfa 147, 155
Coir Fiber	Latex	DC in Diverse series

DP Door panel; *IP* Instrumental panel

3.3.2 Stimuli-Responsive Materials

Stimuli-responsive materials (sometimes called “smart materials”) are receiving significant attention over the last decades (Cao et al. 2015; Roy et al. 2010). Stimuli-responsive materials can be broadly defined as materials that can change their properties, e.g. shape or optical/mechanical/electrical properties, upon the application of external stimuli such as temperature or pH.

Shape memory polymer (SMP) represents an important group of stimuli-responsive materials (Zhang et al. 2014a, b; Meng and Li 2013). However, most of the SMP are based on petrochemical monomers and the resulting SMP are usually not biodegradable. Recently, SMP based on biocomposites has been investigated. Fejos and coworkers fabricated biocomposites based using flax fiber and epoxidized linseed oil. Epoxided linseed oil was cured by anhydride to produce permanent network. Glass transition temperature of this permanent network was determined and used as the switching temperature. Despite the good fixing ratio, the recovery ratio is low due to the low crosslinking density of the network (Fejos et al. 2013). In another study, Tsujimoto et al. prepared SMP using epoxidized soybean oil and polycaprolactone and therefore the SMP is completely biodegradable (Tsujimoto et al. 2015).

Castro and coworkers reported a biocomposite actuator based on flax-reinforced polypropylene (Le Duigou and Castro 2015). A bilayer structure was prepared with flax fiber present in one of the layer. Taking advantage of the water uptake and swelling properties of flax fiber, the biocomposite can be triggered by moisture or water to exhibit self-bending behavior. The structure and the responsiveness of the actuator are illustrated in Fig. 25.

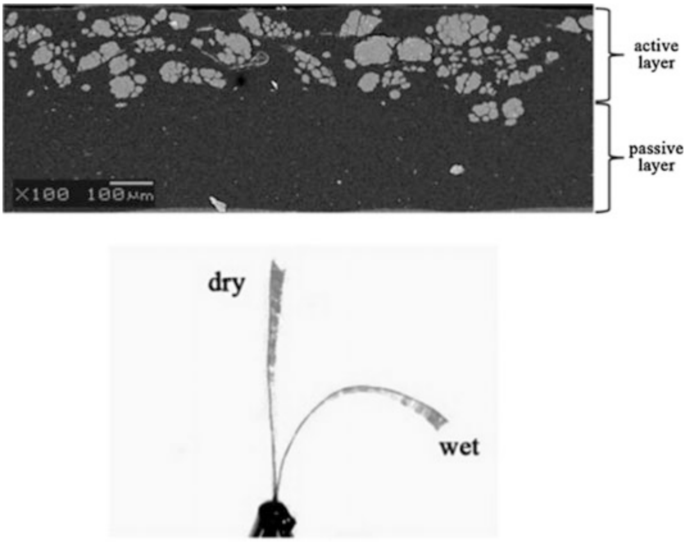


Fig. 25 The microstructure (*top*) and self-bending behavior (*bottom*) of the biocomposite actuator. (Reproduced with permission from Le Duigou and Castro 2015)

3.3.3 Construction

Natural fiber reinforced biocomposites have been used considered as an alternative to conventional building materials, such as concrete and steel. The advantage of using biocomposites as construction materials include wide availability, lightweight, high specific strength, corrosion resistance, sustainable, and easy processing. Compared to concrete and steel, the relatively high cost and the weaker mechanical properties and anti-flammability are the key issues that need to be solved. Biocomposite used for construction purpose have been well reviewed by the book edited by Masuelli (Masuelli 2013).

3.3.4 Other Applications

Various other applications have been explored for biocomposites. Misra and coworkers reviewed some recent progress in the application of biocomposites, including the applications in automobile industry, conducting composites, barrier property, drug delivery, adhesives, etc. (Pandey et al. 2010). Other applications, such as packaging (Islam et al. 2010), or medical (Abdul et al. 2015), are also reviewed recently.

4 Conclusion

Composites from natural fibers are gaining popularity and may have a bright future for development and application as more and more attention is being paid to energy utilization and environmental health. It is highly desired that the composites developed today could be obtained from a renewable, recyclable, and reusable source. The application of natural fiber-polymer composites has been revitalized due to their advantages such as being cost-effective, good performances, easy for modification, and more importantly, environmentally friendly. The performances of natural fiber-polymer composites can be significantly improved via surface modification of natural fibers by various coupling agents. Natural fiber-polymer composites can out-perform traditional composites if designed properly. The market shares of natural fiber-polymer composites are supposed to increase attributed to those advantages.

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Lignin as an Additive for Advanced Composites

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Abstract Lignin, an abundant renewable resource material next to cellulose, can be one of the most essential bio-resources as a raw material for the production of environmentally friendly polymers and polymer composites. Due to its chemical structure, lignin can provide additional functionalities in composites. It can be used as reinforcers, fillers, compatibilizers and even stabilizing agents in polymer composites. In this chapter use of lignin in composites, its additional benefits and possible applications were summarized. Structure—process—property relations were particularly emphasized. Because of the aromatic structure and multifunctional side groups, lignin can be a promising, environmentally friendly additive as a free radical scavenger which prevents oxidation reactions. For the structural composite applications, material properties were found to be highly dependent on process conditions. One can observe controversy in the reported mechanical properties of composites with similar components and similar lignin concentrations. Thus in some studies addition of lignin resulted with enhanced strength and modulus; while lignin just acted as a filler in some others. Those studies should be carefully evaluated considering the process conditions. Further improvements can also be achieved after modifying lignin chemically.

Keywords Lignin · Biocomposites · Additive · Compatibilizer · Filler

1 Introduction

Lignin is the second most abundant polymer on Earth and mainly found in hard and softwood trees which contain 20–30 % lignin. From the total pulp production, approximately 70 million tonnes of lignin are available per year. However only 2 %

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of it is extracted and used as pure lignin, the rest is used as fuel additive(Lignin Product Market Forecast 2016). Except from wood pulp, lignin can also be obtained from different grasses, such as corn stover, sugar cane bagasse, napier grass, annual ryegrass, tall fescue (Fukushima and Kerley 2011). The large variety of sources allows extraction of lignins with different chemical structures. Generally, lignin contains p-coumaryl alcohol, coniferyl and sinapyl alcohol as main components (Glasser 1999). Their ratio into lignin chemical structure depends on the source it is obtained. Hardwood lignins obtained from deciduous plants mainly contain coniferyl and sinapyl alcohol, while coniferyl alcohols are the main component of softwood lignins extracted from conifers plants. The carbon content of lignin attracts attention and puts lignin as one of the most promising materials for production of carbon. Studies on quantification of carbon into lignin structure reveal an average of 50 % carbon content (Lamlom and Savidge 2003). Despite the source, the extraction process also influences the chemical structure of lignin (Liu et al. 1999). The extraction process includes immersion of wood pulp into a solvent (process called pulping), cooking the mixture at temperatures between 150 and 200 °C in order to separate the lignin from the pulp lignocellulose structure and separation of the lignin from the pulp liquor by filtration or centrifugation. The obtained lignin can be further purified in order to remove side products such as ash and carbohydrates. Since the lignin obtained after pulping has high polydispersity —an important parameter on mechanical properties—fractionation can also take place (Dallmeyer 2013). During pulping process the wood may be treated with alkalis, sulfites, organic solvents, enzymes, ionic liquids or steam (Calvo-Flores et al. 2015). Each treatment imparts different functional groups onto lignin structure. The most widely produced structures are Kraft lignin, lignosulfonate and organosolv lignin.

2 Lignin in Polymer Composites

Though lignin is a light-weight (half the density of talc or calcium carbonate), stiff and brittle bio-polymer, it is rarely used as a bio-filler in plastic compounds (Agarwal et al. 2014). However it can improve the thermal properties, process and light stability of polymeric materials because of its phenolic nature (González Sánchez and Alvarez 1999). Lignin is an amorphous polyphenolic material which contains a large number of chemical functionalities in its molecular structure. These chemical functionalities make lignin an appropriate element for the polymeric applications (Satheesh Kumar et al. 2009). The presence of the phenolic groups imparts antioxidant properties to lignin which provides stability to the polymers against thermo- and photo oxidations (Stiubianu et al. 2009). In this chapter functional applications of lignin in polymers and polymer composites were summarized. As emphasized in tens of studies, use of lignin provides additional functionalities in composite structures. It might be speculated that lignin with its processability, low cost and low density can even replace widely used synthetic additives.

2.1 *Lignin as a Stabilizer in the Polymer Composites*

Stabilizers are chemicals that prevent decomposition of polymers induced by oxidation reactions at elevated temperatures or under irradiation (Scott 1979; Yousif and Haddad 2013). Antioxidants and photo-stabilizers are compounds that suppress the action of free radicals on other molecules or prevent their formation. Due to its aromatic structure and multifunctional side groups, lignin can act as a free radical scavenger, can reduce the divalent ions or prevent oxidation reaction (Espinoza-Acosta et al. 2016).

The antiradical activity of lignin can be used in plastic films for packaging applications. Polylactic acid (PLA)/lignin composites are one example that proves the stabilizing property of lignin. PLA extruded films containing different amounts of lignin nanoparticles were investigated by following the radical scavenging activity of these composites. (Yang et al. 2016) Antiradical activity tests based on the radical scavenging activity of the free radical DPPH (2,2-diphenyl-1-picrylhydrazyl) showed increased ability of the film for radical scavenging when increasing the concentration of lignin. The overall mitigation test showed lower migration values with the increase of lignin content when incubated in isooctane, but not in ethanol. However, all the mitigation values were lower than the limits allowed by EU standards, showing possibility of the composite films to be used for fatty food packaging application. The molecular weight of lignin also influences its antioxidant activity (Domenek et al. 2013). Domenek et al. studied this effect on PLA/lignin films. They observed increase in low molecular weight fractions during the thermal degradation of the film showing plastization effect. However, the low molecular fractions formed from high molecular weight increased the generation of molecules with anti-radical activity and thus improved the resistivity of the films against oxidative thermal degradation.

The antioxidant ability of lignin also improves the retention of mechanical properties of polymer composites. Gadioli et al. reported the antioxidant ability of lignin extracted from Eucalyptus wood (Gadioli et al. 2016). Small amount of lignin added into polypropylene (PP) before its extrusion improves its mechanical stability under UV-light exposure. The aging test of PP/lignin mixture reveled elongation loss after 200 h exposure to UV-light, which is double than that of pure PP, and higher than PP stabilized with commercial stabilizer. Improved yield stress and Young's modulus was also observed but with lower intensity. The same group investigated the effect of lignin content into Eucaliptus fibers on the mechanical and thermal properties of PP/Eucaliptus fiber composites (Gadioli et al. 2014). Eucaliptus fibers (30 %wt. respect to PP content) significantly improved the tensile and flexural strength of PP. In order to prove the effect of lignin on composite's thermal and mechanical properties under aging, Eucaliptus fibers with different lignin contents were used. The results showed that increased lignin content not only improves the mechanical stability of the composites after accelerated and environmental aging, but also improves fiber/matrix interaction in PP/Eucaliptus fibers composites and thus their mechanical properties. Antioxidant property of lignin also improved the tensile strength retention in styrene-butadiene rubbers, at a cost of reduction in breaking elongation (Liu and Cheng 2010).

Thermal stability of polymers is another feature that can be improved when adding lignin into polymeric composites. Due to its antioxidant ability lignin can delay the degradation of polymers at elevated temperatures (Gadioli et al. 2014; Liu et al. 2016). Except the increment of the initial degradation temperature and the complete degradation temperature, modified lignin can also act as a flame retardant (Liu et al. 2016).

2.2 Lignin as a Reinforcer in Polymer Composites

The natural polymers are promising materials to replace fossil fuels due to growing concerns on environmental effects. For that reason, there is also a great interest in use of lignin in polymer composites to obtain outstanding mechanical properties (Dias et al. 2016). It is coherent to use lignin as a reinforcing material in polymer matrix, because of the nature of lignin which is supposed to be mechanical support for plants. The advantages of lignin like cost, eco-friendly nature and abundance make it promising material for researchers to be used in high performance polymer composites (Kai et al. 2016).

Although 25–40 % (w/w) was reported to be threshold lignin weight ratio for improving mechanical properties, it is possible to exceed this value via proper homogenization techniques and additives. Li et al. (1997) produced 85 % (w/w) kraft lignin based poly (vinyl acetate) with two plasticizers blends by homogenous mechanical mixing. Solution casting method was used to prepare composites with 85 % (w/w) lignin content with promising mechanical properties. The thermoplastics showed potential for increased mechanical properties. The tensile strength and Young’s modulus of these thermoplastics were increased to 25 MPa and 1.5 GPa, respectively. The mechanical properties are directly related with molecular weight of kraft lignin. Furthermore, the mechanical properties of polymeric materials are depend on production method. And in this study extrusion molding technique was used to produce composite samples with considering melt flow index values which is one of the most critical parameter for extrusion molding.

The most widely emphasized challenge of the lignin is its interaction with matrix polymers. The pure lignin has low miscibility with polymers. Because of the low miscibility, problems like lignin agglomeration and phase separation occur. Many studies have been conducted to observe better compatibility and higher mechanical properties by the modification of lignin with functional groups (Kai et al. 2016). For instance, Sailaja and Deepthi (2010) also studied the effect of compatibilizer on mechanical properties of lignin based composites. In the study, lignin was blended with low density polyethylene (LDPE) up to 40 % (w/w), where maleic anhydride was used as a compatibilizer. The mechanical measurements showed that mechanical properties of most of the composite samples had inferior properties compared to reference sample. However, addition of 20 % lignin coupled with LDPE-g-maleic anhydride resulted with 5 % increase in breaking elongation (Fig. 1). Thought incorporated into a hydrophobic polymer and having a lower molecular weight such an enhancement should be considered promising.

Dias et al. produced lignin reinforced polypropylene and investigated mechanical, thermal and physical properties of composite. Lignin and polypropylene blends were extruded in twin screw extruder and samples were prepared by injection molding. Lignin content varied to see its effects with the use of maleic anhydride compatibilizing agent. To determine mechanical properties of composites, tensile (ASTM D638), flexural (ASTM D790) and impact (ASTM D 256) tests were conducted. The impact test method was notched Izod impact with 5 ft-lb pendulum. The impact strength shows the resistance of material against breakage under high speed forces (Dias et al. 2016). Compared to neat PP films 10 % lignin incorporation reduced the impact around 15 % without the use of compatibilizer according to Table 1. However, at the same lignin content addition of 3 % PP-g-MA induced the impact properties, resulting in similar impact strength. Most promising results were obtained from the flexural strength measurements. Even addition of 30 % lignin in the presence of PP-g-MA, caused 10 % increase in flexural strength. On the other side addition of lignin resulted with up to 25 % reduction in tensile strength because of weak adhesion between materials. Particularly without the compatibilizer, immiscibility had pronounced effects on composite performance. There was a significant reduction in the modulus, which

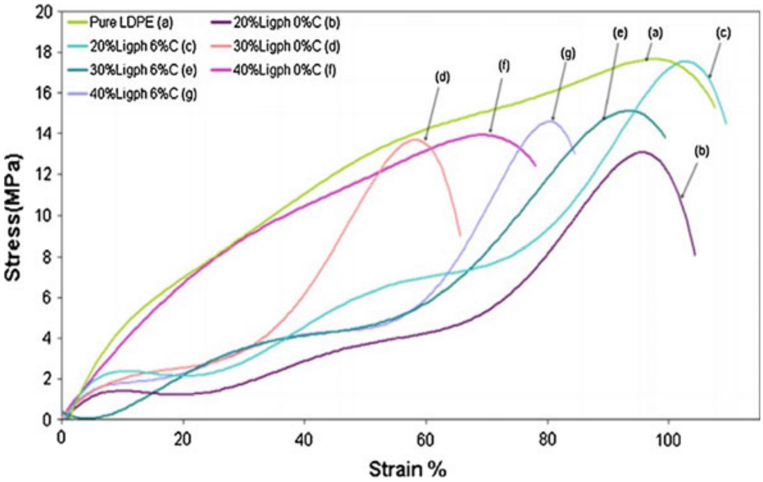

Fig. 1 The stress/strain curves of LDPE/ligph (phthalated lignin) blends (with permission from Elsevier Inc) (Sailaja and Deepthi 2010)

Table 1 Tensile, flexural, and impact properties of composites prepared with kraft lignin, polypropylene (PP) and maleic anhydride (PP-g-MA) (with permissions from Elsevier Inc) (Dias et al. 2016)

(PP/lignin)/ PP-g-MA	Impact strength (J/m)	Flexural strength (MPa)	Tensile strength (MPa)	Flexural modulus (GPa)	Tensile modulus (GPa)
(100/0)/0	16.84 a	36.19 a	24.87 a	1.109 a	1.240 a
(90/10)/0	14.97 a	30.57 b	18.05 b	1.181 a	0.823 b
(90/10)/3	16.77 a	32.04 b	18.38 b	1.059 a	1.060 a
(70/30)/3	16.56 a	40.37 c	17.62 b	1.072 a	1.135 a
CV (%)	11.15	9.10	4.57	16.07	11.55

Means followed by the same letter within a column are not significantly different by Scott-Knot method ($P > 0.05$)

was improved after 3 % compatibilizer incorporation. Resins with the hydrophilic, polar structure might be better matrix for lignin.

According to another study (Thakur et al. 2014) incorporation of lignin had significant effect on mechanical properties of composites. It was showed that flexural and torsion modulus of composite increase with the increase in lignin content, whereas tensile properties decreased with increase in lignin content (Thakur et al. 2014). Dias et al. obtained decrease in flexural strength of PP after 10 % lignin addition, which increased after a threshold value of 30 %. The interfacial adhesion between lignin and matrix material is critical for conservation of flexural properties (Dias et al. 2016). Another study on lignin—polypropylene composite study was conducted by Toriz et al. (2002a). In this study, lignin content was kept between 10 and 60 % (w/w). Incorporation of lignin into polypropylene reduced tensile, flexural and impact strength, whereas increased Young's and flexural modulus which is similar to the work of Dias et al. (2016). When inorganic fillers were incorporated together with lignin, the strength properties increased further compared with only lignin containing composites. This was explained with the better lignin composite interaction and improved lignin filler distribution (Toriz et al. 2002a). Most probably the controversy between different reports arises due to differences in the preparation processes.

Liu et al. produced cheap, environmentally friendly biocomposites from lignin cellulose fibers (LCF) and tall oil based polyamide as thermoplastic material. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and rheology analysis were performed to determine the effects of LCF amount on thermal, rheological and mechanical properties. There is almost no change on relaxation procedure of polyamide after inclusion of LCF. Combining LCF and PA increased the shear modulus and complex viscosity of composite according to rheological tests. When the LCF concentration increased, modulus and strength also increased. On the contrary, breaking elongation of the samples showed reduction with the increase in LCF amount. LCF is reported to be a promising reinforcer for tall oil based polyamide.

By this way, the cost and weight of the polymer decreased, while there is notable increase in the strength of pure PA. PA-LCF biocomposites are speculated to be possible candidates to take the place of petroleum plastics in such applications. However, interestingly the onset of decomposition temperature decreased drastically, when LCF concentration increased (Liu et al. 2015).

Hilburg et al. studied lignin reinforced nanocomposites. Kraft lignin based nanocomposites were prepared by incorporating the lignin separately into polystyrene and poly (methyl methacrylate) with lignin weight concentrations of 3.2, 7.1, 19.6 % and 4.5, 8.3, 22.1 %. According to tensile test results, there was nearly 50 % reduction in modulus, while toughness of all samples increased from 0.15 MJ/m^3 up to around 3.7 MJ/m^3 with the addition of lignin. Furthermore, two polymers exhibited opposite responses with the presence of lignin. The ultimate elongation of lignin based poly (methyl methacrylate) samples is about the double of lignin based polystyrene at high lignin concentrations. Softening temperature was determined via dynamical mechanical analysis (DMA) to observe glass transition temperature. Thermoplastic nanocomposites exhibited higher loss peaks compared to homopolymer, because of durable interaction between lignin and polymer. Lignin based thermoplastics are found to be more promising materials compared with other inorganic based nanocomposites, with the additional cheapness and renewability (Hilburg et al. 2014).

Sahoo et al. produced polybutylene succinate (PBS) and lignin based composites by using melt mixing method. Effects of lignin and compatibilizer on composite properties were analyzed. High amount of lignin (65 % lignin weight content) was successfully incorporated into PBS, which showed an increase in both tensile and flexural properties of composites. The tensile, flexural and impact properties of composite material improved with adding 50 % lignin and 1 % compatibilizer which is polymeric methylene diphenyl diisocyanate (PMDI). Furthermore, addition of lignin and PMDI enhanced the heat deflection properties of pure PBS. SEM images also revealed that PMDI as a compatibilizer improved the interaction between PBS and lignin. In the presence of a functional compatibilizer, enhanced tensile, flexural and thermomechanical properties were observed. Incorporating compatibilizer down to 1 % enhanced mechanical properties because of the improved interface between lignin and polymer (Sahoo et al. 2011).

Luo et al. used lignin as a reactive reinforcing element in biofoam composites. Soy based polyurethane biofoam (BioPU) was prepared via self-rising method in water blowing system. Lignin was incorporated into the foam at the first step of synthesis at various concentrations (0, 5, 10 and 15 %). Prepared composite foams were named according to the lignin content: BioPULignin0, BioPULignin5, BioPULignin10 and BioPULignin15. The mechanical and thermal characterization of samples were realized. As shown in Fig. 2, up to 10 % lignin content, mechanical performance increased continuously. BioPU composites, especially BioPULignin10 exhibited nearly 50 % increase in the specific compression and flexural modulus (Fig. 2). Likewise, dynamic mechanical analysis (DMA) results confirmed that lignin addition enhanced mechanical properties of composite and improved thermal stability of composite (Luo et al. 2013).

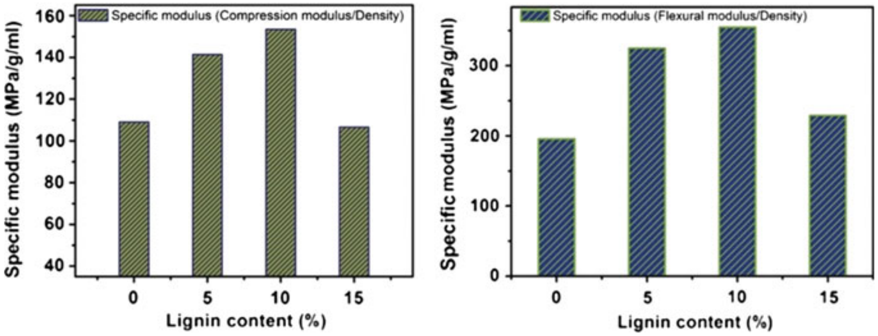

Fig. 2 Specific compressive modulus (ratio of compressive modulus to density) (left) and specific flexural modulus (ratio of flexural modulus to density) (right) of neat biofoam and biofoam composites (with permissions from Elsevier Inc.) (Luo et al. 2013)

Yu et al. studied on the modification of nitrile butadiene rubber (NBR) composites by using lignin and epoxy resin. After preparation of NBR and lignin master batch by latex compounding method, epoxy was added into the mixture via melt compounding procedure. Curing was realized at 160 °C for compounds under press to obtain 1 mm thick sheets. Furthermore, same steps were conducted again without addition of rubber additives such as sulfur to make crosslinking reaction between lignin and epoxy. Lignin epoxy cross-linked samples performed better mechanical properties compared to lignin as direct filler. Additions of 15 % epoxy increased tensile strength from 19.8 to 22.9 MPa, while decrease in elongation from 835 to 551 %. Furthermore, 15 % epoxy incorporation enhanced tear strength nearly 80 % (Yu et al. 2016). The reason for the mechanical improvement of lignin-epoxy cross-linked samples was mentioned to be due to excellent compatibility between lignin and epoxy resin because of polar nature of both lignin and epoxy resin. Table 2 summarizes the mechanical properties of both cross-linked and non-cross-linked lignin results as a reinforcing material (Yu et al. 2016).

Table 2 Mechanical properties of composites (The standard error is presented in brackets) (with permissions from Wiley Inc.) (Yu et al. 2016)

Samples	Tensile strength (MPa)	100 % modulus (MPa)	300 % modulus (MPa)	Elongation (%)	Hardness (shore A)	Tear strength (kN/m)
NBR/50lignin	19.8 (1.1)	1.8 (0.2)	2.7 (0.2)	835 (47)	58	39.8 (2.6)
NBR/50lignin/5F51	19.9 (0.9)	2.4 (0.1)	4 (0.3)	791 (32)	73	46.3 (3.1)
NBR/50lignin/10F51	22.3 (1.5)	4.9 (0.3)	8.4 (0.2)	628 (37)	79	58.1 (2.9)
NBR/50lignin/15F51	22.9 (1.4)	6.9 (0.2)	12.4 (0.5)	551 (42)	83	72.4 (4)
NBR/50lignin/20F51	20.8 (2.1)	8.2 (0.4)	13.3 (0.4)	460 (36)	87	84.5 (4.7)

F51 is a trade name of an epoxy resin

2.3 Lignin as a Filler in Polymer Composites

The effects of lignin as fillers in polymer composite have been investigated in several studies. Those of the applications focused on reduction of composite costs primarily, while moderate mechanical properties were sought.

The research by El-Zawawy et al. (2011) was aimed to investigate the use of lignin precipitated from black liquor of alkaline pulping of rice straw as fillers after modified with transition metal cations, Fe(III), Ni(II) and Co(II), in the production of a polystyrene based composite for polymer packaging applications. The sample preparation of modified lignin by metal cations was done by sorption of cations onto lignin and lignin model vanillin, then followed by stirring of mixtures before its precipitation and filtration process. The composite samples were prepared from powdered alkaline lignin (AL), Vanillin (V), and their complexes, in a 5 % weight, which was extruded with the polymeric matrix, polystyrene (PS) by twin screw compounder system. The resulting composites were molded into films of 0.5 mm thick. Adding both vanillin and lignin resulted in a decrease in the tensile strength, while adding both Co(II) modified vanillin and lignin improved the tensile strength as shown in Table 3. The improvement of the tensile strength with the addition of the complexes is in agreement with the fact that the presence of the vanillin and lignin complexes are compatible with the PS. Filler distribution in polymer composites was studied by change in color under different wavelengths which gives an idea about using the lignin as a remarkable filler for polymer used in packaging. According to test results both cobalt ions (Co II) modified vanillin and lignin complexes mixed with polystyrene matrix caused remarkable change in color. The reason behind color change is that, typical lignin fraction exhibits the basic UV spectra absorption maximum at wavelength of 282 nm, which originates from non-conjugated phenolic groups (aromatic ring) in lignin. The addition to the cobalt (II) chloride solution results in another small peak (λ_{max} = 258 nm) next to the peak at λ_{max} = 282 nm (El-Zawawy et al. 2011).

On the other hand, the values of the glass transition (Tg) for various PS blends was analyzed for their miscibility. The decrease in the Tg can be attributed to the immiscibility between the PS matrix and fillers vanillin and lignin. Furthermore, the addition of both Co(II)–vanillin and Co(II)–lignin complexes to the PS matrix resulted in an increase in the Tg compared to that resulting from the addition of both

Table 3 Physical properties of PS and PS composites (with permission from Elsevier Inc.) (El-Zawawy et al. 2011)

Samples	Tensile strength (MPa)	Elongation at break (%)
Polystyrene (PS)	0.708	5.42
PS- Vanillin	0.566	1.88
PS- Lignin	0.473	2.72
PS- Co(II)–Vanillin	0.797	3.78
PS- Co (II)–Lignin	0.963	1.44

vanillin and lignin to reach ~87 °C. This means that the metal cations results in a slightly better compatibility with PS compared to the unmodified form (El-Zawawy et al. 2011).

In another study lignin and switchgrass were added into poly(butylene succinate) PBS as filler. The effects of mixed fillers of lignin and switch grass (1:1 ratio) was studied and compared with composites from individual fillers and neat polymer. The composite samples fabricated from PBS and 50 wt% of fillers using a micro extruder followed by a microinjection molder. The tensile and flexural properties of the composites were analyzed to characterize the effects of each fillers and also hybrid composites with PBS matrix. The tensile strength of the composites decreased notably with the lignin incorporation, when compared with neat PBS. The only improvement was obtained after compatibilization of hybrid filters of lignin and switchgrass. In contrast incorporation of fillers into the matrix improved the flexural modulus by 283–418 % compared with that of neat polymer. Hybrid filler (1:1 ratio of lignin and switchgrass) proved more beneficial over single filler in the composites that obtained a better flexural strength than the individual filler based composites (Sahoo et al. 2013).

Dynamic mechanical analysis is widely used for the study of viscoelastic behavior of composite materials. The storage modulus gives information about the stiffness and the peak of damping measurement (tan δ) gives information about the glass transition temperature (Tg). The storage modulus and tan δ of PBS and its reinforced composites were analyzed. The storage modulus of the materials at room temperature increased with the filler incorporation. The switchgrass filled composites resulted in higher modulus value and lignin-filled composites showed the lower modulus value among all the composites, which may attribute to the composition and nature of fillers. The storage modulus of the hybrid composites was intermediate between the two individual filler based composites. The SEM micrograph of the tensile fractured surface of the lignin composite as shown in Fig. 3a is comparatively smooth and homogeneous that may suggest a better compatibility of lignin (compared with switchgrass) in the

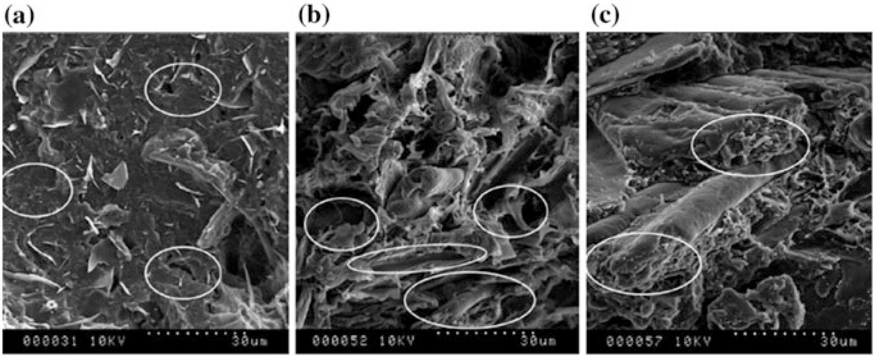

Fig. 3 SEM micrograph of composites at 30 lm scale and 10 kV operating voltage. **a** Lignin composite. **b** Switchgrass composite. **c** Hybrid composite (with permissions from Wiley Inc.) (Sahoo et al. 2013)

PBS matrix. The matching of solubility parameters and possible polar-polar interaction could be the causes of this compatibility(Sahoo et al. 2013).

Diop et al. investigated lignin's dispersion in low density polyethylene (LDPE) using copper (II) sulphate pentahydrate ($CuSO_4.5H_2O$) as a dispersing agent. Lignin concentration was kept under 20 % and it was extracted from softwood kraft black liquor. The composites were manufactured from mixed maleated polyethylene (MAPE) with 20 % LDPE at the first stage. In the second stage, lignin and the remaining LDPE were added and mixed at 60 rpm for 7 min. The specimens were moulded into dumb-bell and pressed under 5 MPa press.

An interfacial agent (i.e., compatibilizer) such as maleic anhydride is needed to increase the compatibility and reduce the interfacial tension between components in immiscible polymer blends to obtain desired final properties. Maleated polyethylene (MAPE) efficiently plays its role by improving the compatibility between the LDPE matrix and lignin. These effects of MAPE could be attributed to the new bonds formed between maleic anhydride group-grafted LDPE and the OH groups of lignin. On the other hand, there is a good compatibility between the LDPE and the PE matrix segments of MAPE. These interactions are thus necessary for improving the composite's mechanical properties. MAPE can improve the interface adhesion but cannot support large deformations.

Composites of LDPE reinforced with lignin showed an improved interface, resulting in increased mechanical properties (tensile modulus and tensile stress). Furthermore, the addition of 3 % MAPE induced an increase of 37 % of the Young's modulus (Diop et al. 2015). Lignin was uniformly dispersed in the presence of $CuSO_4.5H_2O$. It is important to note that $CuSO_4.5H_2O$ could also play an antibacterial role in prospective applications. Generally, it was possible to introduce 20 % (w/w) of kraft lignin as filler in LDPE without the loss of mechanical properties.

Toriz et al. compared the mechanical properties of lignin-PP (polypropylene) blends according to lignin concentration in the mixture. Use of traditional filler combinations such as talc and mica with lignin was also evaluated. Blends were prepared by melt mixing the proper quantities of the components in a container, which was poured into a Brabender bowl mixer. Composite pellets were metered to an injection-molding machine at pressures between 600 and 1000 psi and 170 °C. The effects of adding lignin to PP resulted in decreased tensile strength, proportional to the quantity of lignin. There was a slight loss in flexural strength up to 40 % of lignin content and a marked reduction of flexural strength at 60 % lignin load. Impact strength decreased dramatically with the addition of lignin. Combining lignin and treated mineral fillers improved properties compared to only lignin and PP. For instance, tensile strength of 70:30 PP/Lignin with untreated mica increased from 20.94 to 27.83 Mpa when surface treated mica was added. In 70PP/15L/15 treated mica the tensile strength further increased to 29.82 MPa. This might be due to the better lignin particle distribution and better interaction between the treated fillers and the matrix (Toriz et al. 2002b).

In a similar study, polypropylene was reinforced with wood flour (WF), cellulose and lignin at different loadings to analyze the surface chemistry during weathering. The mixtures were melt-blended in a co-rotating, twin-screw extruder. A hot press was used to produce the composites by compressing the mat at a pressure of 4 MPa for 6 min. The surface characteristics of composites were studied by atomic force microscope (AFM), Fourier transform infrared (FTIR) spectroscopy, and X-ray photo electron spectroscopy (XPS). For different filler-reinforced composites, the changes during weathering in surface morphology, surface chemistry, flexural, and thermal properties were different. Compared to cellulose-based composites, samples containing lignin exhibited smoother surfaces and less loss in flexural and thermal properties compared with composites without lignin after weathering, which suggested that lignin has stabilization and anti-oxidation effects (Peng et al. 2015).

The miscibility of lignin with commercial polyolefin polymers such as polypropylene was aimed to be enhanced via lignin modification by maleic anhydride (MA) and dichloroethane (CE), so as to increase its solubility and compatibility toward PP. The lignin from black liquor was filtered and acidified for purification prior to chemical modifications by MA and dichloroethane. Purified lignin was added to the molten MA in small portions in a separate setup and the reaction mixture was remounted in microwave oven. The resultant reaction product was filtered, and washed with an excess of distilled water. The modified lignin and PP were blended by melt mixing in different proportions (i.e., 5, 10, 15, 20, and 25 wt%) of lignin. Dumbbell-shaped specimens were then prepared by injection molding (Maldhure et al. 2012). Composites fractural surface morphology analysis was done to investigate the interactions between the modified lignin and PP matrix blends. In the case of the PPMA-Lig blends, the MA-Lig particles were well dispersed and also homogeneously distributed within the PP matrix. In this case, better interfacial interaction between MA-Lig and the PP matrix was achieved and also no holes & agglomerations took place, even up to 25 wt% loading. In the case of the CELig blends, the lignin particles were uniformly distributed up to 15 wt% loading. Upon further increases in the CELig loading, agglomeration started and this may have been due to less compatibility of CELig with the PP matrix compared to that of MALig. However, both types of modifications proved advantages in connection to the consequent blends' mechanical properties (e.g., tensile strength, elongation at break, Young's modulus, impact strength) compared to blends arising out of unmodified lignin (Maldhure et al. 2012).

2.4 Lignin as a Compatibilizer in Polymer Composites

Properties of composites materials and blends are strongly related to the interfacial interaction between the reinforce and matrix (Imre and Pukánszky 2013). Synergy between the constituents is possible only if the interaction between them is sufficient to stabilize their phases and transmit the stresses between them. However, not always miscible constituents can be applied, thus their surfaces are chemically modified or tertiary substances are added, which are called compatibilizers.

Compatibilizers have the role to improve the miscibility of the constituents allowing formation of blends and/or composites with the desired properties. Among the other applications, the complex lignin structure allows its usage as compatibilizer in binary and multiphase polymeric composites (Thakur et al. 2014).

Adding lignin in fiber or particle reinforced composites improves the interfacial adhesion between the fiber and the polymer matrix when used up to a certain concentration. Luo et al. (2015) used kraft lignin as compatibilizer in a wood flour/PP composite, The effect of lignin content on its compatibilization was investigated through mechanical tests. They observed that the best interfacial bonding between wood flour and polymer matrix occurs when relatively low amount of lignin is used. Lower lignin concentration enables better control on the molecular movement within the composite and thus improves the adhesion between its components. On the other hand, high concentrations of lignin increase the void volume between the components and thus lignin affects negatively the overall mechanical properties of the composite. These findings were also confirmed by water absorption tests. Larger lignin quantity improves or keeps the water absorption of the composite, as a result of the larger voids between the wood flour and the matrix and their poor interaction. Large cavities, holes and de-bonding areas on the samples with higher lignin content than 2 % were observed through SEM images (Fig. 4). Lignin added into hemp fiber/epoxy composites showed similar trends (Wood et al. 2011). The addition of lignin up to 2.5 wt% resulted in composites with improved flexural and tensile modulus as a result of the reduced pull-out and enhanced interfacial adhesion between the fiber and the matrix. Lignin modified surface of flax fiber/hydrophobic soy-oil based liquid molding resin improves wettability of the fiber, resulting in enhanced stress transfer and mechanical properties (Thielemans and Wool 2005).

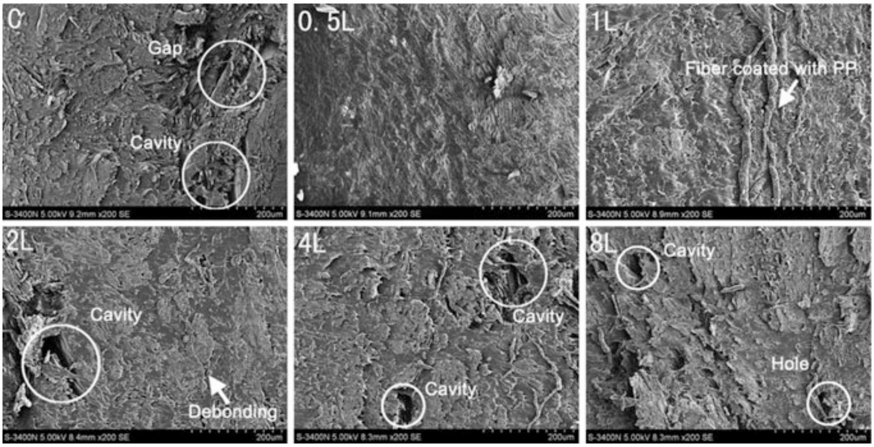

Fig. 4 SEM images of wood flour/PP composites without and with 0.5; 1; 2; 4 and 8 wt. % lignin prepared by extrusion and compression molding (with permission from Wiley Inc.) (Luo et al. 2015)

Due to its polarity and immiscibility with nonpolar polymers and its nonsolubility in common solvents, lignin often requires chemical modifications before its applications. Modified lignin can also be used as compatibilizer in bi- or multiphase composites. Esterification of lignin is one of the ways to modify lignin when used as compatibilizer. Tay et al. (2011, 2013) studied the compatibilization effect of lignin modified with glycidyl methacrylate (GMA) and allyl glycidyl ether (AGE) on oil palm empty fruit bunch (EFB)/PP composites. The addition of more flexible segments between lignin units improved the adhesion between the filler and the matrix. It changed the failure mechanism of the composite, significantly reducing the pullout failure. The chemical modification of lignin improved tensile and flexural modulus, tensile strength and reduced water absorption ability of the composites compared to the samples in which unmodified lignin was used. The increment of the mechanical properties of the composites was enhanced with the addition of more lignin within the compatibilizer structure. Lignin esterified with stearoyl chloride and added into poly(ethylene terephthalate)/low density polyethylene (PET/LDPE) blends improves the shear modulus and the stress at break of the blend (Aradoaei et al. 2010).

Lignin used as co-compatibilizer, together with other polymer can also improve the compatibility of the components within a composite structure. Lee et al. reported lignin modified PP used as compatibilizer in coffee/PLA eco composites (Lee et al. 2015). While lignin itself increased the thermal stability of the coffee reinforced PLA composite, its combination with PP also increased the flexural strength of the composite as a result of the improved interfacial interaction between all the components. The presence of lignin within the composite improved the PP/PLA miscibility, while the presence of PP decreased the phase separation between lignin and PLA.

3 Applications of Lignin Based Composites

In general lignin is a promising chemical for advanced applications due to its low costs and abundancy. Besides lightweight, eco-efficiency in all stages of the product life cycle, recyclability, CO_2-neutrality, nontoxicity were mentioned elsewhere (Bajwa et al. 2016; Naegele et al. 2016; Shankar et al. 2015). Additional functionalities further extended its use in packaging, automotive and electronic industries.

Electronics Special care should be paid for the use of lignin in different resins. For example; while the lignin content might be maximum 5–10 % (w/w) of the resin weight in the phenolic resins, it is possible to add up to 50 % (w/w) into epoxy resin (Stewart 2008). The reason of restriction in phenolic resin is the crosslinking. The crosslinks causes early solidification and high brittleness (Faruk et al. 2016; Stewart 2008). In epoxy resin, lignin provides high impact toughness and stability compared to lignin free phenol epoxy resins. Hence lignin/epoxy composite materials are thought to be promising for electronics industry (Simionescu et al. 1993; Stewart 2008). While the crosslinking is an undesirable for phenolic resins, if the lignin is used as an adhesive additive, crosslinking forms an advantage and makes the shear strength higher (Stewart 2008).

Acoustics Loudspeaker boxes should have high density, stiffness, and storage modulus. According to Naegele et al. lignin based composites seem to be suitable for acoustic applications. Storage modulus depending on temperature is an important criterion for sound attenuation (Thielemans and Wool 2005). Besides, the composites with lignin base exhibits special properties, like dimensional stability under humidity, low thermal expansion, low sound absorbing properties. To provide the required mechanics, purity is an important factor; where several purification processes were proposed so far. Generally extrusion, injection molding, or compression molding processes are preferred to produce lignin based composite materials.

Packaging In general natural biopolymer composites exhibit low mechanical and water resistant properties to be used as packaging materials. Blending or reinforcing plasticizers and crosslinking agents are recommended against such problems (Toriz et al. 2002a). On the other side recent studies showed that natural biopolymers containing lignin significantly influence the physical properties such as, light transmittance, color, water vapor permeability, water solubility, and moisture content. Lignin based composite films can be used as a UV barrier for food packaging film due to low permeation of UV light (Toriz et al. 2002a). Lignin also acts as an antioxidant for both elastomers and polyolefins. Biodegradation is unmanageable not only in plastics, but also polyolefin based products. With the adding of lignin, this biodegradation is getting manageable under favour of lignin's antioxidant property (Cazacu et al. 2004; Stewart 2008).

Fibers Composites might be either in the form of fiber, film, or other 3D shapes. In the fibres lignin deals as a sealant to keep water, protect against biological attack, and provides stiffness, as it behaves as a compatibilizer and functional filler in matrix (Bajwa et al. 2016). Lignin improves the mechanical strength of fibre up to 75 % in Young's modulus while gaining the poor elastic properties to fibers. This makes them usable in biofiber production for textile industry. Biofibers may also be used in biomedical science and automotive industry instead of synthetic polymers under favour of their advantages such as, low production costs, biodegradable nature and environmental-friendliness in fibre reinforced polymers industry (Verma and Dwivedi 2014).

Kadla et al. produced carbon fibers in the first instance using kraft lignin which is a commercially available product. The carbon fiber production was realized by thermal spinning method, and then carbonization procedure was applied without any chemical treatment. In vacuum ambient, thermal pretreatment was conducted to lignin for obtaining fine filament. The lignin poly (ethylene oxide) (PEO) blends could be stabilized with individual fibers melting together. When PEO amount higher than 5 %, blends eased spinning of fiber. Carbon fiber production yield is

45 % from lignin POE blends. After carbonization procedure diameter of fiber decreased, while tensile strength and modulus increased. The mechanical properties are 400–500 MPa and 30–60 GPa for tensile strength and modulus, respectively. According to these values, kraft lignin has promising properties to be precursor for carbon fibers (Satheesh Kumar et al. 2009).

Construction Another area which lignin may be used is mortar and construction materials. In such applications, fluidity is affected by lignin-lignin and lignin-water interactions since lignin functions as a binder (Stewart 2008).

4 Conclusions and Future Prospective

As indicated in relevant literature lignin is a promising composite component with various functionalities. Particularly due to its abundance and natural origin, it is considered as a potential low cost stabilizer with non-cytotoxic and non-carcinogenic properties. However, its complex structure and the variations of lignins obtained from different sources, extraction processes, fractionation and other post treatments do not yet allow its industrial application (Arshanitsa et al. 2013; Rajeswara Rao et al. 2015; Yearla and Padmasree, 2016). On the other side there are controversial results in the final mechanical properties of such composites. In some studies lignin was found to be acting as an excellent reinforcer; while for some composite it was just considered as a filler. However compatibility with the matrix and homogeneity were found to be the main challenge for most of the works. Due to that reason preparation technique is critical to obtain the maximized performance, which will lead larger uses from flexible LEDs to high performance carbon fibers.

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Recent Progress on Rubber Based Biocomposites: From Carbon Nanotubes to Ionic Liquids

**Imran Khan, Mohd Amil Usmani, Aamir H. Bhat,
Jahangir Ahmad Rather, Syed Imran Hassan and Abdul Mumam**

Abstract Currently, reinforcement of a polymer matrix via the integration of fillers is a common industrial exercise which improves the properties of the composite material. Rubber nanocomposites (NCs) demonstrated remarkable properties due to the interaction between the polymer and filler and the homogeneous dispersion of the filler within the polymer matrix. These improved properties included increased stiffness, high strength, reduced elongation to failure, improved resistance to crack growth and tearing and finally various modifications of abrasion, dynamic and fatigue properties, due to their high surface area and significant aspect ratios. Different reinforcing fillers have been incorporated in the rubber to develop elastomeric composites having improved properties. This current chapter focus on development, properties and applications of various elastomeric composites. Secondly, this chapter also emphasis on ionic liquids (ILs) role as additives in elastomer composites as well as effects of nanofillers on elastomer composites.

Keywords Rubber · Nanocomposites · Carbon nanotubes · Ionic liquids

Abbreviations

[Amim][Ntf$_2$]	1-Allyl-3-Methylimidazolium Bis(Trifluoromethylsulfonyl)Imide
CR	Chloroprene rubber
CB	Carbon Black
[Emim][Ntf$_2$]	1-Ethyl-3-Methylimidazolium Bis(Trifluoromethylsulfonyl)Imide

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[Emim][SCN]	1-Ethyl-3-Methylimidazolium Thiocynate
HNBR	Hydrogenated Nitrile Rubber
[Hmim][Ntf$_2$]	1-Hexyl-Methylimidazolium Bis(Trifluoromethylsulfonyl)Imide
FHT	Fluorohectorite
MMT	Montmorillonite
MWCNT	Multiwalled Carbon Nanotubes
NCs	Nanocomposites
NPs	Nanoparticles
NR	Natural Rubber
NBR	Acrylonitrile–Butadiene Rubber
NBR	Nitrile Rubber
SiC	Silicon Carbide
SBR	Styrene Butadiene Rubber
SWCNT	Single-Walled Carbon Nanotubes
T_g	Glass Transition Temperature
XSBR	Carboxylated Styrene Butadiene Rubber

1 Introduction

Natural rubber (NR) is commercially successful bio-based polymer which have been utilized extensively due to their outstanding intrinsic physical properties (Cornish 2001; Rippel 2002). However, it is hardly used under unprocessed condition. Processing of this bio-based polymer material resulted in transformation from a linear polymer into a composite material which provides improved elastomeric properties necessary for most applications. These processes usually takes place by mechanical mixing of a solid masses of NR with compounding additives such as fillers, oils and powders (Hashim 1995). Generally, fillers or reinforcement material are incorporated in NR to increase the tensile strength, improve the tear strength and enhance the abrasion resistance of the rubber product.

On the other hand, biopolymeric materials such as natural, renewable materials like wood, silk, NR, celluloid, amber have attracted attention since a long time (Cipriani et al. 2010). Now, the demand of biopolymeric materials increased drastically due to their effective utilization in different fields. Currently, biopolymer-based materials used together with progressive green composite materials are gaining more attention both in academia and in industry (Thakur et al. 2011). But, they have limited applications in engineering as these fibers can't transfer loads from one to the other. When biopolymers are incorporated in a matrix material to form a composite, the matrix transfers load to bind these biopolymeric fibers in order to protect them against environmental attack as well as to hinder their damage due to handling. This action of matrix has a great impact on several mechanical properties of the composite. The changes in physico-chemical properties of the matrix (melting or curing temperature, viscosity, and reactivity) due to biopolymers are responsible for the choices of fabrication process. The commonly used matrix materials for a composite system are polymers, metals, and ceramics. NR has been used extensively as matrix material due to its high performance and environmental friendliness. NR is a polymer of isoprene in which basically all the isoprene's have the cis 1–4 configuration having high-molecular weight. Comparatively, NR is very essential because it possess the general features of other rubbers as well as it shows highly specific characteristics as Dirt content (0.03 % by mass), Volatile mass (0.50 % by mass), Nitrogen (0.30 % by mass), Ash (0.40 % by mass), Initial plasticity number (38), Plasticity retention index (78) (Geethamma et al. 2005). NR has got much importance because it is renewable, inexpensive, and creates no health hazards due to its biological origin.

2 Overview and Potential Merits of Composites

Generally, composites are any material made of more than one material known as constituent materials with different structural, physical and chemical properties which in turn changes composites behaviour changes compared to system such as blends and alloys. And the characteristics of composites such as permeability, electrical, weight, strength, stiffness, biodegradability and optical properties are usually determined by the combination of their respective properties of the constituent materials (Klyosov 2007). In general, composites can be define as engineering materials made from two or more constituents having considerably different physical or chemical properties. These composites, developed by the combination of different materials, are more strong than the individual materials and may exhibit completely different characteristics than the individual constituents (Thakur 2011). One constituent material of composites basically acts as the matrix (binding material), whereas the other acts as reinforcement (filler). Figure 1 shows the general schematic of a composite.

The matrix material also known as "continuous phase" surrounds the reinforcement (filler). The characteristics of composites are decided by type and level of reinforcement which is also known as "discontinuous phase." The discontinuous phase being harder in nature, generally reveals better mechanical properties as compare to those of continuous phases. These continuous and discontinuous phases have noticeable nature. New characteristics of the resulting composite materials

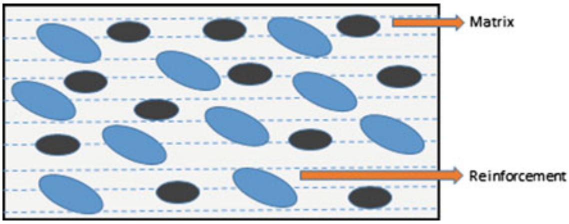

Fig. 1 General schematic of a composite

entirely depend on the distinctive properties of each material. Precisely, the mechanical and physicochemical characteristics of the composite are better to those of the matrix material (Thakur 2011). Composite material has been modified to get specific properties in order meet special needs. Evidently, after modification, composite materials possessed required characteristics such as high fatigue strength, low weight, corrosion resistance, and higher specific properties like tensile, flexural, and impact strengths (Niska and Sain 2008). Composites can be classified either by type of matrix, such as polymer, metal, ceramic, or by the type of reinforcement, such as fibers, particulate, flake, whiskers as demonstrated in Fig. 2. Different types of composite material have been developed to meet the requirements of specific applications. Although, applications of rubber polymers have low cost with application in automotive components or advanced medical devices but in applications like their rigidity and strength they cannot stand with metals. Rubber based polymer composites were designed generally to get the special needs like light weight, high rigidity and thermal stability (Niska and Sain 2008). Also, polymer composites can be characterized into three main classes depending upon their reinforcements, particulate composites, continuous fiber composites, and discontinuous fiber composites. The amazing characteristics revealed by composite materials have directed to their extensive applications in a variety of industries. The advantage and characteristic features of composites consist of increased impact resistance, design flexibility, chemical resistance, and fracture toughness, high strength, light weight and low coefficient of thermal expansion.

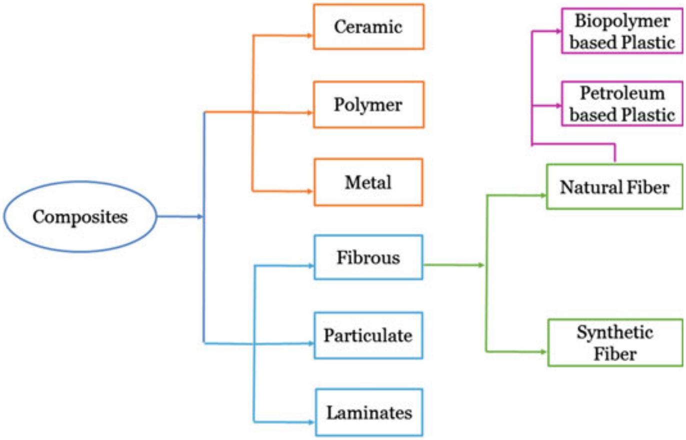

Fig. 2 Composites can be classified either by type of matrix, such as polymer, metal, ceramic, or by the type of reinforcement, such as fibers, particulate, flake, whiskers

3 Manufacturing Techniques of Rubber Nanocomposites (NCs)

Rubber, also known as elastomer, is one of the most important commercial polymers having long and flexible polymer chains with a coiled and bended nature. Atoms are connected in long, randomly coil chains, in the molecular structure of cured rubber, that are interlocked at some positions. In this polymer each bond can rotate freely between a pair of locks without affecting its neighbor. Consequently, rubber demonstrates unique physical and chemical properties. Rubber can aligned their structure under stress by uncoiling molecular chain while upon release of the stress the molecules rapidly gain their original structure due to coiling up of molecular chains. This quality results in material stretch, large free volume fraction, and amorphous and non-orientated state, which reveals specific properties, such as low hardness, high elasticity and high elongation at break. These useful characteristic properties of rubber can be obtained only after its chemical modification by sulfur atoms or other curing agents with the help of vulcanization process. In this process more sulfide bonds are created between chains which cause each section of free chain shorter. As a result, the chains become stiffen more rapidly for a given length of strain and makes rubber harder because of increases in the elastic force constant. Therefore raw rubber reveals enormous applications in the real world only after its vulcanization.

3.1 Conventional Manufacturing Techniques

Traditionally, a typical manufacturing sequence comprises mixing, forming and vulcanizing in the rubber manufacturing industry.

3.1.1 Mixing

Mixing of dry rubber with softeners, fillers, vulcanizing agents or additives can be done using either by using two-roll mill or an internal mixer. For mixing in rubber latex with the other compound must be in the form of emulsions or dispersions which may be prepared by milling the substances with distilled or softened water in ball or gravel mills, which revolve from a few hours up to several days. Gelatin, casein, glues, soaps and so on, are used as wetting or dispersing agents. The latex is stabilized with surfactants, which act by developing a charge on the tiny rubber particles surface or by surrounding water around the particle which in turn prevents any type of aggregation.

3.1.2 Forming

After following the process of mixing, the compounded rubber is now ready to be formed into a shape for vulcanization. The most common process is by molding under pressure in a heated mould. There are three important variants of the process-compress ion, transfer and injection molding-of these, the compression mold is the most widely used.

3.1.3 Vulcanizing

After mixing and forming the final process in the manufacturing sequence is vulcanization process where heat are applied at higher temperature for a given time to cure the product. Basically the curing is done with the aim to produce the crosslinking which is achieved by the chemical reactions which occur in the rubber mixture. There are various vulcanizing methods like economically important method which uses enlarged pressure and temperature and other methods include hot air vulcanization or microwave vulcanization.

3.2 Rubber Nanocomposites

Recently, fiber-reinforced elastomers have acknowledged by the composite industry because of their low cost, high strength and simple processing method. Glass fiber–reinforced rubber composites have been broadly studied owing to its high strength, high modulus and low creep. It has been observed that the quality of developed fiber reinforced rubber composite significantly followed by the amount of loaded fiber in the matrix, uniform dispersion, orientation of fiber, fiber-rubber adhesion and the length to diameter ratio of the fiber. These composites have their applications in sheeting, tires, roofing, hoses, conveyer belts, complex-shaped articles and industrial rubber products. Together with glass fiber-reinforced rubber composites, extensive studies on natural fiber–reinforced rubber composites have also been reported (Geethamma et al. 1998). Natural fibers and rubbers (synthetic rubbers and NR which act as the matrix in the composite) are being major components of these composites. Rubber has been successfully used as matrix for preparation of composite because to its unique, versatile and adaptable material nature. Rubber has an extraordinary property of swelling in various organic solvents and can modified its state without dissolving in these solvents (Vajrasthira et al. 2003). It has much higher elastic strain and impact strength as compare to metals and plastics. Therefore, it showed great performance under high strains. For instance, it can be stretched rapidly even under small load to about 1000 % elongation and again occupied its original shape quickly on releasing the applied forces.

The bioreinforcement in NR composites showed great effects on its mechanical properties which include increased modulus and strength, decreased elongation at failure, significantly better creep resistance and increased hardness together with a considerable improvement in cut, tear and puncture resistance. The reinforcement effect of grass (bagasse) in NR showed appreciable increase in tensile strength retention (Nassar et al. 1996). Also, an increase in rheometric and mechanical properties was observed in composites comprising kenaf and NR (Anuar et al. 2008). Pineapple and jute have been proved potential reinforcement in NR (John and Thomas 2008). The loading of sisal and coir as reinforcement in NR caused an increase the dielectric constant of the composites. And the biocomposites formed exposed various applications as antistatic agents and composites containing waste paper in NR along with boron carbide and paraffin wax showed applications in radiation shielding (Madani et al. 2004). While, sisal and oil palm fibers, in a unique combination, has been incorporated in NR to design hybrid biocomposites. It has been found that the final biocomposite showed an increase in modulus. Also, chemical alteration of sisal and oil palm fibers was found effective in increasing interfacial adhesion which caused in improved properties like dielectric, viscoelasticity, stress relaxation and water sorption (Jacob et al. 2006).

3.2.1 Advantages of Rubber Nanocomposites

The main advantages of nanoreinforcements in comparison with conventional composites, are summarized as follows:

i. Smaller fraction of nanomaterials as reinforcements causes a significant improvement of the matrix properties developed light weight, low cost and easy processable NCs.
ii. The load transfer phenomenon from the matrix to the reinforcement is more effective in case of NCs due to their high surface area and good adhesion at the interface.
iii. Smaller size of nanomaterials causes an increase in crack propagation length at the interface, which improves both strength and toughness.

Reinforcing ability of a reinforcing agent are determine by three main factors such as the particle size, structure and surface characteristics. Among these three factors, particle size is most effective parameter (Hamed 2000). Evidently, reinforcement of nanofillers is essential for rubber products especially.

3.2.2 Challenges of Rubber Nanocomposites

In spite of improvement in overall material performance by nanoreinforcements, NCs are still facing few challenges.

i. Nanoparticles (NPs) as nanoreinforcements lean to aggregate during manufacturing processes which may affect the thermal as well as mechanical properties of the NCs. And homogeneous dispersion of NPs to obtain high performance NCs in matrix is critical.

ii. The production, use and disposal of NPs may cause health and environment related problems. NPs used in consumer products may threaten public health as they can damage the body's natural defenses or cause increased responses to common allergens.

3.3 Reinforcing Agent

3.3.1 Carbon Black

Since a long time, carbon nanomaterials attracted attention of researchers due to its exceptional physical and mechanical properties. Evidently, carbon black (CB) has been used as significant filler for elastomers as well as to improve the electrical conductivity of polymers. Small particles of CB (ranging 10–100 nm diameter) always combine into aggregates which form irreversible and anisometric structures. These aggregates produce loosely-bounded agglomerates ranging 100–500 nm in diameter, due to van der Waal bonds attraction among them. Later on, Herd et al. (1992) distributed these different structural morphologies into four categories such as spheroidal, linear, branched and ellipsoidal. The mechanical performance of final composites generally determines by degree and size of aggregates.

The presence of organic groups on the CB surface is responsible to adsorb elastomers molecules have high chemical and/or physical affinity. This makes CB the most frequently considered and used filler for elastomers (Kurian et al. 1995). The particle size effect was examined by means of two types of CB structures, firstly structure (particle size within the ranger 40–48 nm) and secondly coarse structure (particle size within the range 201–500 nm), on the mechanical performance of polyurethane-based fluoro elastomer (Griffini et al. 2012). It has been observed by dynamic mechanical analysis that the fine-structure filler can reinforce the matrix more effectively, while the coarse filler reveals poor reinforcement ability. Recent progress for the reinforcing mechanisms of CB by using advanced characterization tools that could be pursued to progress high performance elastomers. In this contrast, Chodák et al. (2010) studied tensile testing and electrical conductivity of styrene butadiene rubber (SBR)/CB composites and found that the fracture mechanisms of the CB network under various deformation phenomena by quantifying by electrical current measurement and the filler–filler networks through dynamic mechanical analysis and dielectric spectroscopy (Meier and Klüppel 2008). Similarly, filler effect on the viscoelastic behaviour of elastomer/CB composites has been reported (Lv et al. 2008). Also, Sahoo et al. (2011) conducted studies on dielectric constant and electrical resistance of ethylene acrylic dipolymer elastomers loaded with CB, but no electrical conductivity threshold was observed. Although CB is predominant reinforcing filler in elastomer industry, but it makes negative environmental effect since produced from petroleum industry which make a reasonable question to find alternates which have less negative effect on the environment and which may be applied at low volume fractions. Thus, more and more efforts have been made to search for alternatives (Sengupta et al. 2007).

3.3.2 Clays and Clay Minerals

Clay is an inexpensive natural raw material that would widely used for several years as filler for rubber and plastics to reduce costs of material. In general the clay minerals fits to the specified category of layered silicates or phyllosilicates because of its arrangement of silica and alumina sheets in a defined way. Clay is composed of silicates layers of size 1 nm thick and 200–300 nm wide in the lateral dimension. The layered silicate structure of clay is generated by 2-D arrays of silican-oxygen tetrahedral and aluminium-or magnesium-oxygen/hydroxyl octahedral units. The most commonly used layered silicates for the preparation of polymer/layered silicate NCs belong to the family of 2:1 phyllosilicates, in particular montmorillonite (MMT). The layered thickness is normally about 1 nm and the lateral dimensions of these layers can vary from 100 nm to several microns depending on the type of layered silicate. In MMT, the isomorphos substitution of Al^{3+} by Mg^{2+}, Fe^{3+} etc. in the octahedral sheet results in a net negative charge in sandwiched layers.

The dispersion of the layered silicate is understood correctly when all layers are enough distanced from each other in the polymer matrix. In general, the distance between two successive layers in MMT is too small to permit polymer molecules to enter into it. And one of the method Organic modification increases the gap between the layers and this method be used to overcome this problem. In this method, the resulted organo clay is formed by exchanging the original interlayer cations for organo cations. The organo cations decreases the surface energy which in turn increase wetting and intercalation by the polymer matrix with the consequences in the larger interlayer spacing. The organic cations may deliver functional groups and which may react with monomer or polymers to improve interfacial adhesion between the clay nano layers are quaternary alkyl ammonium ions as shown in Fig. 3. This modification allow s formation of an organophilic surface in

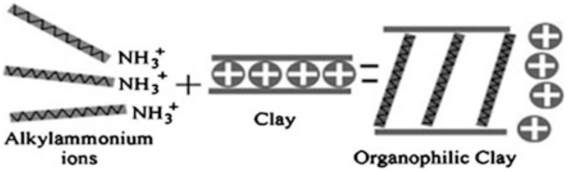

Fig. 3 The organic cations may deliver functional groups and which may react with monomer or polymers to improve interfacial adhesion between the clay nano layers are quaternary alkyl ammonium ions

the clay structure but elastomers matrix the organic modification itself is not enough to get intercalated or the exfoliated structures.

4 Natural Rubber Green Nanocomposite

The biodegradability of the natural fibers is related to a healthy ecosystem, while their low cost attributes the economic interest of industry. Jute, sisal, coir, pineapple and banana like lignocellulosic fibers have already been used as reinforcement in thermoset matrices (Sreekala et al. 1997). Numerous studies have been done to develop a new class of fully biodegradable green composites by combining natural fibers with biodegradable resins (Drzal 2002). All most in all studies an improvement in strength of the composites were reported, particularly for optimal range length of the reinforcing fibers. Green composites developed by loading short fibers in rubber compounds causes increased strength and stiffness to the rubber matrices. Also, low cost, easy processability and improved physical, chemical, and electrical properties can be achieved in the final compound. The incorporation of bio-fibre reinforcement into NR greatly affects the mechanical properties of composites. Ismail et al. (1997) investigated the effect of fibre concentration on the mechanical properties of oil palm reinforced NR composites. A general trend of reduction in tensile and tear strength with increasing fibre concentration has been observed. Nassar et al. (1996) were presented an interesting report on the reinforcement effect of grass fibre bagasse in NR and observed 97 % retention in tensile strength of developed composite. Pineapple (Bhattacharya et al. 1986) and jute fibre (Arumugam et al. 1989) have also been used successfully as potential reinforcements in NR. Similarly, Mathew et al. (2004) have used isora fibre in NR. In another study, Madani et al. (2004) investigated composites contain waste paper in NR along with boron carbide and paraffin wax for radiation shielding applications. In an innovative study, Jacob et al. (2004) developed hybrid biocomposites by using a unique combination of sisal and oil palm fibres in NR. The author reported an increase in modulus of resulted biocomposite. It has also been observed that chemical treatment of sisal and oil palm fibres caused an increase in interfacial adhesion. In contrast, Derringer (1971) developed biocomposite comprising short glass fibers and rubbers. The author found a high modulus, good mechanical strength and low creep in the resulted composites. Coran et al. (1974) conducted studies on cellulose fiber elastomer composites and observed that the properties of resulted composite mainly depend on fiber concentration, fiber aspect ratio, type of elastomer and fiber orientation. In a similar study, Abrate (1986) reviewed the micromechanics of short fiber reinforced rubber composites whereas Murthy and De (1982) investigated the effect of fillers on short jute-fiber reinforced NR composites. Chakraborty et al. (1982) considered the effect of bonding agents in the composites synthesized by short silk fiber and NR. Varghese et al. (1994) reported relaxation in stress in short sisal fiber reinforced rubber composites. The properties of short coir fiber reinforced NR composites were reported by Geethamma et al. (1998). In a similar study, Shaji et al. (2006) investigated the mechanical properties of green composites of oil palm fiber and NR as a function of fiber length, orientation, and loading. The author observed low breakage of fibers during milling, superior mechanical properties of the composites in the longitudinal direction and found 6 mm fiber length optimal to attain valuable reinforcement in NR composites. Further, it has been observed that tensile strength and tear strength decrease while modulus increases on addition of oil palm fiber. Oil palm fibers treated with NaOH (5 %) showed higher fiber orientation and properties than untreated ones.

5 Carbon Nanotube Reinforced Rubber Composites

Fine particles like CB, silica or calcium carbonate have been used in rubber compounds in the form of reinforcement since a long time of the rubber industry. These reinforcements are incorporated into the matrix in order to get a significant changes in the physical and mechanical properties of the compound (Donnet 2003). However, to attain the desired properties, high concentrations of conventional reinforcements are required which causes a damaging effect on the process ability of the compound, increases the final weight and limits their applications.

In the past few years, carbon nanotubes (CNT) have encouraged scientific world for a range of prospective applications (Bokobza 2007). CNT are allotropes of carbon having covalently bonded carbon atoms arranged in the form of cylinders with diameters in the range 1–50 nm following a wide variety of lengths. CNT reveals exclusive characteristics like high aspect ratio (300–1000), high flexibility (Cooper et al. 2001) together with great combination of mechanical, electrical and thermal properties (Uchida and Kumar 2005). Consequently, due to very low mass density (Gao et al. 1998), they turn out to be potentially useful reinforcing fibers for the progress of high-performance polymer composites. Elastomers have limited applications because of their low mechanical properties; therefore, most of the studies are concentrated on the development of interface between the filler and the matrix following functionalization of CNTs or with various preparation methods. Also, thermal conductivity of elastomer/CNT composites are limited because of their effective high cost and viscosity (Likozar and Major 2010). Therefore, to get an appreciable development in the thermal conductivity, a large amount of CNTs must be loaded into elastomers. Three methods are generally used to produced CNT; arc discharge, laser ablation and chemical vapor deposition. Synthesis and purification techniques following the specific growth conditions are responsible for quality and yield of CNT (Shaffer and Sandler 2006). On the basis of cylindrical wall CNTs have been divided in two categories: single-walled carbon nanotubes (SWCNT) and multiwalled carbon nanotubes (MWCNT). SWCNT consists of single layer of graphite called graphene into a seamless cylinder having important electric properties comparatively. While, MWCNT possess multiple layers of graphite arranged in concentric cylinders.

Although, a lots of research work have been done on elastomers/CNT composites, but still it is not confirmed whether elastomer/CNT composites are appropriate to scale up in a commercial manner or not due to handling problem of their bundles and high manufacturing cost compared to CB (Sherif Araby et al. 2015). Generally, NPs loaded within the polymer matrix by mechanical dispersion in solution or melt processing struggling with numerous critical issues:

i. Lack of uniformity in the dispersion of nanoreinforcements within the polymer matrix.
ii. Higher viscosity of the compounds due to the nanofiller high aspect ratio.
iii. Lesser control of the orientation of CNTs in the resulting composites.

Consequently, functionalization of CNTs is required in order to generate an efficient interphase in polymer matrix NCs.

5.1 Functionalized Carbon Nanotubes

CNTs showed great characteristics for the synthesis of high performance nanostructured materials with outstanding mechanical, thermal and electrical properties following low density with respect to organic and inorganic tubes. However, the incorporation of CNTs as reinforcement is not an insignificant job if a good dispersion is mandatory to maximize the advantage of CNT reinforcement. Indeed, the ability to hold to each other varies as developed SWCNTs are intractable and indispersable in common solvents (Baughman et al. 2002). As a result, CNT have been used ultimate materials for reinforcing fibers owing to their excellent mechanical properties. Functionalization of CNTs is one of the most effective techniques to load these nanofibers into the polymer matrix. Low amount or well dispersed nanoreinforcements developed more strong interfaces that has ability to slow down the progress of the crack (Andrews and Weisenberger 2004). But, CNT-based NCs can only be synthesized by solving two main problems: (i) the large contact area of CNTs and the strong attraction among them which is responsible for the non-uniform dispersion of nanoreinforcements in polymeric matrices, and (ii) the poor interfacial attraction between the CNTs nanoreinforcements and the matrix. Recently, CNT-based NCs has been development adopting different approaches that have been used to disperse CNTs through the wrapping of the cylindrical surface with the help of various species of polymers (Andrews et al. 2002), aromatic compounds (Nakashima et al. 2002) and surfactants (Islam et al. 2003).

5.2 Elastomeric Nanocomposites

5.2.1 Natural Rubber

NR is a diene monomer of hydrocarbon having repeating unit is cis-isoprene. NR considered as the chosen material in several engineering applied field due to its exceptional strength, good creep, stress relaxation resistance and its low cost. CNT/NR nanocomposites have been effectively prepared by several procedures: melt mixing (Shanmugharaj et al. 2007), solution blending (Zhao et al. 2006) and latex compounding (Wang et al. 2006). López-Manchado et al. (2004) reported the effects of the loading SWCNTs on the physical and mechanical properties of NR. A strong interaction filler and matrix, which showed a great increase in the storage modulus and appreciable shift of the glass transition temperature (T_g) towards higher temperatures. These effects were more noticeable in comparison with CB/NR nanocomposites.

In another study, Bokobza et al. (2006) synthesized MWCNTs-NR nanocomposites, it is reported that a noticeable increase in the stress can be observed from a filler content of 2.4 wt% at a particular strain level and the reinforcing effect increased with increasing the CNT incorporation in the composite. Also, Zhao et al. (2006) observed that the modulus of the SWCNT/NR composite developed with toluene as a solvent increased about 20 % compared to the pure NR material by loading 0.25 wt% of SWCNTs. They ascribed this enhancement to the formation of additional sources of embarrassments or physical crosslinks in the network in presence of CNTs. While, Sui et al. (2007) studied that CNTs dispersed well in the rubber matrix and interfacial interaction between them was improved after being treated with acid and ball-milling. Finally, Shanmugharaj et al. (2007) observed that 3-aminopropyltriethoxisilane functionalized CNT was able in increasing the scorch time and optimum cure time in the sulfur vulcanization of NR. Further, it has been experienced that NR/silane functionalized CNTs composites exhibited tensile strength, higher modulus and elongation at break compared to NR vulcanizates owing to the higher polymer-filler interact ion between the silanized CNTs and NR vulcanizates.

5.2.2 Styrene-Butadiene Rubber

Styrene-butadiene rubber (SBR) is an elastomeric copolymer having repeating units of styrene and 1,3- butadiene. SBR is mostly synthesized by emulsion polymerization but some time solution polymerization technique also used. It is synthetic rubber extensively used in the elastomer industry due to its good abrasion resistance, aging stability and low-temperature properties. SBR has more applications in tire industry which needs approximately 70 % of its total production. In the production of SBR, CB being the most used reinforcing filler. Recently, CNTs/SBR composites have fascinated interest due to the opportunity to attain improved properties at low filler loadings. The performances of MWCNTs/SBR compounds were found better than those of CB (N330)/SBR composites. Bokobza et al. (2007) showed the intrinsic potential of MWCNT as a reinforcing filler in elastomer matrices, in particular, styrene-butadiene copolymers. While, De Falco et al. (2007) developed an easy technique to fabricate cured styrene-butadiene rubber/MWCNT composites.

5.2.3 Polyurethane Rubber

Polyurethane (PU) generally produced by the polyaddition reactions of higher-molecular-weight diols and diisocyanates, which led to a two-phase morphology of alternating soft and hard segments. PU have shown numerous applications due to its properties like excellent flexibility, elasticity, and damping ability (Xiong et al. 2004). However, in its pure form PU has some drawbacks, related to low mechanical strength, high water absorption, and poor thermal stability. Therefore, these drawbacks can be removed by incorporating fillers such as CNTs into PU, which possesses high thermal stability. However, the incorporation of CNTs in PU is usually difficult due to low interfacial interaction between CNTs and polymer matrix, and hence the development of the desired characteristics is not easily attained in PU/CNT nanocomposites. Evidently, functionalized CNTs have been used to get improved mechanical and thermal properties of NCs (Sahoo et al. 2006). Functionalized CNTs have been used in most of the studies to improve their compatibility and dispersion (Buffa et al. 2007). The addition of functionalized CNTs into PU matrices was mainly done by solvent mixing (Curtzwiler et al. 2008). The first reported studies on CNT/PU systems were independently carried out by Koerner et al. (2005) and by Sen et al. (2004). Koerner et al. (2005) observed that the uniform dispersion of CNTs in PU is responsible to produce a material which was able to store and release up to 50 % more recovery stress than the pristine resin. Similarly, Park et al. (2006) reported the used of CNT filled polyurethane foam in radar-absorbing structures in the X-band (8.2–12.4 GHz) frequencies. Recently, Jana and Cho (2008) reported comparison between MWCNT/PU prepared by solvent cast and oxidized and MWCNT/PU prepared by in situ polymerization.

5.2.4 Silicone Rubber

Silicone elastomers are unusual synthetic polymers having repeating unit of “inorganic” that is, silicon to oxygen bonds. Further, these silicon atoms are also attached to organic groups, such as methyl. These inorganic and organic units provide silicones some unique properties following thermal and chemical stability. Consequently, silicone NCs have attracted attention of academia and research in recent years (Paul et al. 2006). The first study on CNT/Silicone NCs was reported by Frogley et al. (2003), who compared systems loaded with up to 1 wt% SWCNTs and up to 4 wt% CNFs. A number of studied have been carried out to synthesize new nanocomposite systems so as to get exclusive properties from different polymers including silicone rubber. Ahir and coworkers have reported the first study on silicone-based nanocomposite as a new photomechanical actuator (Ahir et al. 2006).

6 Cellulosic Fibril–Rubber Nanocomposites

Cellulose is the chief component of plant structures, bacteria and tunicates having annual production about 1.56 × 10^{12} t (Klemm et al. 2005). Cellulose showed significant load-bearing capability due to the chain conformation and microfibrillar morphology. The cellulosic units have a complicated layered structure having a thin primary wall deposited during cell growth surrounding a secondary wall. The secondary wall consists of three layers, among them the thick middle layer responsible for the mechanical properties of the fiber. This middle layer made up of numerous helically wound cellular microfibrils produced from long-chain cellulose molecules Fig. 4 (Zimmermann et al. 2004).

Cellulose microfibril have diameter about 5–10 nm and their length varies from 100 nm to several microns, according to the resource. They can be separated by chemical and mechanical treatments. Cellulose microfibrils undergo transverse cleavage on acid hydrolysis and formed microcrystalline cellulose or whiskers. This crystalline arrangement of whiskers provides high modulus and force cellulose micrifibrils to be act as effective reinforcing agents (Hamad 2013). Till now, we have limited information about cellulosic nanofiber-reinforced latex composites except few studies. The reinforcements effects of cotton microfibrils in latex emulsion was investigated by Orts et al. (2005). It has been found that the load holding capacity of resulted composite increased several-fold together with twofold increase in elongation at maximum stress. Similar results were also reported for the

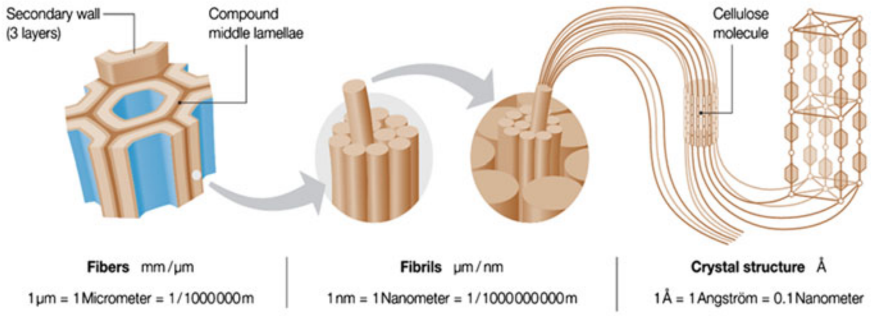

Fig. 4 The cellulosic units have a complicated layered structure having a thin primary wall deposited during cell growth surrounding a secondary wall

composites formed by reinforcing straw derived microfibrils into latex (Imam et al. 1999). Hajji et al. (1996) conducted studies on the tensile behavior of NCs from latex and cellulose whiskers and found significant improvement. In a similar study, banana nanofibers developed by the process of steam explosion were loaded in NR latex to form composites (Bana and Banthia 2009).

7 Graphene-Rubber Nanocomposites

The unique honeycomb like structure of graphene having monolayer of sp^2-hybridized carbon atoms revealed exceptional physicochemical properties (Wang et al. 2011). As a result, graphene display broad range of application, especially in the field of graphene/polymer composites. Graphene can be synthesised by reducing graphene oxide (GO) following chemical or thermal treatment. Graphene oxide (GO) has received incredible research interest because to its effective physical and chemical properties (Gan 2015a, b). This is because product obtained by chemical oxidation of the graphite; the GO, encloses a large number of oxygen-containing groups within its backbone. Evidently, GO becomes highly compatible with numerous organic polymers, particularly with those having polar groups (Yadav et al. 2014). Thus, the GO is considered as suitable filler to developed GO filled polymer composites (Lu et al. 2014). Reduced GO (RGO) demonstrates its characteristics between those of graphene and GO. Recently, some reports about the effects of reduction degree on the properties of graphene itself and graphene/polymer composites have emerged. Most of these studies focused on the mechanical, thermal, and electrical properties of graphene/polymer composites (Wu et al. 2015). In addition, the silicone rubber (SR), extensively used industrial material, has revealed various applications in different research fields. The SR also has been used in numerous materials production due to its elastic, biocompatible, thermo stable and chemically stable nature (Yan et al. 2015). But, the SR considered mechanically weak without the incorporation of the reinforcing fillers. Therefore, the GO seems to be a potential as the reinforcing filler in SR to modify its mechanical properties (Gan 2015a, b). Gan and jiang (2016) synthesised SR/GO composites and found that GO could increase both the thermal and mechanical properties of the SR composites.

High performance GO/rubber composites can be developed by homogenous dispersion of GO sheets into rubber matrix. For this purpose, solution mixing (Li 2012) method has been found an operative way to reach the desired dispersion, but the removal of organic solvents creates persistent problems for the useful functioning of the method. Yingyan Mao et al. (2013) conducted studies on GOsilica/SBR composite by mixing the GO/SBR composite with silica/SBR composite. GOsilica/SBR composite demonstrated better static and dynamic mechanical properties in terms of wonderful wear resistance and low-rolling resistance as compare to silica/SBR composite. Although significant studies has been reported on thermal stability of composites filled with GO or graphene. Thermal stability of graphene nanoribbon/silicone rubber (SR) nanocomposites was reviewed by Gan et al. (2015a, b). The author observed uniformly dispersion of graphene nanoribbon in the matrix due to the excess of oxygen containing groups and had interactions with matrix; as a result, thermal stability of SR was improved. In a similar study, Wang et al. (2013) investigated improvement in the thermal stability of carboxylated acrylonitrile butadiene rubber vulcanizates by incorporating GO. It was observed due to significant interactions between the rubber matrix and the fillers, which causes exfoliation, high aspect ratio and the hydrogen bonding between GO and the polymer. On the other hand, it has been found that thermal stability of several polymer matrices was not significantly affected by non-reduced GO (Bastiurea et al. 2015), whereas RGO was able to improve the thermal decomposition temperature of polymer, accountable for the high surface area and good dispersion of RGO sheets (Gavgani et al. 2014). Study conducted by Yulian Bai et al. (2015) showed that RGO improved the mechanical properties of SR nanocomposites. The author found homogeneous dispersion of RGO in the SR matrix and better interactions between them due to the huge surface area, wrinkled morphology and high extent of exfoliation of the RGO sheets which causes significant improvements in thermal stability compared with the blank sample.

8 Effect of Nanofillers in Rubber-Rubber Blends

Rubbers showed generally lots of applications and they are blended to get their enhanced performance in all conditions. Synthetic rubbers have been reinforced with fillers to obtain composites consisting specific properties. Generally, CB and precipitated silica considered as the conventional fillers for these requirements. Depending upon their dimensions in polymer matrices, nanofillers can be considered in three ways. For instance, if the three dimensions of the particle are in the order of nanometers than it appear as spherical particles like CB, silica, aluminum oxide, titanium dioxide, zinc oxide and silicon carbide NPs fillers. But, if only two dimensions of a nanofiller are in the nanometer scale and the third is larger such as CNT, carbon nanofibers, cellulose whiskers, boron nitride tubes, boron carbon nitride tubes and gold or silver nanotubes, then they constitutes second category. While, the nanofillers having only one dimension of the filler is in the nanometer range, formed third category and provides a layered appearance, for instance, layered silicates, layered graphite flakes and layered double hydroxides layered nanofillers. They showed a strong tendency to form aggregates and agglomerates because of high adsorption surface energies.

9 Effect of Nanofillers in Rubber Nanocomposites

The most highly used fillers in the rubber industry include CB and silicone dioxide (silica), while organically modified layered clays, CNT or polyhedral oligomeric silsesquioxanes emerging as new candidates (Goettler et al. 2007). There are some other possible nanoscale reinforcements which include particulate silica metal oxides, silica-based molecular networks, haloysite tubular silicates, smectic-layered silicates, CNT, fullerenes, graphite platelets and carbon nanofibrils. Commonly used rubber reinforcement, CB, can be varied in both its aggregate structure and particle size. While, a higher modulus caused by higher structure at lesser loading leading to less hysteresis, high elasticity and low rolling resistance. Therefore, a smaller particle size leads to better interfacial effects that eventually improve grip and abrasion resistance. Though, the attraction of polymer chains to the surface of matrix would be advantageous to reduce hysteresis, which produces high heat and rolling resistance. Another form of particulate carbon, fullerenes, can strongly contribute as good reinforcement in rubber by producing physical crosslinks due to its highly active and curved surface. But, due to their toxic nature and higher cost still conventional fillers like CB or silica has been utilizing as reinforcements. In the same way, MWCNTs are also another good option for carbon-based nanoscale reinforcement. They can be excellently loaded into rubber matrices by solution processing. MWCNTs have high reinforcing efficiency due to which they can increase modulus greatly together with elongation to fail and hence results in a new compound after incorporation into the matrix having great characteristics like higher stiffness, stronger and more ductile. Furthermore, silica has also showed good reinforcement capability in the size range between nanoscale and microscale as a potential replacement for CB. At the stage of finer grading high viscosity produces due to strong particle–particle forces, resulting flow processing and dispersion complicated. In addition, sulfur vulcanization of the rubber formulation decreases because of its high acidity. Meanwhile, silane can be used to reduce the particle–particle interactions and increase particle–polymer interactions to enhance dispersion and improve reinforcement together with abrasion resistance without increasing hysteresis, making it appropriate for tire treads. A typical silane for bonding silica while also preventing interference with rubber cure is bis (3-triethoxysilylpropyl)-tetrasulfide (TESPT). Silane is able to improve some properties without the presence of silica but the treatment cost would be high (El Fray and Goettler 2010). Simultaneously, layered silicate especially montmorillonite, possesses high surface area and high aspect ratio, both of which makes it highly efficient reinforcing agent. The nonpolar organoclay when incorporated in brominated isobutylene-co-paramethylstyrene (BIMS), results increased mechanical properties and T_g temperature with decreases in cure time (Maiti et al. 2004). Although, layered silicates, being highly effective polymer reinforcements, are less efficient than conventional reinforcements like CB in strengthening rubber, and also results in high hysteresis (Kato et al. 2006). Thus, they are not being used for structural applications, such as stress-supporting tire components. Apart from that the high aspect ratio makes them more appropriate for stiffening than strengthening of the polymer matrix (El Fray and Goettler 2010).

It has also been found that the existence of ammonium ions on the gallery surfaces of rubber matrix result an increase in sulfur vulcanization, consequently, cure time and the shear modulus at cure temperature reduces due to the presence of organoclay, which indicates a looser crosslink network (Al-Yamani 2007). It has been investigated that addition of a dispersion agent to the treated clay that result an increase in the rubber modulus by enhancing the degree of dispersion of the clay platelets by Al-Yamani and Goettler (Al-Yamani 2007). Montmorillonite can also be added as a secondary reinforcement to nanoscale CB or silica because of their two mesoscale dimensions in the plane of the platelet. For instance, duel reinforcement of nitrile rubber with layered silicates and wood cellulose pulp fibers causes synergy effect in nanoscale hybrid composites, with respect to tear resistance (Benes 2002). However, layered silicate insertion improves tear resistance with or without the presence of cellulose fibers. On the other hand, cellulose fibers offer more reinforcement for tensile strength compared to nanoscale platelets. Evidently, these two reinforcements together developed a multiscale composite having more strength and high tear resistance. Therefore, these reinforcements can be used in rubber products like hosing pipes, belts, seals and mouldings. For application, the layered silicate platelets, as filler, resist compressional stresses in the pulley grooves in transmission v-belts, allowing some measure of axial flexibility. Alignment of the silicate platelets in the plane of sheet like matrix produces longitudinal stability in die cut nanocomposite seals and improves swell in thickness provide a tight joint. Also, layered silicate rubber nanocomposite can be used for the formation of effective short fiber reinforced rubber hoses in extrusion dies (Goettler 1979).

10 Effect of Ionic Liquids in Rubber Nanocomposites

Ionic liquids (ILs) usually consist of bulky organic cations and small inorganic anions which in turn of the does not form closed packed crystal structure and thus remain liquid at room temperature. ILs have unique physical properties such as negligible vapor pressure at room temperature, low melting points, non-flammability, high thermal stability, make them attractive for the industrial applications. ILs have been explored as powerful electrolytes for electrochemical systems such as lithium ion batteries (Park et al. 2010), fuel cells (de Souza et al. 2003), and solar batteries (Ye et al. 2013) and many other application (Taha et al. 2016a, b; Srinivasa Reddy et al. 2016; Nayeem et al. 2016; Khan et al. 2014a, b, c, 2015, 2016a, b; Passos et al. 2014). Depending upon their exclusive properties, they can also be employ in polymers as plasticizers (Scott 2003) and antistatic additives (Pernak et al. 2001). ILs performance as additives in rubber compound revealed drastic changes due to their extraordinary characteristics such as chemical stability, thermal stability, low vapor pressure, non-flammability and high ionic conductivity (Ferreira et al. 2012; Sowmiah et al. 2009; Leys et al. 2008; Armand et al. 2009; Vila et al. 2007). ILs

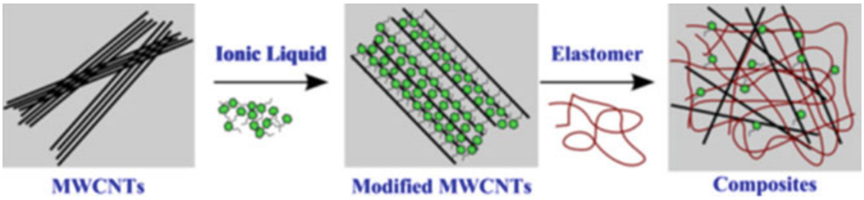

Fig. 5 Electro-conducting and truly elastic materials with MWCNT

attracted a lots of attention because of their ability to improve filler dispersion in elastomeric composites such as in CNT (Likozar 2011; Subramaniam et al. 2011; Das et al. 2009; Le et al. 2012; Tunckol et al. 2012; Kim et al. 2012), CB (Tunckol 2012), halloysite nanotubes (Lei et al. 2011; Guo et al. 2010), and silica (Lei et al. 2010, 2012), for hydrophobic matrices. Subramaniam et al. (2011) prepared rubber composite using IL with highly electro-conducting and truly elastic materials with MWCNT (Fig. 5). Further, ILs have also been used to improve ionic conductivity together with thermal and mechanical properties of polymer composites. ILs have been showed great interaction towards various fillers such as SWCNT, silica and clays through the mechanisms like π–π stacking, cation–π interactions, hydrogen bonding, van der Waals forces and electrostatic forces (Lei et al. 2010). Consequently, ILs, in combination with rubbers, have been utilized to fabricate unique materials like solid-state polymer electrolytes or electroactive polymers (Cho et al. 2006, 2007; Marwanta et al. 2005; Liu et al. 2010). Although high IL quantity is required to develop a specific composite having desired properties which may affect the curing process of rubbers. ILs have already been employed in elastomer composites of HNBR (Likozar 2011), polychloroprene rubber (CR) (Subramaniam et al. 2011; Das et al. 2009; Le et al. 2012), SBR (Guo et al. 2010; Lei et al. 2010, 2011, 2012; Kreyenschulte et al. 2012) and acrylonitrile–butadiene rubber (NBR) (Cho et al. 2006, 2007; Marwanta et al. 2005). It has been reported that imidazolium ILs are able to change crosslinking behavior of rubber composites (Lei et al. 2011; Pernak et al. 2010). Moreover, some ILs have been found to accelerate vulcanization process or decreases the vulcanization time of rubber compounds by catalyzing the interface crosslinking reactions (Pernak et al. 2010; Przybyszewska and Zaborski 2010). The vulcanization acceleration efficiency of ILs depends on the type of anion, for example, rubber compounds having alkylimidazolium chlorides and bromides showed higher cure rate of NBR vulcanized with sulfur, while rubber compounds with alkylimidazolium hexafluorophosphates exhibited longest vulcanization times (Przybyszewska and Zaborski 2010). Currently, anion is being used to control the water miscibility, hydrophobicity or hydrogen bonding ability of elastomer composites (Pringle et al. 2002). Elastic polymer electrolytes have been developed using NBR and ILs by Cho et al. (2007) and Marwanta et al. (2005). On the other hand, Fukushima et al. (2007) reported imidazolium based room temperature ILs can be used to disperse SWCNTs by means of cation–π/π–π interaction. However, latter on Heinrich (Subramaniam et al. 2011) investigated the effect of varying the IL proportions on the elastomers properties and discussed the effectiveness of IL modified MWCNTs on CR. Similarly, Likozar (2011) conducted studies on the properties of HNBR polymer films containing different ionic liquids. In an interesting study, Laskawska et al. (Laskowska et al. 2013) accounted an increase in the conductivity from 10^{-10} S cm^{-1} up to 10^{-7} S cm^{-1} approximately at 15 phr loading of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][Ntf$_2$])/XNBR composite. Incorporation of [Emim][Ntf$_2$] in XNBR produced a shift T_g temperature towards lower temperature, from 23 to 31 °C, at 15 phr loading, which is responsible for the plasticizing action of [Emim][Ntf$_2$] in the XNBR system. It is also observed that the use of [Emim][Ntf$_2$] more efficiently improved the ionic conductivity without a deterioration of mechanical properties in comparison to 1-ethyl-3-methylimidazolium thiocynate [Emim][SCN]. Further, hydrophobic IL was contributed more in filler dispersion compared with the hydrophilic IL. While, Marzec et al. (2014a, b) conducted studies on mechanical properties NBR/SiO$_2$/IL. The author found lowest values of elongation at break and tensile strength, as well as the highest stiffness (highest modulus) for NBR/SiO$_2$/[Emim][SCN]composite which showed that the hydrophilic liquid [Emim][SCN] not only accelerates the crosslinking during vulcanization but also supporting to a faster degradation of the polymer. Moreover, the study also confirmed a better stability of the hydrophobic ILs such as [Emim][Ntf$_2$] and 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([Amim][Ntf$_2$]) in the polymer matrix compared to the hydrophilic IL, [Emim] [SCN]. It has been reported that the hydrophobic ionic liquids, ([Emim][Ntf$_2$]) and ([Amim][Ntf$_2$]) retarded the aging process of nitrile rubber composites exposed to outdoor conditions.

However, it is also observed that ILs based on anion [Ntf$_2$]$^-$ revealed a variety of electrochemical applications in super capacitors, sensors and biosensors because of their high conductivity and high electrochemical stability as compared to those ILs which contains dicyanamide [N(CN)$_2$]$^-$ or thiocyanate [SCN]$^-$ ions having high conductivity but much less electrochemically and thermally stability (Miran Beigi et al. 2013). The relationship between the length of the cation alkyl chain in a TFSI-based IL and the improved ionic conductivity of the XNBR/IL-LDH composite was also investigated by Laskowska et al. (2014). As already stated, the [Ntf$_2$]-based imidazolium salts act as plasticizers in the rubber matrix and contribute to the reduction in the T_g of the composites. It was observed that 1-hexyl-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Hmim][Ntf$_2$]) reveals the highest plasticizing effect in the XNBR/LDH composite and significantly increases the ionic conductivity of the composite. Furthermore, the effect of cation alkyl chain length was found less significant in ionic conductivity. Therefore, it has been concluded that the loading of ([Emim][Ntf$_2$]) (or ([Bmim][Ntf$_2$])) in rubber composites resulted better mechanical properties and ionic conductivity as compared to ([Hmim][Ntf$_2$]). Similar study by Laskowska et al. (2014) showed the influences of the alkyl chain length of an imidazolium cation and the IL concentration on the properties of NBR/SiO$_2$ composites. The author reported an increase in AC conductivity with the increase of IL quantity in the NBR/silica composites. The T_g of NBR/SiO$_2$ composites decreased as the length of the suspended alkyl chain in the IL cation increased. Moreover, the alkyl chain length was not contributed much in the ionic conductivity of the polymers. Though, the NBR/SiO_2 composites demonstrated improved conductivity in the presence of ILs. The IL with a TFSI anion showed superior dispersion of the silica filler at each concentration; but, the mechanical properties were declined. However, ([Emim][Ntf_2]) provided most significant function to the formation of crosslinks and accelerated curing process. In addition, [Ntf_2] anion based imidazolium ILs are more compatible with hydrophobic rubber matrices due to their hydrophobic nature (Huddleston 2001) prevents leakage (migration within the polymer matrix), facilitate rubber processing and improve filler dispersion throughout the elastomer matrix. These ILs have been applied in elastomers like hydrogenated nitrile rubber (HNBR) (Likozar 2011), chloroprene rubber (CR) (Steinhauser et al. 2012; Subramaniam et al. 2013), nitrile rubber (NBR) (Laskowska 2013; Marzec et al. 2014a) and solution styrene butadiene rubber (SBR) (Subramaniam et al. 2011).

11 Application of Rubber Nanocomposites

11.1 Rubber Nanocomposites in Membranes

The incorporation of impermeable particles reduces light gas and vapor permeability as particle loading increases in polymeric membranes of rubber which makes nanofilled polymers attractive membrane materials. It has been found that the different aspect ratio of organoclays such as montmorillonite (MMT) and fluorohectorite (FHT) having the same type of intercalant, revealed the best oxygen permeation measurements for hydrogenated nitrile rubber (HNBR)/organophilically layered silicate NCs (Gatos 2007). Further, nonporous metal oxide NPs dispersed in rubbery polymer in order to develop higher light gas permeability membranes that have little or no change in selectivity relative to the neat polymer (Barrer 1963). NCs developed by graphite/NBR showed significantly better wear resistance and gas barrier properties together with superior electrical/thermal conductivity (Yang 2007). While, NCs synthesised by loading layered silicates such as sodium bentonite and sodium fluorohectorite into NR, carboxylated styrene butadiene rubber (XSBR) and their 70/30 latex blend were investigated for membrane applications which showed reduced swelling rate due to the tortuosity of the path and the reduced transport area in polymeric membrane (Stephen 2006). In addition, butyl rubber/vermiculite NCs revealed brilliant gas barrier properties (Choudalakis 2009).

11.2 Rubber Nanocomposites in Tires

Addition of NCs into tire components is aimed to increase overall performance of vehicles in terms of fuel efficiency by reducing weight and energy consumption from rolling resistance. In this regard, loading of reinforcements like silica, alumina and fullerene black into tire tread formulations results a greater latitude in composition and better optimization of overall tire performance by allowing relaxation of formulation constraints in balancing heat build-up, traction and abrasion resistance. The compounds used in SBR tread like AlOOH reduces 8–20 % hysteresis, almost the same as for silica reinforcement. It has been observed that a 20 % decrease in hysteresis yields 4 % fuel savings and also reduced CO_2 emission (Myers 2008). Silica has greater reinforcing power as a filler, thus it improves tear strength, abrasion resistance, age resistance and adhesion properties as compared to CB (Ou 1996). However, CBs of high surface area provide good traction and abrasion resistance in tire treads, while large particle diameter or wide range of aggregate size causes reduction in rolling resistance. Fullerene, another form of carbons, possessed a lower specific gravity than conventional CB, but can be used inexpensively along with CB to optimize the performance characteristics of tread compounds (Lukich 1998). In a related study, silicon carbide (SiC) has been used to prepare elastomeric NCs that exhibit superior properties over conventional materials (Wang 2002). The author observed highest improvement in wet skid resistance together with nearly 50 % decrease in abrasion. It has also been reported that NCs developed from silicon carbide perform better than those products developed without additives or composites with conventional additives. Enhanced wet skid resistance provides extended life due to superior safety, and reduced abrasion. Recently, CBs, silicas and a new rubber silane have been used in tire systems to enhanced rolling resistance (Klockmann 2007). It has been also found that CB especially dedicated for application in truck tire treads because of its extremely low surface area which provides an excellent compromise between hysteresis and abrasion resistance. In addition, many pneumatic products are made up from elastomers like tire inner liners, and they periodically refilled with air. Therefore, high aspect ratio fillers have been used to improve the barrier properties of elastomers, for instance exfoliated clay minerals (Usuki 2002). The high roughness and planar geometry makes exfoliated layered silicates perfect barriers for penetration and slow down air loss through the tire inner liner. For instance, a new class of elastomeric nanocomposite barrier coatings, that maintain a high degree of flexibly along with excellent barrier properties, have been developed by elastomeric dispersions using exfoliated vermiculite as layered silicate filler, having good dispersion and stability in butyl rubber (Takahashi 2006). Superior barrier properties, for rubber products, can be achieved with the help of these coatings. As a result, different layered clay minerals have been dispersed in the elastomers matrix which permits sufficiently low air permeability in tire inner liners (Feeney 2006). It has also been found that CB/NR or CB/SBR composites developed by intercalation of montmorillonite nanoclay with a tetralkylammonium salt results in lower hysteresis, heat resistant and reduced compression (Cataldo 2007). Other related pneumatic applications utilizing the permeation reduction produced by incorporation of layered silicates could include tire innertubes, air springs and curing bladders (Gent 1992).

11.3 Rubber Nanocomposites in Medicine and Healthcare

One of the best known example of elastomer used in medicine is a medical grade silicone elastomers filled with silica and saline have been used for breast growth and reconstruction (Brody 1997). Whereas, InMat's elastomer nanocomposite, has been tested for coating in medical packaging and NR latex (NRL) containing silver salt has been found another interesting material for medical applications (Abu Bakar 2007). In an another interesting study by Dundee University researchers, a novel nanocomposite coating was developed to create antibacterial coatings (De Coster 2003). Correspondingly, natural properties of elastomers which provides good sealing properties, low gas and water permeability, outstanding oil resistance and a low level of migrating substances from rubber products are also make use of NBR rubbers in food, pharmaceutical and cosmetics (Myers 2007). A new group of composite biomaterials for tissue engineering scaffolds and biomedical implants and devices developed by biocompatible thermoplastic elastomer matrices and inorganic NPs fillers. Moreover, the incorporation of ceramic NPs, like alumina or titania, to polymer matrices greatly affects their mechanical, physical and biological properties (Piegat 2008).

11.4 Rubber Nanocomposites in Sporting Goods

Rubber composites have also been applied in sporting goods, for instance, vermiculite filler is incorporated into butyl rubber as the matrix in very high aspect ratio to produced flexible coatings with gas permeability 30–300 times lowers than butyl rubber. This technology first time used long life double core tennis ball, the official ball of the Davis Cup (Kato et al. 2006). In another interesting study nanosized $CaCO_3$ has been used in combination with different elastomers such as NR and NR/NBR blends for sport goods like laminated sheet for inflated balls and NR based cycle tubes with improved barrier properties and air retention (Chakravarty and Chakravarty 2007). Similarly, exfoliated graphite nanostructures incorporated in elastomeric matrix of NR, polyisoprene, polybutadiene, SBR, styrene-propylene or ethylene-diene block copolymer rubbers contains an intermediate nanocomposite layer in golf ball (Sullivan and Ladd 2006). While, thermoplastic elastomer polyurethanes (TPU) have already been captured market attention in foot wears as shoe soles. Thus, number of formulations with NPs has been developed to improve the dry sliding behaviour of TPU (Karger-Kocsis 2006).

11.5 Rubber Nanocomposites in Airspace Industry

Organoclay and other nanofillers incorporated into HNBR elastomers to develop high-performance NCs working at extremely high operating temperatures and extended material service lifetime for aerospace industry (Gatos et al. 2004; Anmin et al. 2007). First material developed of this kind was metal rubber (Lalli et al. 2005). Metal rubber is a new nanocomposite synthesized by self-assembly processing of metal NPs and elastomeric polyelectrolytes. Metal rubber elastomers are being used as sensors to detect fatigue, impact and large strain in aerospace applications. Polymer composites are also potential materials for microwave absorbers, sensors and other aerospace applications. For instance, electromagnetic absorbers are being used as electromagnetic shielding for air vehicles and wireless communications (Guo 2007). But, present electromagnetic absorption materials have numerous weaknesses like less durable and effective only over fixed frequency bands. Therefore, the current electromagnetic absorbers can be improved with the help of polymer composites reinforced with magnetic NPs.

12 Conclusion

A broad insight of elastomer composites have been focused in this chapter showing the excellent performance of composites with the emphasis on ILs used as additives in elastomer composites and fillers that have been incorporated in rubber matrix so as to enhance the final properties of composites successfully. It has been concluded that the use of ILs as additives in elastomeric composites greatly improved filler dispersion and ionic conductivity by affecting the vulcanization process. On the other hand, fillers having higher structure possessed higher modulus causes less hysteresis at lesser loading leading, high elasticity and low rolling resistance. While, a smaller particle size produces better interfacial affects that ultimately improve grip and abrasion resistance. Therefore due to much progress that has been gained by elastomer composite development, their broader range of applications has been conversed in this chapter.

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Manufacturing of Natural Fiber/Agrowaste Based Polymer Composites

Debora Puglia, Fabrizio Sarasini, Carlo Santulli and José M. Kenny

Abstract Most recently, there has been an increasing interest for the production of laminates for semi-structural applications using sustainable materials. In this field, a possible option is the use of composites including ligno-cellulosic fibers, which are normally obtained as by-products from the textile industry, therefore mainly in the form of fabric or mats. Despite a reasonably large amount of studies on thermosetting composites reinforced with vegetable fibers also exist, in the view to replace fiberglass e.g., in the automotive industry, it is clear on the other side that the evolution of natural fiber composites has a much stronger drive towards the use of thermoplastic matrices and possibly biodegradable ones. Moreover, in terms of life cycle analysis (LCA), it is recommendable that both matrix and fiber are obtained from by-products or even better waste from an industrial or agricultural process, so that their use may represent as such a reduction in the environmental impact of the whole process. Therefore, this chapter discusses first the opportunities offered and challenges encountered in the production of natural fiber composites, then concentrating on the possibilities to obtain a polymer matrix alternative to petrol-based ones, especially in the particular case of manufacturing biopolymers by using agrowaste as received or with limited structural transformations rather than simply as a monomer (e.g., dextrose) source for polymer synthesis.

Keywords Lignocellulosic fibers · Natural fiber composites · Thermoplastic starch · Biobased thermosets

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1 Natural Fiber/Agrowaste Based Thermosetting Composites

1.1 General Considerations

Thermosetting resins play an important role in industry due to their high flexibility for tailoring desired ultimate properties, leading to their high modulus, strength, durability, and thermal and chemical resistances as provided by high cross-linking density. Recent years have viewed an increasing demand of natural products in industrial applications for environmental issues, waste disposal, and depletion of non-renewable resources (Jenck et al. 2004; Raston 2005). Renewable resources can provide an interesting sustainable platform to substitute partially, and to some extent totally, petroleum-based polymers through the design of bio-based polymers that can compete or even surpass the existing petroleum-based materials on a cost-performance basis with high eco-friendliness values (Kaplan 1998; Stewart 2008b). In the case of thermosetting materials, the most widely applied renewable resources include plant oils as the most important renewable raw material for the production of bio-based polymer materials. Plant oils are triglycerides (triesters of glycerol with long-chain fatty acids) with varying composition of fatty acid depending on the plant, the crop, the season, and the growing conditions. Recent reviews have focused on the development of cross-linked plant oils and their derivatives for thermosetting applications, such as coating and resins (Biermann et al. 2000; Derksen et al. 1996; Meier et al. 2007; Raquez et al. 2010; Sharma and Kundu 2006). In addition to plant oils, other raw renewable materials of interest in the design of bio-based thermosetting materials include lignin and proteins due to their vast abundance and high functionality (Derksen et al. 1996; Stewart 2008a). Due to its aromatic nature, lignin has been considered as a promising substitute for phenol in phenol–formaldehyde-based resins. In non-food applications, the use of plant proteins like soy proteins and wheat gluten may be also a promising way to produce thermosetting (bio)materials with a large range of applications. In this framework, there has been also overwhelming interest in using biobased thermosetting polymers as matrix in natural fiber composites, not only because they are from renewable sources, but also since they have comparable mechanical properties to other conventional thermosetting polymers. Interestingly, many studies have been performed as regards the use of natural fibers as reinforcements in composites, but only quite a few investigations have been carried out on the possibilities of using polymers from renewable resources as matrix (Herrmann et al. 1998; Williams and Wool 2000). In the following paragraphs, the different thermosetting materials obtained from agrowaste material will be considered, and special attention will be given to composites containing natural macrofibers.

1.2 Phenolic Resins

Among different renewable resources, cashew nut shell liquid, an agricultural by-product abundantly available in tropical countries such as India, is one of the major and economical resources of naturally occurring phenols. Cashew nut shell liquid (CNSL) occurs as a reddish brown viscous fluid in the soft honeycomb structure of cashew nut shell, containing four major components with an unsaturated C15-chain, namely cardanol, cardol, anacardic acid and 2-methylcarbol (Fig. 1) (Voirin et al. 2014). The phenolic nature of resulting cardanol makes it possible to react with formaldehyde under a variety of conditions to form Novolac or Resole resins. Compared with conventional phenolic resins, cardanol–formaldehyde resins have improved flexibility (due to the internal plasticization effect of the long chain), leading to better processability (Quirino et al. 2014). The side chain imparts a hydrophobic nature to the polymer, making it water repellent and resistant to weathering. There are examples in which an epoxy resin crosslinked with a cardanol based novolac was used as matrix and jute fibers as reinforcement (Barreto et al. 2010; Campaner et al. 2010; Maffezzoli et al. 2004), or cardanol based composites containing sisal (Barreto et al. 2011), or buriti fibers (Da Silva Santos et al. 2010). Other examples of natural fibers that have been used to reinforce CNSL-based novalac or resole type resins include oil palm fibers (Tiamiyu and Ibitoye 2012), kenaf and hemp bast fibers (Aziz and Ansell 2004), coconut coir fibers (Barreto et al. 2012). Other renewable fillers include rice husks (Ofem et al. 2012), coffee husks (Bisanda et al. 2003) and sawdust (Lubi and Thachil 2007). Natural fiber reinforcements are frequently pretreated with an alkali solution (i.e. 5–12 % sodium hydroxide solution), to increase the number of hydroxyl groups on the surface of the fiber (Fig. 1).

As suggested above, due to its similar structure with phenol, lignin has been also considered as another natural substitute for phenolic based resins. Traditionally, lignin is viewed as a waste material available in large quantity derived from the wood pulp in the paper industry. Only 1–2 % of overall lignin is utilized for more specific applications, the remaining primary serving as a (bio)fuel. Similar to phenol–formaldehyde resins, lignins have an aromatic and cross-linked structure, together with a great variety of functional groups such as ether and hydroxyl groups, depending on the origin of lignin and the extraction technology (Laurichesse and Avérous 2014). Through the functionalization of its hydroxyl groups, lignin becomes a good candidate as a building block unit for polymer synthesis to elaborate innovative macromolecular architectures (Matyjaszewski and Möller 2012). Several attempts have been made to integrate lignin into industrial processes to emphasize its use as a renewable feedstock, for example for replacement of synthetic phenols in binders and in epoxy or phenol-formaldehyde resins formulations (Kouisni et al. 2011). Literature reports include several methods to synthesize lignin based epoxy resins. They have been applied for polyesters and phenolic resins applications, following different strategies (Mansouri et al. 2011), such as (i) blending lignin with epoxy resins (Yin et al. 2012), or (ii) modifying

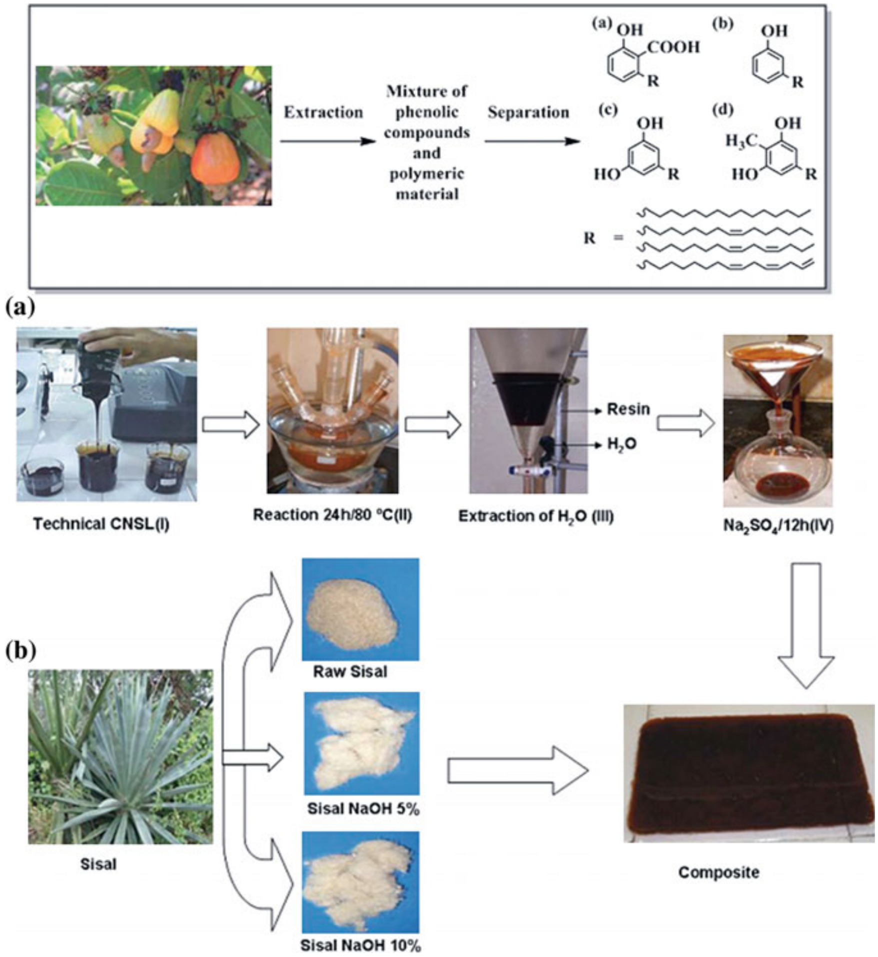

Fig. 1 Components in CNSL (Lochab et al. 2014) and flow chart of preparation of the biocomposites: **a** synthesis of polymer resol and **b** chemical treatment employed in the sisal fibers

lignin by an epoxidation reaction, usually with epichlorohydrin (Sun et al. 2007). Examples are also reported in literature in which lignin modified phenolics are used as matrices in natural fiber composites based on jute (Sarkar and Adhikari 2001), sisal (Faulstich de Paiva and Frollini 2006), flax and kenaf (Mahendran et al. 2013).

Tannin compounds, extracted from the wood, bark, leaves, and galls of plants can be also considered as another raw renewable material in the design of phenolic resin composites reinforced with natural fibers. Frollini et al. (2008) used tannin as a partial substitute of phenol in the preparation of composites reinforced with bark from the Acacia Mimosa tree (fibers and particles) and sisal (Fig. 2). The tannin used as the substitute of phenol was also extracted from the bark of the Acacia

Mimosa tree, because this tree is rich in tannin. In a companion paper, Barbosa et al. (2010) used the tannin–phenolic matrix in the preparation of composites reinforced with coir fibers.

1.3 Epoxy and Polyurethane Resins

In the formation of sustainable epoxy monomers, epoxidized plants oils and fatty acids have been largely utilized. Vegetable oils, such as linseed oil, soybean oil, castor oil, appear as excellent renewable raw materials for thermosetting polymers as they are expected to be inexpensive and abundant, they have been also studied as bio-based precursors through their epoxidation for the synthesis of bio-based epoxy prepolymers (Wang and Schuman 2013). Vegetable oil-based monomers containing reactive functional groups, such as conjugated double bonds, acrylates, and norbornene groups, have been successfully synthesized. These monomers can be polymerized by themselves or copolymerized with petroleum-based monomers using different polymerization methods to afford biorenewable thermosetting materials. Thermal and mechanical properties of these thermosetting materials can be finely tuned by controlling structures of vegetable oil-based monomers or using different kinds of co-monomers. Green vegetable oil-based composites can also be obtained by adding fillers, including natural fibers, into these vegetable oil-based thermosets to further improve their thermal and mechanical properties. Several researchers have investigated the synthesis and mechanical characterization of networks based on epoxidized vegetable oil epoxy monomers using various approaches (Liu et al. 2006). Park et al. (2004) synthesized and characterized epoxidized soybean oil (ESO) and epoxidized castor oil (ECO), which proved one of the most important functionalization reaction involving C=C double bonds. Soy based polyols derived from ESO have also been widely used to produce polyurethanes that are comparable in many aspects with polyurethanes obtained from petrochemical polyols (Lligadas et al. 2010). While epoxidized vegetable oils could

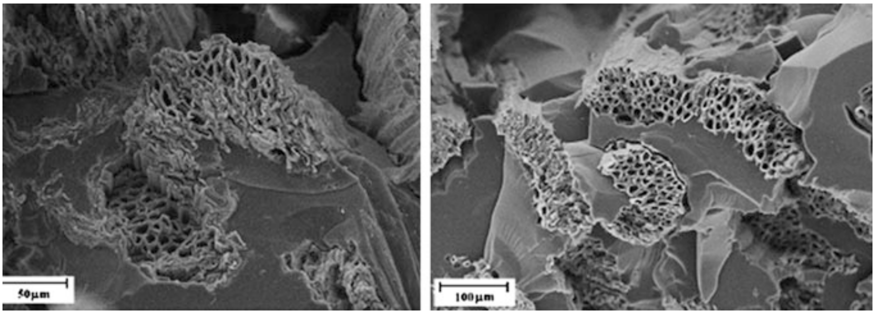

Fig. 2 SEM images of impact fractured surfaces of tannin–phenolic composites (TPC) reinforced with 50 wt% of sisal fibers (Ramires and Frollini 2012)

be interesting renewable materials for adhesives and plasticizers, they could not lead to high performance materials if fiber reinforcement is not considered. Taking into consideration this limit, most ESO industrial uses are thus limited to non-structural, additive applications, such as plasticizers or stabilizers: in this context, many attempts have been done to improve the properties of bio-based epoxy by using natural reinforcements. Quite a few publications exist in the field of bio thermoset-based natural fiber composites (Adekunle et al. 2010; Liu et al. 2007; Liu and Erhan 2008; Müssig 2008). Examples can be found for natural fiber composites manufactured with flax (Liu et al. 2006), jute (Masoodi and Pillai 2012), hemp fiber (Boquillon 2006) or composites prepared from corn, soybean, fish, and linseed oils using up to 75 wt% of different natural fibers, such as corn stover, wheat straw, and switch-grass fibers (Pfister and Larock 2012). Large scale natural fiber composite 'unit beams' of sandwich construction were successfully manufactured at the University of Delaware from flax mat, chicken feathers, recycled paper and structural foam using epoxidized soy-bean oil and a modified vacuum assisted resin transfer molding (VARTM) process (Dweib et al. 2006; Hu et al. 2007).

Vegetable oils can also be converted to polyols, which can further react with diisocyanates to provide polyurethanes. In sustainable thermosetting materials, polyurethanes are currently prepared starting from renewable polyols, while the second partner, isocyanate, is mainly made from petroleum-resources.

Examples of biobased polyurethanes containing natural fibers can be found for castor oil-based polyurethanes with banana fibers processed by hand lay-up of short random fiber-mats, followed by compression molding at room temperature (Merlini et al. 2011). A natural polyol of alcoholysed castor oil with triethanolamine-based rigid polyurethane foam and wood flour composite was prepared and characterized, revealing a decrease in compression modulus and yield strength with increasing wood flour content, although good interaction of wood flour with isocyanate was noticed (Mosiewicki et al. 2008) (Fig. 3).

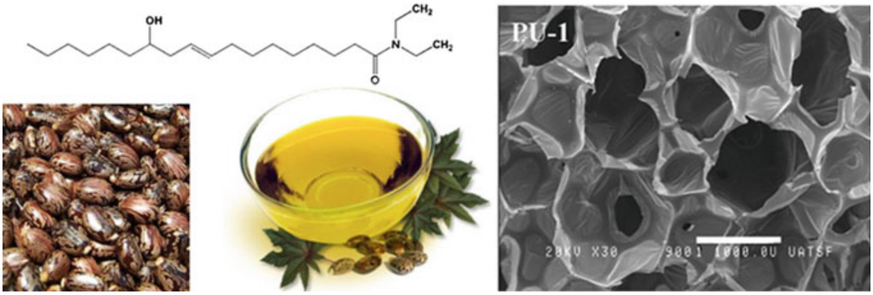

Fig. 3 Castor oil (chemical formula, seed and oil) and SEM image of flexible polyurethane foams based on castor oil (Kozak and Lobko 2012; Spontón et al. 2013)

The same oil-based polyurethane composites of natural fibers such as sisal, coconut short fibers and woven sisal fabric have been studied. The results showed that the performance of coconut fiber composites is generally inferior to that of sisal fiber and even to the neat polyurethane matrix, whereas the best performance was displayed by the sisal fabric composite (Chen et al. 2006). Two types of environmentally friendly jute fiber reinforced green composites have been studied. These are based on *Mesua ferrea* L. seed oil based poly(urethane ester) and poly(urethane amide) resin blends with commercially available partially butylated melamine–formaldehyde and epoxy resins by solution impregnation and hot-curing methods (Dutta et al. 2010).

1.4 Polyester Resins

Polyester resins currently used for decorative coatings and for a wide range of commodity composite materials (in industrial equipment such as tanks, boat building, truck roofs, and so on) are a class of unsaturated polyester derived from the polycondensation of a polyol and a polyvalent acid or acid anhydride. These building blocks can be substituted for renewable-based analogous, either partially, or to some extent, totally. For example, fatty acids or oils can be used as polyacids, while rigid carbohydrates, such as isosorbide, can be used as polyols. Isosorbide is a sorbitol derivative obtained from starch through hydrolysis and subsequent hydrogenation of the glucose into sorbitol.

Recently, lignin esters have been also proposed for use as unsaturated ester thermosets: following a fast and simple procedure, kraft lignins were esterified with anhydrides to render them more soluble in styrene, improving toughness and connectivity in the polymer network (Raquez et al. 2010). Epoxidized vegetable oils can be used as a replacement for polyester resins. Rösch et al. prepared cross-linked partially bio-based polyesters by curing epoxidized soybean oil with various dicarboxylic acid anhydrides (Rösch and Mülhaupt 1993). In the case of composites, an example can be found in the work of Haq et al. (2008), where the synergy between natural fibers (industrial hemp) and the biobased resins obtained by partial substitution of unsaturated polyester (UPE) with epoxidized soybean oil (EMS) was exploited. In Yeganeh and Mehdizadeh (2004), John et al. (2002) methacrylated soybean oil, methacrylic anhydride modified soybean oil (MMSO) and acetic anhydride modified soybean oil-based resins and flax fiber composites were manufactured by a compression molding technique. The fiber to resin ratio was 60:40, where air-laid fibers were stacked randomly, the woven fabrics were stacked in a crosswise (0/90) configuration and impregnation was performed manually. The resultant cured bio-based composites exhibited significantly improved performance.

1.5 Natural Fiber/Agrowaste Based Thermosetting Elastomers

Several works were carried out employing vegetable oils as precursors for the synthesis of vegetable oil-based polymers, in which the resulting polymers had elastomeric or rubbery properties (Visakh et al. 2013). In these works, the vegetable oils such as linseed, tung, soybean, corn, castor oils and others, or the modified vegetable oils, were crosslinked by vinyl monomers, such as styrene, a-methyl styrene, divinyl benzene, cyclopentadiene and others. Moreover, a promising alternative for the production of elastomeric polymers is also the use of furanic molecules, such as furfural and hydroxymethyl furfural. From these two compounds, furfural and hydroxymethylfurfural, many monomers can be produced through their functionalization, can be polymerized and the resulting polymers may have thermoplastic properties and even rubbery properties. However, except for natural rubber, all other molecules from renewable sources by themselves or in a polymerized form do not exhibit the characteristics of elastomers. The polymers produced from these molecules are mostly thermoplastic, and to provide elastomeric characteristics they need to be modified by grafting, copolymerization or blending.

Extensive literature is present for the case of thermoplastic biobased elastomers, especially in the case of polyurethanes (Ghassemi and Schiraldi 2014; Tang et al. 2014), while very few examples can be found in the case of thermosetting elastomers. In the paper of Gopalakrishnan and Linda (2011), novel thermosetting polyurethanes from novolac type hydroxyalkylated cardanol-formaldehyde resins, polypropylene glycols (PPG-1200 and PPG-2000) and aliphatic diisocyanates, such as hexamethylene diisocyanate and isophorone diisocyanate, were prepared in the form of thin sheets, while in Wang et al. (2012), a novel cross-linkable, high molecular weight poly(diisoamyl itaconate-co-isoprene) (PDII) elastomer was prepared by emulsion polymerization based on itaconic acid, isoamyl alcohol, and isoprene. In Zhu and Wool (2006), a new bio-based elastomer synthesized from soybean oil was filled with nanoclay to generate an elastic nanocomposite, while Andjelkovic and Larock (2006) studied the synthesis and characterization of novel rubbers from cationic copolymerization of soybean oils and dicyclopentadiene. To the best of our knowledge, fully green elastomeric composites have never been produced and studied, being the production of elastomeric polymers from molecules from renewable sources, to be used as a matrix in these composites, still a big challenge. This is an area in which there are still many possibilities to explore and research efforts must be concentrated on solving this problem and thus opening new opportunities in the preparation of fully green elastomer composites, generating new applications for them as replacements for conventional elastomer composites.

1.6 Natural Nanofillers in Biobased Thermosets

The use of nanofiller in bio-based polymers for fiber reinforced polymer composites can provide value added properties to biocomposites. In such composites, the natural fibers remain the main reinforcement for stiffness and strength, while the nanofiller could enhance the matrix properties.

Few examples of nanocomposites in which the cellulosic nanostructure is used in bio-based thermosets can be also found. Due to the fact that these environment friendly composites suffer from several limitations, such as low mechanical properties due to low strength in reinforcement plus inadequate interfacial strength, and that cellulose nanostructures have been shown to have significant potential as reinforcement, the possibility of using cellulose nanofibers as reinforcements in a bio-derived resin was revised. In Masoodi et al. (2012), cellulose nanofibers were used as reinforcements in the forms of layered films, while in Lee et al. (2011) the stability of the gas-soybean oil foam templates and the mechanical properties of the polymer nanocomposite foams are enhanced upon the addition of bacterial cellulose nanofibrils. Other examples of bio-based thermosets containing cellulosic nanoreinforcements are the work of Shibata and Nakai (2010) in which the use of a bio-based epoxy was revised, and systems in which cellulose nanocrystals are incorporated in bio-based polyurethanes (Lin et al. 2013; Wik et al. 2011). Few examples exist also in the literature on the polymerization of furfuryl alcohol in presence of cellulosic nanoreinforcements (Pranger and Tannenbaum 2008); in these papers, the authors established the feasibility of producing furfuryl alcohol reinforced by cellulose nanowhiskers and montmorillonite using in situ polymerization without using any solvent or surfactants. They found that sulfonic acid residues at the cellulose nanowhiskers surface, which were left over from the acid hydrolysis treatment, acted as catalyst for the polymerization reaction of furfuryl alcohol. Results on the use of nanocellulose in fiber reinforced traditional thermosets can be found in Phillips et al. (2013), where the infusion of an epoxy reinforced with nanocellulose in presence of flax was studied.

Limited examples can be also found in which the biobased natural fiber composite contains cellulosic nanostructures. A waterborne polyurethane synthesized from castor oil and polyethylene glycol crosslinked with isophorone diisocyanate was used as matrix in a cellulose nanocrystals (from *Eucalyptus globulus*) based composite with concentrations from 0.2 to 5 wt% (Gao et al. 2012). The use of bio-based thermosets clearly represents an area of significant interest, since further combination of environmental friendly high performance materials with cellulosic nanostructures can surely give the opportunity of creating new high performance hybrids.

2 Natural Fiber/Agrowaste Based Thermoplastic Composites

2.1 Production of Natural Fiber Composites: Perspectives and Difficulties

The manufacturing of natural fiber composites can represent a tough challenge due to the inherent properties of natural fibers that differ significantly from those of synthetic ones such as glass, aramid and carbon fibers. The key parameters for successful processing of natural fiber composites are related to their hygroscopic behavior and low resistance to high temperature that have so far limited the possibilities for selection of polymers to be effectively used as matrix in a composite material. Also, the use of natural fibers would require, at least in principle, the subsequent adoption of biopolymer matrices, in order to obtain a fully biodegradable, if not compostable, composite material, so to yield substantial environmental advantages, which are strongly desirable in some fields of application. In addition, the suitability of traditional manufacturing techniques for natural fiber reinforced polymer composites is still under evaluation due to the fact that mechanical and thermal properties of both natural fibers and biodegradable polymers are somehow different from those of synthetic fibers and petroleum-based polymers (Ho et al. 2012). In practice, the way natural fibers are introduced as reinforcing material in polymer composites has to be adjusted to the available production techniques so as to make easier for industries their adoption in viable industrial products. Composites manufacturing processes can be broadly divided into two main manufacturing categories according to the nature of polymer matrix, namely thermoset or thermoplastic but, in the case of natural fiber composites, the processing parameters are usually dependent also on the type of natural fiber. Manufacturing methods for processing thermoset composites offer the following advantages (Mazumdar 2001):

- processing of thermoset composites is much easier because the initial resin system is in the liquid state and fibers are easy to wet with thermosets, thus voids and porosities are less;
- heat and pressure requirements are less in the processing of thermoset composites than thermoplastic composites, thus offering energy savings;
- a simple low-cost tooling system can be used to process thermoset composites.

The disadvantages are related (i) to the lengthy cure time that results in lower production rates than thermoplastics, (ii) to the impossibility of reform thermoset composites once cured to obtain different shapes and (iii) to the difficulty in their recycling at the end of service life.

Low viscosity thermosetting polymers that can be cured at room temperature are considered a right choice as they can easily impregnate natural fibers without the damage associated to their thermal degradation. Resin transfer molding (RTM), vacuum assisted resin transfer molding (VARTM) and sheet molding compound

(SMC) represent some of the most ordinary techniques used for impregnating and forming thermoset-based natural fiber composites (Francucci et al. 2012; Kong et al. 2014; Richardson and Zhang 2000; Rodriguez et al. 2004; van Voorn et al. 2001).

The long cycle times and high cost (mainly due to post molding operations such as trimming) in processing thermoset composites have shifted the attention to natural fiber composites based on thermoplastic matrices. In the case of thermoplastic composites, the initial raw material is in solid state and needs to be melted to obtain the final product. The advantages of processing thermoplastic composites include:

- the process cycle time is usually very short because there is no chemical reaction during processing, and therefore can be used for high-volume production methods;
- thermoplastic composites can be reshaped and reformed with the application of heat and pressure and are therefore easy to recycle.

Selection of the production technique depends on the production rate and the product status (semi or finished). Injection molding requires prepared pellets of composites whilst the pultrusion and extrusion processes can deal directly with fibers to have a profile product. Moreover the production technique affects the fiber aspect ratio and fiber orientation and hence the mechanical properties of the resulting composites. For example, in pultrusion long and unidirectional fibers are obtained within the produced profile, while more randomness in the fiber direction is achieved in extrusion and injection molding. It is important to emphasize that these processes involve heating of the material above the melting point of the chosen matrix. Since the degradation temperature of most natural fibers lies in the range of 150–220 °C, attention should be paid to minimize the exposure of natural fibers to these high temperatures. The thermal decomposition of fibers generates volatiles and the resulting composites are always characterized by low mechanical properties (Gassan and Bledzki 2001; Kim et al. 2005; Ouajai and Shanks 2005). For this reason, the polymers presently used as matrices are those with low to moderate melting temperatures, that is to say polypropylene (PP), polyethylene (PE), poly(vinyl chloride) (PVC) and polystyrene (PS) (Abdelmouleh et al. 2007; Faruk et al. 2012; Khalil et al. 2013; Ku et al. 2011; Van den Oever et al. 2000; Singha and Rana 2012; Zampaloni et al. 2007). Strictly related to the choice of thermoplastic matrix is the poor compatibility between the mostly hydrophobic thermoplastic polymers and the hydrophilic natural fibers that makes it necessary the use of coupling agents and fiber surface treatments (Belgacem and Gandini 2005; Fuqua et al. 2012; Keener et al. 2004; Mohanty et al. 2001). Another concern that can affect in a significant way the composites is related to moisture content of natural fibers that is usually in the range of 6–12 wt% and should be reduced to less than 3 wt% in order to enable the production of molded parts of good quality.

In the following subparagraphs special attention will be given to the manufacturing processes and issues related to agro green thermoplastic composites reinforced with natural fibers both on a micro and nanoscale even though very often the manufacturing route is only secondary to the mechanical and thermal properties obtained.

2.2 Starch Based Thermoplastic Composites

In the past decades there has been a renewed interest in the use of environmentally friendly alternatives to petroleum based polymers that has triggered the development of the biodegradable polymers, whose taxonomy is schematically summarized in Fig. 4. Except the last family that is of fossil origin, most polymers are obtained from renewable resources: in particular, this subsection will be devoted to the first family that represents the so called agro polymers obtained from biomass by fractionation and in particular on starchy materials.

Starch is a polysaccharide mostly produced by higher order plants as a means of storing energy. It is stored intracellularly in the form of spherical granules 2–100 μm in diameter with multilevel structures from macro (native granules) to molecular scales, i.e. starch granules, alternating amorphous and semicrystalline shells (growth rings) (100–400 nm), crystalline and amorphous lamellae (periodicity) (9–10 nm), and macromolecular chains (~nm) (Xie et al. 2012). Most commercially available starches are isolated from grains such as corn, rice and wheat, and from tubers such as potato and cassava (tapioca) (Wollerdorfer and

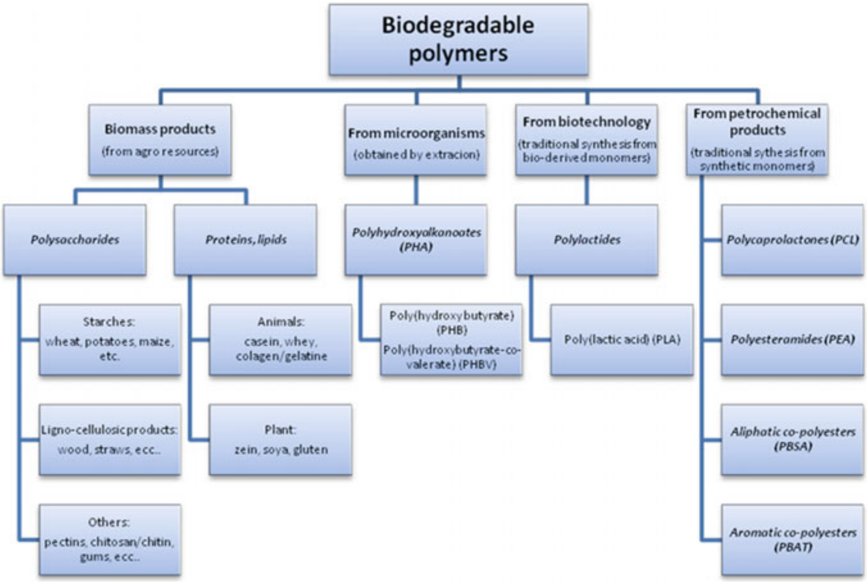

Fig. 4 Classification of biodegradable polymers

Bader 1998) (Teixeira et al. 2012). Starch is a polysaccharide consisting of D-glucose units with two major biomacromolecules that are amylose and amylopectin. Amylose is a sparsely branched carbohydrate mainly based on α(1–4) bonds whereas amylopectin is a highly multiple-branched polymer based on α(1–4) (around 95 %) and α(1–6) (around 5 %) links, with constituting branching points localized every 22–70 glucose units. Moreover, in starch granules are also found very small amounts of proteins, lipids and phosphorus depending on the botanical source (Xie et al. 2012). Depending on the source, amylose content of starch can lie in the range from 1 to 70 % and most native starches are semicrystalline with a crystallinity of about 20–45 % (Liu et al. 2009).

Processing these materials is much more complex than using traditional polymers due to the multiple chemical and physical reactions that take place, e.g. water diffusion, granule expansion, gelatinization, decomposition, melting and crystallization.

Gelatinization is particularly important because it is the basis of the conversion of starch to a thermoplastic and refers to the destruction of the crystalline structure in starch granules. In fact, native starches are non-plastic due to the intra- and inter-molecular hydrogen bonds between the hydroxyl groups in starch molecules, which represent their crystallinity. Thermal processing is used to disrupt and transform the semi-crystalline structure of starch granules to form a homogeneous and amorphous material. This transformation is usually accomplished using small amounts of molecular substances commonly known as gelatinization agents or plasticizers (water, glycerol, glycol, citric acid, urea). The transformed material is known as thermoplastic starch (TPS). Furthermore, since materials consisting mainly of pure starch normally offer unfavorable final product properties such as poor mechanical characteristics, limited long-term stability and high moisture sensitivity, TPS is regularly blended with other polymers such as poly(lactic acid) (PLA), polycaprolactone (PCL), poly(butylene succinate adipate) (PBSA), poly (hydroxy ester ether) (PHEE) and polyvinyl alcohol (PVA) (Liu et al. 2009). In addition to blending, another approach consists in the use of cellulose-based fillers. Starch based materials can be processed with the same techniques used for conventional polymers, such as extrusion, injection molding, compression moulding and film casting even though the formulation and processing conditions have to be carefully selected, optimized and controlled due to the singular phase transitions that can occur. A detailed investigation of the thermal processing and the rheology of these materials can be found in Liu et al. (2009) and Xie et al. (2012).

2.2.1 Biocomposites Based on TPS and Natural Fibers

Several types of fibers have been tested along with TPS: bleached leafwood fibres (Averous and Boquillon 2004; Avérous et al. 2001a, b; Funke et al. 1998), fibres from bleached eucalyptus *urograndis* pulp (Curvelo 2001), fibers from paper pulp (Averous and Boquillon 2004), flax fibers (Wollerdorfer and Bader 1998), jute fibers (Wollerdorfer and Bader 1998), ramie fibers (Wollerdorfer and Bader 1998), hemp fibers (Gironès et al. 2012), oil palm fibers (Wollerdorfer and Bader 1998), sisal fibres (Gironès et al. 2012; Leblanc and Saiter 2009), bagasse fibers Kaewtatip and Thongmee (2014) and luffa fibers (Kaewtatip and Thongmee 2012). Averous and Boquillon (2004) tested various formulations based on plasticized starch matrix, varying matrix formulation (glycerol/starch ratios = 0.257 and 0.538), fibers length (from 60 μm to 1 mm), filler content (up to 30 wt%) and fibers' nature (natural cellulose fibers from leafwood and paper pulp fibers). A wheat starch was used in order to prepare two different TPS matrices characterized by a dissimilar amount of glycerol as plasticizer, namely TPS_1 (less amount of glycerol and therefore brittle at room temperature) and TPS_2 (higher amount of glycerol and therefore soft at room temperature). After dry blending, native wheat starch and glycerol were added to a turbo-mixer (2000 rpm). After dispersion in the mixer, cellulose fibers were added and the final mixture was obtained at higher speed (2500 rpm). The blend was then extruded in a single screw extruder and the pellets, after a first granulation, were again extruded to allow a better dispersion. Final pellets were then injection molded (100–130 °C, 1500 bar) to obtain the specimens for the mechanical characterization. The authors found that both Young's modulus and tensile strength increased with the fiber length and content in comparison with the neat matrix whereas the elongation at break decreased. These improvements are consistent with a good compatibility at the filler/matrix interface as found in other investigations (Avérous et al. 2001b; Funke et al. 1998). In particular, cellulosic fibers showed a better interface adhesion compared to the lignocellulosic ones and a higher amount of plasticizer was found detrimental to the properties of the composites due to the formation of glycerol rich domains that affected in a negative way the filler/matrix adhesion. The introduction of these agrofillers was found positive also for the thermal resistance (Dufresne and Vignon 1998) of the biocomposites with lignocellulosic fibers that caused higher degradation temperatures in the resulting composites.

Similar positive results were found by Wollerdorfer and Bader (1998) who tested several formulations of natural fibers and thermoplastics such as biodegradable polyesters, polysaccharides and blends of thermoplastic starch. A wheat starch was plasticized with glycerol and sorbitol using a co-rotating twin screw extruder at 115 °C and 50 rev/min. The extrudate was then pelletized and processed by injection molding. Depending on the type of polymer matrix, a maximum fiber content of 20–35 wt% was attained. The chemical similarity of polysaccharides and plant fibers resulted in a fourfold increase of tensile strength of the reinforced polymer compared to the neat TPS (Fig. 5). The Young's modulus also increased in a similar way to the tensile strength while the elongation at break was drastically reduced (from 45 % up to 1.3–2.0 %).

In addition to injection molding, compression molding has been extensively investigated for processing starch based polymers. In (Kaewtatip and Thongmee 2014) pregelatinized cassava starch, glycerol and NaOH treated bagasse fibers at different contents (0–20 wt%) were mixed in polyethylene bags until a homogeneous dispersion was achieved. The mixture was then compressed at 160 °C for 10 mins under a pressure of 200 kg/cm^2 and subsequently cooled down to room

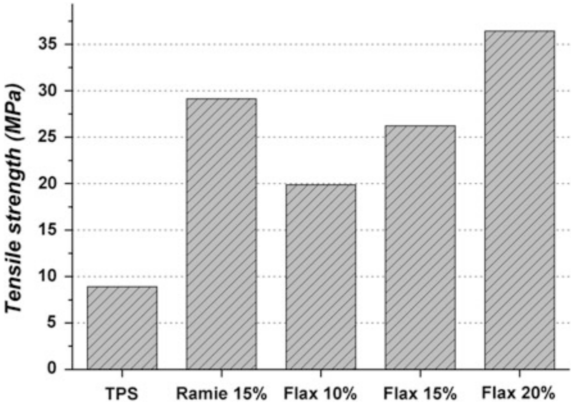

Fig. 5 Tensile strength of TPS reinforced composites

temperature. The authors found that there was a good adhesion between the treated fibers and the TPS matrix as a result of the fiber's surface roughening caused by the NaOH treatment (Cao et al. 2006) and of the chemical similarity of fibers and starch that makes it easy the formation of hydrogen bonds in the structure (Kaewtatip and Thongmee 2012). The water absorption of the TPS reinforced composites was lower compared to the neat TPS due to fiber-matrix interactions and to the higher hydrophobic character of the cellulose that is related to its high crystallinity (Curvelo 2001; Dufresne et al. 2000; Dufresne and Vignon 1998). In addition, maximum weight loss of TPS reinforced composites was measured at a higher temperature compared to that measured for the neat matrix: the difference was by about 12 °C for 20 wt% of treated bagasse fibers, which also inhibited the retrogradation of the starch, The beneficial effects of introducing natural fibers into TPS matrices can be further confirmed by the results obtained on sisal fiber reinforced TPS composites obtained through a combination of extrusion and compression molding (Fig. 6) (Leblanc and Saiter 2009).

2.2.2 Starch-Based Nano-biocomposites

Several types of nanofillers have been used with plasticized starch that can be broadly subdivided in organoclays (montmorillonite, hectorite, sepiolite and so forth), polysaccharide nanofillers (nanowhiskers/nanoparticles from cellulose, starch, chitin, and chitosan) and carbonaceous nanofillers (carbon nanotubes, graphite oxide, and carbon black). In this section only the use of polysaccharide nanofillers from cellulose will be addressed. A detailed review of the state of the art in the field of starch-based nanocomposites can be found in Xie et al. (2013). There is a wide range of cellulose particle types currently under investigation for various commercial applications. The diversity of cellulose particle types depends on cellulose source and extraction processes. There are basically two families of nanosized cellulosic particles, the former consisting of cellulose nanocrystals (CNC) or

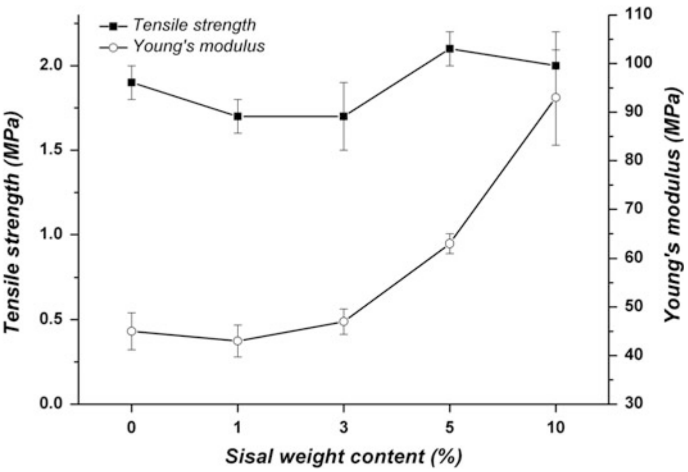

Fig. 6 Tensile strength and Young's modulus of TPS reinforced composites as a function of sisal content

nanowhiskers (CNW), whilst the latter is microfibrillated cellulose (MFC) (Brinchi et al. 2013; Lu et al. 2008). CNC has been isolated from a variety of cellulosic sources, including plants, animals (tunicates), bacteria and algae and in principle can be extracted from almost any cellulosic material. The isolation of CNC from cellulose source materials occurs in two stages, where the first one is a pre-treatment of the source material that for wood and plants involves the complete or partial removal of matrix materials—hemicelluloses, lignin, etc.—and isolation of the cellulosic fibers. The second one is a controlled chemical treatment, generally hydrolysis with a concentrated mineral acid (usually sulphuric acid), in order to remove the amorphous regions of the cellulose polymer and obtain a highly crystalline structure. Usually the manufacturing process of choice is the solution casting (Cao et al. 2008; Lu et al. 2006) even though also melt blending techniques have been explored (Teixeira et al. 2009). According to the literature, the mechanical properties (tensile strength and Young's modulus), thermal property (T_g), and moisture resistance generally show improvement with addition of CNWs to starch-based materials (Cao et al. 2008; Chang et al. 2010; Kvien et al. 2007). This can be related to both the good nanofiller dispersion in the matrix, resulting from the chemical similarity, and the strong nanofiller–matrix adhesion by hydrogen bonding interactions (Cao et al. 2008; Lu et al. 2006). In particular, the increase in mechanical properties can be assisted by the formation of a rigid network of the CNWs, the mutual entanglement between the nanofiller and the matrix, the efficient stress transfer from the matrix to the nanofiller along with an increase in the overall crystallinity of the system stemming from the nucleating effect of the CNWs. The increase in T_g is due to the restriction of mobility of the amorphous starch chains by the contact with the CNW surface or by the increased crystallinity, and to the relocation of the plasticizers (including water) from the starch matrix to the CNW surfaces that can decrease the overall plasticization effect on the amorphous regions. As for cellulose-based microfibers, moisture resistance improves and this behavior can be explained by the less hydrophilic nature of cellulose and the geometrical hindrance created by the CNWs, by the constraint of the starch swelling due to the presence of the rigid CNW network, and by a decrease in the mobility of the starch chains, resulting from an increase in the T_g or the crystallinity as previously discussed (Xie et al. 2013).

3 Conclusions

As a whole, the production of natural fiber/agrowaste based thermoplastic composites represents a promising possibility in the way to produce a biodegradable material, aimed at applications such as packaging and automotive, with additional benefits for the environmental impact of the whole process. Some difficulties persist nonetheless, in particular: it is not obvious to ensure a good compatibility between the biopolymer matrix and the vegetable fiber if they have not been obtained using waste from the same agricultural crop. In other words, polysaccharides extracted from agrowaste show a non negligible influence deriving from the botanical species they were obtained, which in turn affects a number of properties in the final composite, such as interaction with water and bacteria, crystallinity, glass transition temperature, etc. To enhance crystallinity, the fabrication of nanocomposites could be recommended, which needs in turn a further degree of chemical complexity that may not always be desirable, especially when the final properties of the filler are not outstanding, an outcome that may be attributed to the diversity of dimensions and characteristics of cellulose particles.

In the future, it is suggested that study over possible agrowaste sources will be expanded, with the aim both to lead to a sound characterization of their respective properties and merits and to come to a suitable selection of plant-derived materials based on their inherent characteristics rather than simply on their local availability and limited cost.

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Tribological Characteristics of Green Biocomposites

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Abstract Owning to the environmental concerns and sustainable development, green biocomposites are increasingly explored and developed to replace conventional composites. Polymer composites used in tribological application have received great attention from researchers due to its self-lubricating properties, versatile fabrication process, low in cost and easy to tailor their properties with wide range of functional fillers. The past research in using green biodegradable materials reinforced polymers in tribological study has established a good understanding on tribological behaviour of natural fibre-reinforced polymer composites (NFRPCs). In this chapter, the tribological performance of various natural fibres reinforced polymer composites reported in the literature is reviewed. Furthermore, the effect of different important factors of natural fibre on wear and friction of polymers is discussed. Most of the polymer materials showing certain degree of enhancement in tribological properties after reinforced with natural fibre. Further optimization of its performance is possible by selecting optimum fibre loading, fibre length, fibre treatment, sliding orientation and combining with other fillers to form hybrid system composites. Finally, based on our current understanding, we have speculated some future trends and directions of NFRPCs in the field of tribology.

Keywords Natural fibre · Biocomposites · Tribology

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1 Introduction

Today's fast-paced urbanisation and industrialisation have posed serious threats to the ecological system raising environmental concerns. Product waste disposal and depletion of petrochemical resources have escalated the demand for biodegradable and eco-friendly renewable materials. Greater environmental awareness has the potential to increase regulations on pollution, product end life disposal, productivity and green innovation. Many countries like the United States of America and European Union are currently leading the world in terms of environmental protection thanks to the implementation and reinforcement of numerous environmental legislations. In case of developing countries, the United Nations Industrial Development Organization (UNIDO) has drawn out the Green Industry Initiative with the objective to enhance the operations of enterprises the world over through better and efficient use of energy resources, raw materials, innovative practices and applications of new green technologies. Green industry involves the creation of industrial operations, processes and products by efficient consumption of resources and transformation of the energy system towards greater sustainability by expanding renewable energy sources. Developing green industries includes establishing new industries that supply eco-friendly goods and services, reduce negative environmental effects, limit depletion of resources, and improve material recycling management. Such efforts can further reduce wastage, decrease manufacturing cost and reduce pollution risks. Meanwhile, green industries are a step towards long term techno-economic progression and ecological development.

In terms of using green materials, many industries in Malaysia have replaced synthetic materials with natural ones. Companies like Proton and Perodua have shifted from synthetic fibre-reinforced composite to kenaf fibre-reinforced composite in automotive trim components like door panels, seatbacks, headliners and package trays (Nur Suraya Mustafar 2016). Several Malaysian construction companies have started using natural and green materials in their production processes. Some local companies like Duralite Sdn Bhd, Everise, Crimson Sdn Bhd, KPC Manufacturing, IRM Composite and Kencana Fibre Composite Sdn Bhd are producing panels and profiles from wood wool and kenaf fibre, in line with the latest contraction requirement. The products, including external and internal walls, roof decking and concrete shuttering, with cost effectiveness, high thermal insulation value, fire resistance and acoustic properties, are beneficial in the construction field (Nur Suraya Mustafar 2016).

After the introduction of the Industrialized Building System (IBS) by the government, composite materials are being used extensively in Malaysia. The Composite Building System has become an important part of IBS which is used widely due to easier installation, light weight and easy handling. IBS is also extensively used because the conventional building system is unable to cope with the hugely demanding construction industry (Nur Suraya Mustafar 2016).

Polymer materials are rarely used in their pure form because of their lack of mechanical properties. Reinforcements like micro- and nano-fillers, fibres, organic and inorganic fillers, polymer blends have been extensively studied and proven to improve the mechanical properties of polymer after reinforcement. They are widely used by manufacturers owing to properties such as light weight, easy processing, modification and operational procedures, and low cost. Lately, industries are focusing on incorporating polymer materials with natural fibres for natural fibre-reinforced composites. Composites include one or more materials in the matrix to form multiphase systems which are chemically and physically distinct and separated by interfaces. Some of the benefits of composites are light weight, high strength and stiffness, and the ability to be tailored. However, most of the polymer composite products in the market have synthetic fibres such as glass, carbon or aramid as reinforcement. This is due to the promising properties of synthetic fibres as against polymer composites reported by a fair amount of researchers from around the world in the last decade. Despite great performance, as much as 50 % of the volume of these conventional fibres i.e. glass persists as unburned residue, thereby adversely affecting the environment (Zini and Scandola 2011).

Lately, the composites used in aircraft fabrication are being made from natural fibres with the aim of reducing the weight of aircraft components (McMullen 1984). The uses of natural fibre-reinforced composites range from small-scale household components such as table tops, chairs, bookshelves, panels, false ceilings and garden furniture to advanced industrial applications such as structural components in drainage cover, building industry and interior components in the automobile. These are called green biocomposites mainly due to their degradability and sustainability. A substantial number of studies have been performed on developing biocomposite materials with natural fibres and biopolymers such as starch (Shibata et al. 2008), polylactide (PLA) (Oksman et al. 2003), polycaprolactone (PCL) (Arbelaiz et al. 2006) and poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) (Bhardwaj et al. 2006). The development of green biocomposites is highly beneficial to various industrial sectors.

Sources of natural fibres can be sub-divided into animal and plant fibres. The review presented in this chapter focuses on plant fibre-reinforced conventional polymer and bio-degradable polymer. Natural fibres from plants such as cotton, bamboo, wood, flax, hemp, abaca, kenaf, banana, sisal, oil palm and jute have a number of techno-economic and ecological advantages over synthetic fibres like glass. A combination of the mechanical and physical properties of natural fibres together with their eco-friendly characteristics has made the industrial sector, notably the automobile industry; develop a profound interest in these fibres. In Europe, car makers are using mats made from abaca, flax and hemp in press-moulded thermoplastic panels for door liners, parcel shelves, seat backs, engine shields and headrests. For consumers, natural fibre composites in automobiles provide better thermal and acoustic insulation than fibre-glass, and reduce irritation to the skin and respiratory system (Tilborg 2009). The low density of plant fibres also reduces vehicle weight, thereby reducing fuel consumption and carbon dioxide emissions (Tilborg 2009). Natural fibres have a lower cost (US$200–1000/ton) and energy to produce (4 GJ/ton) than glass (cost: US$1200–1800/ton and energy to produce: 30 GJ) or carbon (cost: US$ 12,500/ton and energy to produce: 130 GJ) (Thomas and Pothan 2009). Their manufacturing processes also consume less energy than those of fibre-glass, and produce less wear and tear on machinery, cutting production costs by up to 30 % (Tilborg 2009).

The market size for natural fibre-reinforced composites is projected to reach $5.83 billion by 2019 with a compound annual growth rate of 12.3 % (Ali et al. 2016). In addition, European Union's end-of-life of vehicles (ELV) directive requires that components for all new vehicles should be 95 % recyclable by 2015 (Chand and Fahim 2008). For example, vehicles in some BMW series contain up to 24 kg of flax and sisal fibres. Released in July 2008, the Lotus Eco Elise features body panels made with hemp, along with sisal carpets and seats upholstered with hemp fabric. Japan's car makers are also 'going green'. In Indonesia, Toyota manufactures door trims made from kenaf and polypropylene and Mazda is using a bioplastic made with kenaf for car interiors. The use of natural fibre composites for various components by different automotive manufacturers is illustrated in Table 1. These industries have taken a huge step towards a bio-based economy and environmental protection while expanding sustainable development globally. Hence, natural fibre-reinforced polymer composites (NFRPCs) are poised to be prominent materials in the engineering composite industry.

There are many researches in progress for green biocomposites made using natural fibre—reinforced synthetic matrix or resin. One of the main examples of biodegradable polymer is poly-(lactic acid) i.e. PLA which can be synthesised by ring-opening polymerisation or the condensation polymerisation process of lactic acid monomer obtained through the fermentation of dextrose from starch feedstock (Suryanegara et al. 2009). High-molecular-weight PLA is a colourless, glossy, stiff thermoplastic polymer with properties similar to those of polystyrene. PLA can be degraded by a simple ester bond and the presence of enzymes is not essential to catalyse this hydrolysis. The rate of degradation depends on the size and shape of

Table 1 Application of natural fiber reinforced composites in automobile (Hill et al. 2012; Cicala et al. 2010; Koronis et al. 2013; Ahmad et al. 2015)

Manufacturer	Model	Application
BMW	3, 5 and 7 series	Door panels, headliner panel, boot lining, seat backs, noise insulation panels molded foot, and well linings
Audi	A2, A3, A4, A4, Avant, A6, A6, Avant, A8, Roadster, Coupe	Seat backs, side and back door panel, boot lining, hat rack, and spare tire lining
Ford	Mondeo CD 162, focus	Door panels, B-pillar, and boot liner
Mercedes-Benz	Trucks	Internal engine cover, engine insulation, sun visor, interior insulation, bumper, wheel box, and roof cover
TOYOTA	Brevis, Harrier, Celsior, RAUM	Door panels, seat backs, and spare tire cover
Volkswagen	Golf, Passat, Variant, Bora, Fox, Polo	Door panel, seat back, boot lid finish panel, and boot liner

the article, the isomer ratio and the temperature of hydrolysis (Garlotta 2001). PLA also exhibits properties such as high strength, superior modulus, biodegradability and easy processing (Garlotta 2001). However, due to its relatively high cost, PLA cannot compete with conventional, economical polymers. To reduce its cost and produce a reasonably priced composite, PLA can be combined with inexpensive fillers such as natural fibres.

Besides PLA, other biodegradable polymers such as poly(butylene succinate) (PBS) (Kim et al. 2011), Polyhydroxyalkanoates (PHA) and poly (hydroxybutyrate-co-valerate) (PHBV) have been introduced to replace fossil-based polymers due to the shortage of oil supply, global environmental concerns over CO_2 emissions and the problem of plastic from fossil-based products (Kim et al. 2011). These biocomposites have several beneficial properties bringing them in close competition with the existing fossil plastic materials. However, the present level of production and high cost restrict the industrial applications of biocomposites. In addition, its hydrophilic properties make it a challenge to design products with outdoor applications.

Many engineering components fail due to wear and tear. Therefore, the selection of materials in engineering components depends on tribo-performance. Numerous studies have demonstrated that NFRPCs have good mechanical and tribological properties which are comparable to those of conventional fibre-reinforced polymers (Chin and Yousif 2009; Wambua et al. 2003). Despite legal enforcements on using renewable materials in composites fabrication, there are numerous challenges in terms of the performance of natural fibre-reinforced composites. The inconsistency in the quality of natural fibres, flammability, moisture absorption and expansion are the main shortcomings in natural fibre composite products. There are also significant problems in the fibre-matrix interaction which reduce the mechanical and tribological properties of the product (Beckermann and Pickering 2008). The main goals when designing good tribological properties of NFRPCs are to reduce the wear volume loss or wear rate and COF.

In order to better understand the role of natural fibres in the tribological process, this chapter will review and explore various tribological characteristics of green biocomposites and the contribution of natural fibres in enhancing their tribological behaviour. Bio-waste material-reinforced polymer composites are not reviewed or discussed in this chapter.

2 Fabrication Techniques of Green Biocomposites

Natural fibres such as jute, sisal, kenaf, abaca and hemp are commonly used in industrial applications to produce NFRPCs. The most interesting benefit of natural fibre-reinforced composite is its availability and readiness to be used with various manufacturing processes that have previously been associated with synthetic fibres. The literature has reported many well-established techniques such as hand layup, vacuum infusion, injection moulding, extrusion, compression moulding, sheet moulding and resin transfer moulding—the major manufacturing processes for NFRPCs (Faruk et al. 2012; Ticoalu et al. 2010). Fong et al. (2015) reported work on flax fibre-reinforced composites fabricated by the hand layup method. Du and his team reported the fabrication of PLA/softwood composites using the film-stacking method (Du et al. 2014). Pramendra et al. (Bajpai et al. 2013) used three different types of natural fibres i.e. nettle, grewia optiva and sisal incorporated into PLA polymer to develop laminated composites using a hot compression technique. Jute and flax reinforced PLA composites were also fabricated using the extrusion method (Hinchcliffe et al. 2016). Many research findings and reviews on processing and mechanical properties of natural fibre-reinforced polymer have been published previously (Saheb and Jog 1999; Ku et al. 2011; Pickering et al. 2016). The incorporation of natural fibres into PLA is receiving attention mainly for its potential to create materials that are more environmentally sustainable. Table 2 illustrates a list of some of the recent works (2013–2016) reported by different researchers on natural fibre-reinforced polymeric biodegradable composite materials.

Many processing methods can be used to produce green biocomposites. Each processing technique and condition can produce composite materials that are different in dimensions, shape complexity, mechanical properties and performance. More techniques are definitely needed in the future to further modify and use NFRPCs to improve their performance and widen applicability.

3 Surface Modification and Compatibility of Green Biocomposites

The hydrophilic nature of natural fibres has resulted in poor compatibility between fibres and polymer matrices. The moisture absorption and expansion of fibres can affect the fibre-matrix interface bonding and mechanical properties of the composites (Saheb and Jog 1999). Therefore, moisture absorption of natural fibres and

Table 2 Recent reported works on fully degradable biocomposites

Type of natural fiber	Matrix	Fabrication technique	Reference
Grewia optiva and nettle	PLA	Hot press	Bajpai et al. (2013)
Bamboo, vetiver grass and coconut	PLA	Injection molding	P et al. (2013)
Oil palm empty fruit bunch	PLA	Extrusion	Alam et al. (2014)
Kenaf	PLA	Extrusion and compression molding	Shukor et al. (2014)
Bamboo	PLA	Hand lay-up	Sukmawan et al. (2016)

fibre-matrix compatibility are major limitations in producing well-performing natural fibre-reinforced composites. In order to reduce the moisture absorption capability of the fibre and promote good bonding of fibre-matrix interface, fibre pre-treatment and coating have been widely employed and investigated (Ahmad et al. 2015; Saheb and Jog 1999; Riccieri et al. 1999).

Interfacial bonding between fibre and matrix plays an important role in determining the mechanical properties of composite materials. This is because stress is transferred between matrix and fibres across the interface. Thus, good interfacial bonding is required to achieve optimum reinforcement and strengthen the composites. Nevertheless, there is usually limited interaction between the hydrophilic fibres and hydrophobic matrices leading to poor interfacial bonding and mechanical performance in natural fibre composites. This consequently affects long term properties. For good bonding, the fibre and matrix must have good contact or wetting. Insufficient fibre wetting results in interfacial defects which can act as stress concentrators and cause ineffective stress transfer throughout the interface of the composites (Ahmad et al. 2015). Fibre wettability affects the toughness, tensile and flexural strength of composites (Ahmad et al. 2015). Physical and chemical treatments can improve the wettability of the fibre and thus improve the interfacial strength (Sukmawan et al. 2016).

A great number of researches have been carried out to improve the natural fibre-matrix compatibility by modifying the fibre surface. A variety of cellulose-based natural fibres and chemical treatments including coupling agents have been applied for improving the mechanical properties of biocomposites. Jang et al. (2012) used plasma treatment on the surface of coconut fibres to improve the interfacial adhesion between the fibres and matrix. They found enhancement in the mechanical properties such as tensile strength and Young's modulus of the coconut fibre-reinforced PLA composites. Treatment by alkali and silane, and a combination of both treatments were studied on sisal fibre-reinforced PLA matrix biocomposites (Orue et al. 2015). The results showed that the alkali treatment gave more surface area which promoted mechanical interlocking adhesion with PLA polymer; while the silane treatment increased mechanical properties—this could be due to the chemical bonding between PLA and fibres through the silane agent. Biodegradable polymer composites prepared from short jute fibre reinforced-PLA were studied by Rajesh and Prasad (2014). The short fibre was treated with NaOH at various concentrations and the composites were prepared with different weight fractions of untreated and treated jute fibres in the PLA matrix. Results indicated that the tensile properties of composites with treated fibre at higher fibre loading showed better performance than those of composites with untreated fibre (Rajesh and Prasad 2014). Orue et al. (2016) studied the effect of different chemical treatments on the tensile properties of sisal fibre bundles and sisal fibre reinforced-PLA composites. They concluded that composites treated by alkali and a combination of NaOH, and silane treated fibres showed the highest tensile strength values. In another study, jute fibre was modified by alkali, permanganate, peroxide and silane treatment reinforced-PLA biocomposites (Goriparthi et al. 2012). The results showed that silane treated composites gave better thermal stability to the biocomposite sample.

Chemical treatments and coupling agents such as silane may create thin layers of newly developed functionalities on the fibre surface. Such layers can further act as a bridge between the polymer matrix and natural fibre within the composite materials and help improve interfacial bonding of treated fibre and the matrix materials (Mohanty et al. 2004). The modifications caused by the alkaline treatment can lead to the disruption of hydrogen bonding in the network structure, thereby increasing surface roughness. This treatment removes a certain amount of lignin, wax and oils covering the external surface of the fibre cell wall, depolymerises cellulose, resulting in better mechanical interlocking and efficient stress transfer between the matrix and fibre (Rajesh and Prasad 2014).

4 Tribological Performance of Green Biocomposites

Natural fibres started being used extensively in polymer tribology around late-1990s. This was the time when issues like environmental changes, global warming and pollution were being emphasised globally. Tribological performance and the wear mechanism of polymer composites have been widely investigated and reviewed by many researchers (Friedrich et al. 2005; Chang et al. 2007; Briscoe and Sinha 2002; Friedrich and Schlarb 2011; Sinha and Briscoe 2009; Stachowiak 2006; Nirmal et al. 2015). Wear of polymer composites is not an intrinsic material property; it depends on the wear mechanism (adhesive or abrasive) and external conditions such as applied load, sliding speed, temperature and surface roughness. Increase in the load-carrying capacity and effective stress transfer in the composite system leads to an increase in the wear resistance of polymer after addition of fillers. This can be achieved by reinforcing the polymer with an optimum amount of fillers such as micro- and nano-particulate reinforcements (Bahadur and Schwartz 2008; Xue and Wang 1997; Chang et al. 2008), continuous (unidirectional), woven fabric and short (chopped) fibres.

In general, at low load and sliding speed or low product of pressure-velocity (PV) condition, wear mass loss is relatively low. This is probably due to an insufficient load. Under such conditions, the penetration is low and there are fewer abrasive particles in action with the contacting surface, resulting in less wear. At high load or high PV conditions, the wear mass loss is substantially high. When the load increases, the degree of penetration gets higher i.e. deeper grooves are formed. Most of the abrasive particles (sharp asperities) penetrate the surface and create more grooves. This results in more material removal by a severe plastic deformation which appears as a series of grooves parallel to the sliding direction. These phenomena are apparent when the worn surfaces of samples are observed in SEM examination. The increase in applied load increases the real area of contact between sample and counterface affecting the coefficient of friction (COF). In terms of sliding speed and surface roughness, wear volume loss normally increases with increasing sliding speed and abrasive particle size. An increase in sliding speed generally leads to a reduction in coefficient of friction. However, this depends on the type of material. The high sliding speed can increase the temperature of contacting surface, leading to thermal softening of polymer and decreasing its surface hardness. This can cause a rapid increase in both wear and friction. Some studies have reported that good thermal conductivity of reinforcement materials can lead to a reduction in wear and friction of the polymer (Chang et al. 2008).

The use of natural fibre-reinforced polymer for tribological applications has been an area of wide interest. Natural fibres have been found to be beneficial for their mechanical properties and the wear resistance of polymers. Several studies have summarised the mechanical and tribological properties of polymer matrix composites reinforced with natural fibres as green biocomposites (Saheb and Jog 1999; Ku et al. 2011; Omrani et al. 2016; Shalwan and Yousif 2013).

4.1 Effect of Fibre Loading

Fibre reinforced-polymer can be an effective method of improving the mechanical and tribological properties of polymer composites (Friedrich 1993). The mechanical properties of a natural fibre depend on its cellulose type because each type of cellulose has its own cell geometry. In the theoretical sense, fibre reinforcement in polymers can cause an increase in the mechanical properties of the polymer composites due to the stress transfer support from the fibre. This phenomenon can also contribute positively to the tribological properties of the polymer materials and further broaden their applications. However, Shalwan and Yousif (2013) have pointed out that there is no remarkable correlation between the mechanical and tribological performance of major polymeric composites.

In recent years, there is an increasing trend of studies reporting the tribological properties of natural fibre-reinforced polymer composites (NFRPCs) in an attempt to investigate the potential of these materials in applications concerning wear and friction (Mutlu 2009; El-Sayed et al. 1995). For example, the addition of rice straw and rice husk dust in the composites has proved to be useful in brake pad formulation due to the improved tribological properties after reinforcement (Mutlu 2009). Many scholars have reviewed and summarised the technical aspects of NFRPCs in terms of properties and applications (Ku et al. 2011; Pickering et al. 2016; Mohammed et al. 2015; Saheb and Jog 1999; Ticoalu et al. 2010; Zini and Scandola 2011; Nguong et al. 2013; Ramamoorthy et al. 2015; Saba et al. 2016; Omrani et al. 2016; Ahmad et al. 2015; Fowler et al. 2006). The tribological properties of natural fibre- and fibre fabric mat-reinforced polymer composites show promising results as compared to those for unfiled polymer. A reduction of 85 % in the wear rate has been achieved when epoxy was reinforced with kenaf fibre (Chin and Yousif 2009). The incorporation of woven jute fabric into polypropylene (PP) matrix increases the wear resistance of PP (Xavior et al. 2014).

Majhi et al. (2012) studied the tribological behaviour of modified rice husk-reinforced epoxy composite. A variation of fibre loading of 5–20 wt% weight fraction of rice husk was incorporated with epoxy resin. It was found that 10 wt% of rice husk reinforced epoxy composites exhibited the lowest wear rate as compared to other loading amounts. The wear resistance increased on increasing the rice husk fibre loading. However, above 10 wt% of fibre loading, the wear rate trend showed a rise. This was due to the agglomeration of fibres in the composite which lead to poor interfacial adhesion between the fibre and the matrix (Majhi et al. 2012).

Another study on the effect of fibre loading on tribological performance of coir fibre-reinforced polyester was reported (Divya et al. 2014). The results showed that an addition of 1 wt% of coir fibres improved wear resistance of the composites. Addition of 2, 3, 4, and 5 wt% of coir fibre resulted in an increase in the wear rate of the composites. Studies on polyvinylpyrrolidone (PVP) composites have shown that date palm leaves (DPL) fibre is effective in reducing the COF and wear of PVP (Mohanty et al. 2014). It was observed that the wear rate decreased by increasing the weight percentage of DPL fibre. The lowest wear rate was observed when the composites were filled with 26 wt% of DPL fibre and thereafter, the wear rate increased with increasing DPL content. In addition, the 26 wt% of DPL fibre loading also showed the minimum value of COF. When the fibre content increased beyond the optimum value, DPL fibres agglomerated. This consequently reduced the interaction between DPL fibres and PVP matrix, causing debonding of fibres from the matrix. Hence, at higher fibre loading, the interfacial adhesion between the fibre and matrix was not enough to resist the sliding force, resulting in higher wear rate.

Table 3 summarises the tribological behaviour of polymer matrix composites with data taken from numerous published literatures (Omrani et al. 2016; Chand and Fahim 2008). Generally, all the reported optimum wear rates and COF values are approximations based on published results and have been selected from specific wear test conditions (speed and load) reported by the authors. Most of the scientific paper reported on the tribological properties of NFRPCs focused on natural fibre-reinforced synthetic polymer matrix. There is a lack of studies on the tribological behaviour of natural fibre-reinforced biodegradable polymer matrix.

The type of fibre material is a key consideration in manipulating the tribological properties of polymer composites. Shuhimi et al. (2016) reported the comparison study of tribological performance of oil palm fibre/epoxy (OPF/E) and kenaf fibre/epoxy composites (KF/E) under dry sliding conditions. It was found that the wear rate of OPF/E composite is lower than KF/E composite at high temperatures. In addition, by selecting an optimum fibre-matrix ratio, shape and size of fibre, good fibre distribution (chopped fibre), fibre orientation, fibre treatment and compatibility of fibre-matrix interfacial bonding, the properties of the composites can be enhanced several-fold as compared to monolith polymer materials. Above the optimum level of loading, the fibre tends to agglomerate and makes the fibre-matrix interaction less effective. Hence, higher wear rate and fibre pull-out can be observed when fibre loading exceeds the optimum amount. Thus, it can be concluded that fibre types and optimum loadings are crucial steps to be taken into account by researchers when designing durable tribology performance requirement of NFRPCs.

Table 3 A summary of the tribological properties of green biocomposites

Number	Matrix	Natural fiber	Fiber orientation	Fiber treatment	Fiber volume fraction	Lowest wear rate	Lowest COF	Sliding parameter	Reference
1	Polyester	Jute	Normal	–	15 %	9×10^{-8} g/cm	0.60	Low pv (0.61 MPa ms^{-1})	El-Sayed et al. (1995)
2	Polyester	Jute	Normal	–	15 %	20×10^{-8} g/cm	0.77	High pv (1.65 MPa ms^{-1})	El-Sayed et al. (1995)
3	Polylactide (PLA)	Jute	–	Silane	50-wt%	0.03 g (weight loss)	–	0.418 m/s sliding speed, 9.8 N	Goriparthi et al. (2012)
4	Polypropylene	Chopped jute	–	MA-g-PP	23-wt%	0.00025 (cm^3/m)	–	2.56 m min^{-1} sliding speed, 7 N	Chand and Dwivedi (2006)
5	Polypropylene	Chopped sisal	–	MA-g-PP	23-wt%	0.0072 g (weight loss)	–	2.56 m/min sliding speed, 7 N	Dwivedi and Chand (2009)
6	phenol formaldehyde	Sisal	–	Borax	15 wt%	$\sim 0.45 \times 10^{-7}$ cm^3/Nm	~0.4 (at 300 ℃)	480 rpm, 0.98 MPa load	Wei et al. (2015)
7	Polyester	Sisal	–	–	2–5-wt%	0.16 mm^3/Nm	–	480 rpm, 0.98 MPa load	Lv et al. (2015)
8	Polysulfide-modified epoxy (PSEP)	Sisal	Normal	–	20/80 ratio	0.014 gm (weight loss)	–	2.56 m/min sliding speed, 7 N	Chand and Dwivedi (2007b)
9	Polyester	Sugarcane	Anti-parallel	–	3.45–4.18 wt %	0.06 g (weight loss)		0.47 m/s 25 N (abrasive)	El-Tayeb (2008a)
10	Polyester	Chopped sugarcane (5 mm)	–	–	3.45–4.18 wt %	0.098 g (weight loss)		0.47 m/s 25 N (abrasive)	El-Tayeb (2008a)
11	Polyester	Corn straw (Particles)	–	–	40 % (coarse particles) 25 % (soft particles)	0.005 g/min (coarse particles) 0.01 g/min (soft particles)	0.51 (coarse particles) 0.48 (soft particles)	0.8 m/s 2–6 N	Ibrahim (2016)

(continued)

Table 3 (continued)

Number	Matrix	Natural fiber	Fiber orientation	Fiber treatment	Fiber volume fraction	Lowest wear rate	Lowest COF	Sliding parameter	Reference
12	Polyester	Jasmine leaves (particles)	–	–	30 %	0.02 g/min	0.6	0.8 m/s 2–6 N	Ibrahim (2016)
13	Epoxy	Kenaf	Normal	–	48 vol.%	0.15×10^{-5} mm^3/Nm	0.52–0.68	30–100 N, sliding distances (5 km) sliding velocities (1.1–3.9 m/s)	Chin and Yousif (2009)
14	Epoxy	Rice husk	–	Benzoyl Chloride	10 wt%	0.09×10^{-6} mm^3/Nm	–	10 N 300 RPM speed	Majhi et al. (2012)
15	Polyurethane	Kenaf	AP	NaOH	25 wt%	3.2 × 10–8 mm^3/Nm	0.02	80 N 2.8 m/s 0–2.7 km	Singh et al. (2011)
16	Unsaturated Polyester	Coir/montmorillonite	–	Silane	1 wt%	2.8×10^{-6} mm^3/Nm	–	33 N 200 rpm 500 m (abrasive)	Divya et al. (2014)
17	Polyvinyl pyrrolidone	Date palm leaf	–	Acrylic acid	26 wt%	0.48×10^{-11} mm^3/Nm	0.12	5–20 N 0.392, 0.471, and 0.549 m/s 376 m	Mohanty et al. (2014)
18	Polyester	Oil palm	–	–		37×10^{-4} mm^3/Nm	0.59	70 N 3.9 m/s 5 km	Yousif and El-Tayeb (2007a)
19	Unsaturated polyester	Betelnut (fiber mats)	AP-O	–	12 mm thickness	0.01×10^{-5} mm^3/Nm	–	30 N 0–7 km	Yousif et al. (2008)
20	Polyester	Cotton/graphite	–	–	25 wt%/ 20 phr	$<0.2 \times 10^{-14}$ m^3/Nm	~0.4	80 N 2.22 m/s 4 km	Hashmi et al. (2007)
21	Polyester	Cotton/UHMWPE	–	–	25 wt%/ 14.19 vol.%	$<1.3 \times 10^{-14}$ m^3/Nm	~0.5	80 N 2.22 m/s 4 km	Hashmi et al. (2006)
22	Epoxy	Agave (chopped 3 mm)	–	–	30 vol.%	0.2 mm^3/Nm	0.3	15 N 1.413 m/s	Mylsamy and Rajendran (2011)

(continued)

Table 3 (continued)

Number	Matrix	Natural fiber	Fiber orientation	Fiber treatment	Fiber volume fraction	Lowest wear rate	Lowest COF	Sliding parameter	Reference
23	Polypropylene	Wood		*N*-2-aminoetil–3-aminopropil-trimetox-isilane	40 wt%	5×10^{-6} min^3/Nm	0.35	100 N 1 m/s	Aurrekoetxea et al. (2008)
24	Bio-epoxy	Nano-cellulose (aerogels)		–	1.4 vol.%	0.1 mm^3 $\times 10^{-6}$	0.31	4, 7, 10 N 0.15, 0.25, 0.35 m/s	Barari et al. (2016)
25	Bisphenol-A	Pineapple Leaf (8 mm length)		NaOH alkali treatment	30 vol.%	2.84×10^{-3} mm^3/Nm	0.60	15 N 1 m/s 180 m	Supreeth et al. (2014)
26	Epoxy	Bagasse			20 vol.%	5.8×10^{-5} gm^3/Nm	–	10 N 1000 mm/min 27 m	Mishra and Acharya (2010)

Note All the reported optimum wear rates and COF values are approximations based on published results and have been selected from specific wear test conditions (speed and load) reported by the paper's authors

4.2 *Effect of Fibre Surface Treatment*

Studies show that treating natural fibre can aid improvement of the mechanical properties of NFRPCs (Yu et al. 2010; Venkateshwaran et al. 2013). As mentioned earlier, improved mechanical properties can lead to better wear resistance of the composites. This can be attributed to effective stress transfer of fibre-matrix and increase in load-carrying capacity during the wear process. The surface modification after chemical treatment leads to an improvement in the interfacial bonding between fibre and matrix. Numerous natural fibre surface treatments such as electric discharge, alkalisation, acetylation, peroxide, permanganate, benzoylation, silane and cyano ethylation have been published. These chemical agents can react with hydroxyl group of the fibres and enhance interface interaction. However, the type of chemical treatment and loading content are also crucial in optimising the performance of NFRPCs. Through the works of Bhanu et al. (Goriparthi et al. 2012), Fig. 1 shows the abrasive wear loss of jute fibre reinforced-PLA composites (jute fibre/PLA) as a function of sliding distance and types of treatments applied. Surface modified jute fibre composites have higher wear resistance when compared to untreated jute fibre/PLA. Among all the treatments applied, silane treated jute fibre/PLA shows the highest wear resistance. This is due to the strong interaction in the silane treated jute fibre/PLA as compared to other treatments in the composites' adhesion and tensile test results (Goriparthi et al. 2012). Similar findings were reported by Divya et al. (2014) about the effect of surface treatment on wear performance of coir reinforced treated and untreated hybrid composites. For all fibre loadings of coir fibre-reinforced polyester composites, the treated fibre-reinforced polyester composites showed better wear resistance due to improved interfacial bonding between polymer chains and coir fibres. Among the two different treatments, the lowest wear rate was observed in silane treated composites (Divya et al. 2014).

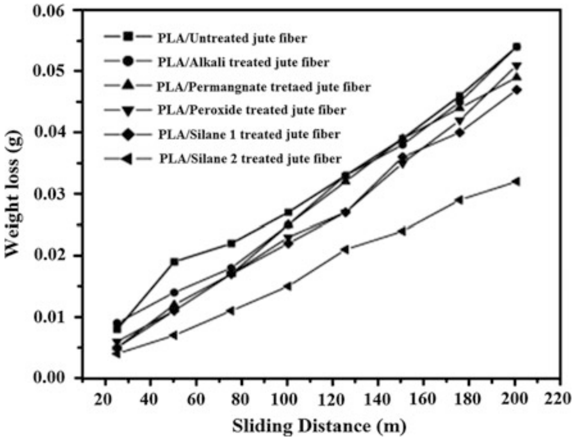


Fig. 1 Abrasive wear loss of jute fibre reinforced-PLA composites as a function of sliding distance and types of surface treatments applied (Goriparthi et al. 2012)

Chand and Dwivedi (2007a) investigated the effect of Maleic anhydride-grafted polypropylene (MA-g-PP) on the wear behaviour of bamboo fibre-reinforced polypropylene composites. MA-g-PP was added as a coupling agent and was found to give better wear resistance when compared to the composite without a coupling agent. In their other works on wear behaviour of jute fibre-PP and chopped sisal fibre-PP composites (Chand and Dwivedi 2006; Dwivedi and Chand 2009), the effect of MA-g-PP on abrasive wear performance of jute fibre-PP and chopped sisal fibre-PP composites was also found to have increased in wear resistance after addition of a coupling agent. Addition of MA-g-PP coupling agent significantly influenced the wear resistance of sisal fibre reinforced PP composites. It was observed in chopped sisal fibre reinforced polypropylene composite that initially at low loads (i.e. 1 N and 3 N), the sample having 1-wt% MA-g-PP exhibited maximum wear resistance; but at higher applied loads (i.e. 5 N and 7 N), the sample having 2-wt% MA-g-PP offered maximum wear resistance. The enhancement of wear properties by the addition of coupling agent MA-g-PP may be due to the reduction in fibre pullout and lower fibre–matrix debonding (Chand and Dwivedi 2006). The higher concentration of MA-g-PP i.e. 5-wt% increased the internal slippage of chain molecules, leading to lowered wear resistance of the composite (Dwivedi and Chand 2009).

In a comparative study conducted by Wei et al. (2015), borax treated sisal fibres showed the best heat resistance, consistent friction coefficient and low wear rate under different temperatures as compared to alkali treated and organosilane treated in sisal fibre/nano-silica-reinforced phenol formaldehyde composites. This was due to the thermal stability of borax which absorbed the frictional heat during the wear process. Yousif and El-Tayeb (2008) evaluated the wear characteristics of treated and untreated oil palm fibre-reinforced polyester composites. The wear test results confirmed that the treated oil palm fibre-reinforced composites exhibited better wear properties than the untreated reinforcements due to good interfacial adhesion. Nirmal et al. (2010) developed composites with treated betel nut fibres as reinforcements in polyester matrix. They found that 6 % NaOH treatment to the fibres improved the wear resistance of composites better than the untreated ones. Aurrekoetxea et al. (2008) reinforced pine wood in polypropylene matrix (WPC) and confirmed that the wear performance of WPC was superior to that of pine wood and neat polypropylene. Boopathi et al. (2012) conducted a tribological experiment on borasus fruit fibre reinforced epoxy composites and demonstrated that 5 mm long alkali-treated fibre-reinforced composites exhibited superior wear properties.

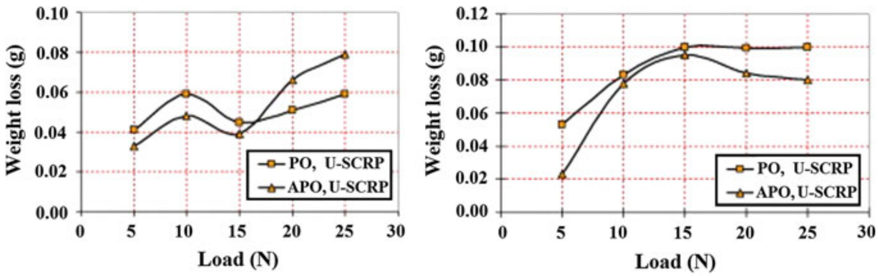
Another study revealed that the COF was lower for sisal fibre treated with NaOH as compared to that of untreated sisal fibre in epoxy composites (Ashok Kumar et al. 2010). The effect of bleaching and NaOH alkali treatment as compared to untreated coir fibre-reinforced polyester was reported by Yousif et al. (2009). Among the two, alkali treatment showed lower COF and wear weight loss as compared to bleached, treated and untreated coir fibre reinforced-polyester composites. Reviewing the research carried out by various researchers, it can be seen that fibre-matrix adhesion is a key factor in determining the tribological performance of polymer composites.

4.3 Effect of Fibre Orientation Against Sliding Direction

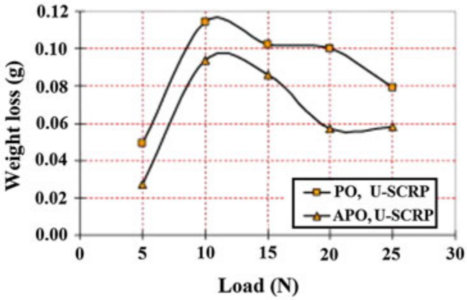
It is worthwhile to understand the effect of fibre orientation on the tribological behaviour of composites. Wear rate is sensitive to the orientation of the fibre axis with respect to the sliding direction (Lhymn et al. 1985). Chand and Dwivedi (2007b) reported that the abrasive wear rate of the epoxy can be reduced by the incorporation of sisal fibre. Minimum wear rate is observed in normal orientation (N-O) direction to the sliding counterface; while the wear rate is found to be maximum in parallel oriented (P-O) (longitudinal) fibre alignment direction to the counterface (Chand and Dwivedi 2007b). The wear rate for the P-O in sisal/epoxy composite is highest as compared to that in anti-parallel oriented (AP-O) (transverse) and N-O directions but lower than the wear rate in pure epoxy. When sisal fibres are aligned in parallel to the wear direction, the contact area is maximum when sliding as compared to that in case of AP-O fibres. The abrasion in fibre composite is due to the removal of the complete layer of fibre, micro-cutting of cell, delaminating of fibres, formation of micro-fibrils, and micro-cutting and breaking of resin leading to debris formation. In the AP-O direction, fibres are cut but the removal of complete fibre is hampered due to the matrix phase between the fibres. A simple explanation can be provided for the observed behaviour based on the exposed fibre area, which is larger in case of P-O and AP-O directions (Chand and Dwivedi 2007b). In P-O and AP-O, the detachment of fibres is easier from the bulk composite; whereas for N-O, the fibres are deeply embedded in the bulk matrix and cause less detachment during sliding (Chand and Dwivedi 2007b).

The influence of different fibre orientations on abrasive wear performance of untreated sugarcane fibre (SCF)-reinforced polyester is also reported by El-Tayeb (2008a). The SCF-polyester composites were oriented P-O and AP-O against the sliding direction. As shown in Fig. 2, P-O showed higher abrasion weight loss as compared to AP-O. This was due to the high interaction along fibres and abrasive particles in P-O. There was no interaction or contact in the fibre-matrix interface during the wear process. This increased the extent of micro-cutting and micro-ploughing in the matrix and shearing or tearing of the fibre followed by delamination. In AP-O sliding direction, the sliding counterface moved through different interfaces and deferent layers of matrix and fibre bundle during the wear process. The micro-cutting and micro-ploughing action was hampered due to phase discontinuity which hampered the wear sliding. In addition, the wear debris was trapped against counterface which caused less material removal in this mode of fibre orientation.

El-Sayed et al. (1995) investigated the frictional and wear properties of linen fibre-reinforced polyester and jute fibre-reinforced polyester with different fibre orientations for a bearing application. The test was carried out in dry conditions at



(a) 0.157m/sec, 400 SiC abrasive paper **(b)** 0.314m/sec, 400 SiC abrasive paper



(c) 0.47 m/sec, 400 SiC abrasive paper

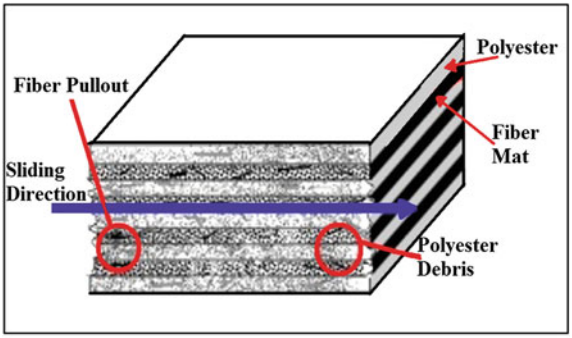
Fig. 2 Abrasion wear of sugarcane fibre-reinforced polyester composite as a function of applied loads and sliding speeds (El-Tayeb 2008a)

low and high pressure-velocity product (pv limit) of 0.61 MPa m s^{-1} and 1.65 MPa m s^{-1} respectively. Results showed that the COF increased and the wear rate decreased with an increase in the fibre volume fraction of both fibres. Among the three fibre orientations, N-O displayed the lowest wear rate as compared to that displayed by P-O and AP-O directions. However, normal direction sliding for the three sliding conditions showed the highest COF. Similar results were reported on kenaf fibre-reinforced epoxy composites for bearing applications where the wear resistance of the composite was substantially and consistently high in N-O as compared to that in P-O and AP-O (Chin and Yousif 2009).

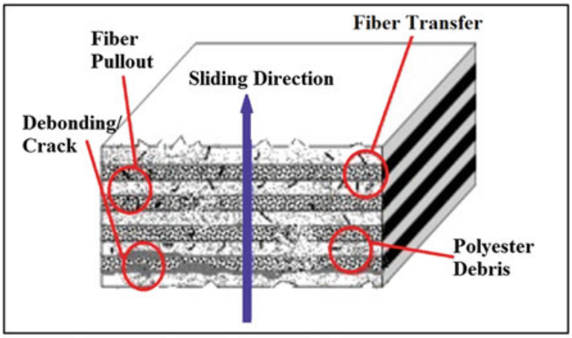
In contrast to these trends, different wear properties of NFRPCs were observed under different sliding wear conditions. The wear behaviour of treated kenaf fibre-reinforced polyurethane composites was investigated by Singh et al. (2011) with applied load of 50–80 N, 2.81 m/s and 2.71 km under wet sliding conditions. Better wear performance was reported when the kenaf fibre was oriented perpendicular to the sliding direction at 50 and 60 N applied loads. However, under 70 and 80 N applied load, AP-O showed the lowest wear rate as compared to that by the N-O and P-O directions.

Besides the NFRPCs discussed above, some studies have reported on the different orientations of natural fibre mats (sheets)-reinforced polymer composites in tribological applications (Yousif et al. 2008). The wear rate of betel nut fibre reinforced-unsaturated polyester (BFRP) is compared at three different sliding orientations. Figure 3 shows a schematic illustration of natural fibre mats-reinforced polymer composites against the sliding direction. Results revealed that the wear performance of the BFRP composites in the three tested orientations follows the order of AP-O > P-O > N-O. In P-O, the sliding direction of the counterface was parallel to the polyester layer and betel nut fibre mat. The possibility of transferring fibre and/or polyester debris to either one of the faces was low for this orientation.

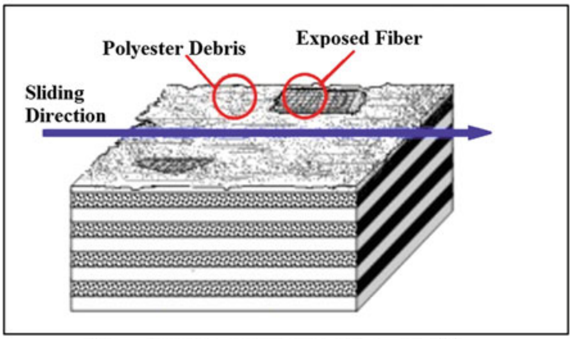
Fig. 3 Schematic illustration of fibre mat-reinforced polymer composites against sliding direction (Yousif et al. 2008)



(a) Parallel Orientation (P-O)



(b) Anti-Parallel Orientation (AP-O)



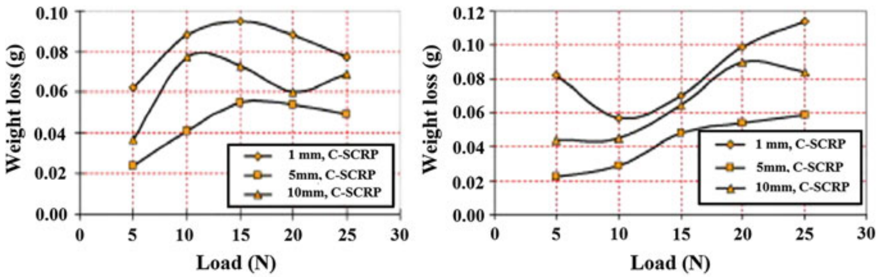
(c) Normal Orientation (N-O)

Fibre mats did not strongly support the fibrous region. Therefore, pull-out and removal of fibre was observed (Yousif et al. 2008). In AP-O, due to the perpendicular sliding of the counterface to both fibres and matrix regions, there was a high possibility of transferring broken and pulled out fibres to the matrix regions. Furthermore, polyester debris could transfer to the fibres. This kind of rubbing could form a strong surface at the sliding surface, which in turn reduces the material removal of the composite. On the other hand in N-O, all the published work discussed (Yousif and El-Tayeb 2007b) confirms that N-O gives very poor results i.e. high removal of material. The delamination of fibre mats contributes to high removal of material.

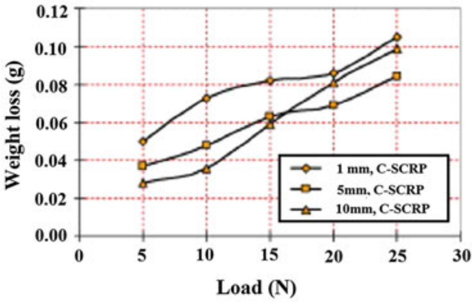
4.4 *Effect of Fibre Length*

The strength value of fibre reinforced-polymer composites is not solely based on fibre loading in the matrix. The fibre length plays a crucial role in affecting the overall properties of the composites. Theoretically, increase in fibre length can directly increase the interfacial contact between fibre and matrix as long as the interfacial adhesion is good. Several works have reported the effect of fibre length on the tribological behaviour of NFRPCs (El-Tayeb 2008a, b). In the work reported by El-Tayeb (2008a), as illustrated in Fig. 4, the weight loss of chopped sugarcane reinforced-polyester composite decreased when the fibre was lengthened from 1 to 5 mm. However, a reverse trend was observed when the fibre length was increased from 5 to 10 mm showing higher wear weight loss. The reinforcement with 5 mm of sugarcane fibre exhibited the lowest weight loss. This was attributed to the fact that the entanglement of fibre increases when the fibre length increase, resulting in increased difficulty in removing the fibres from the matrix (El-Tayeb 2008b). On the other hand, the high wear weight loss of 1 mm of sugarcane fibre reinforced-polyester composites could be due to the easy removal of 1 mm fibre from the matrix of the composites. In random distribution of chopped fibre, the fibres have a high possibility of being subjected to sliding wear along their length and end. Short fibres receive less support from the matrix during the wear process as compared to longer fibres. A higher interaction between the fibre and matrix surface can be expected for longer fibres as compared to shorter ones, leading to lower wear loss. In another experimental study on the influence of fibre length on the tribological behaviour of agave fibre reinforced-epoxy composites, it was found that 3 mm of agave fibre exhibited the lowest wear rate in all sliding conditions tested as compared to 5 and 7 mm long fibres (Mylsamy and Rajendran 2011).

The effect of fibre length on sisal/GF reinforced-epoxy hybrid composites was reported by Ashok Kumar et al. (2010). Three different lengths of fibre i.e. 1, 2 and 3 cm in the ratio of 1:1 of sisal and glass fibre reinforced-epoxy composites were tested using a pin-on-disc tester. The coefficient of friction decreased with an increase in the fibre length from 1 to 2 cm. The coefficient of friction (COF) increased with further increase in fibre length. Optimal frictional coefficient



(a) 0.157m/sec, 400 SiC abrasive paper (b) 0.314m/sec, 400 SiC abrasive paper



(c) 0.47 m/sec, 400 SiC abrasive paper

Fig. 4 Effect of fibre length on abrasion wear of chopped sugarcane fibre reinforced-polyester composite as a function of applied loads at different sliding speeds (El-Tayeb 2008a)

measurements were found at 2 cm fibre length. It was also observed that the COF considerably decreased with increased fibre length at higher sliding speeds. The lowering of the friction promoted better tribological properties which were significant at 2 cm fibre length. It can thus be concluded that optimum fibre length can effectively improve the tribological behaviour of NFRPCs. The nature of natural fibre behaviour and the degree of fibre-matrix interactions are of importance as well.

5 Transfer Film Forming

A transfer film is formed by the removal of soft polymer in the form of debris due to the sliding action against counterface asperities. This film significantly affects the wear rate of materials. The chemical reaction and attachment of sliding composite materials to the counterface are complicated processes. It was confirmed that the formation of a uniform transfer film during sliding wear contact can slow down the wear process of materials and lower the wear rate (Bahadur and Schwartz 2008). This is due to the cushioning effect of the transfer film given by the composites and sliding counterface. In the absence of a protective transfer film between sliding surfaces, the removal of materials from wear continues to increase.

The transfer film formation is greatly dependent on the types of reinforcements, the fibre-polymer composition and the bond strength developed from the samples to the counterface. Bahadur and Sunkara (2005) extensively investigated the formation of transfer films and bond strength developed for polyphenylene sulphide (PPS) filled with ZnO, TiO_2, CuO and SiC nanoparticles. The bond strength was measured with the tangential shear stress needed to peel the transfer film off the counterface. The film was further analysed using XPS analyses. It was found that the film formed for 1–2 vol.% of CuO and TiO_2 in PPS was thin and uniform, and the wear debris was finer than the one for unfilled PPS. As the vol.% of the CuO and TiO_2 increased above 2 vol.%, the transfer film lost its uniformity and turned lumpy, failing to fully cover the sliding counterface. This phenomenon was the effect of the wear loss, where the wear loss of CuO and TiO_2 filled PPS composites was higher than that for unfilled PPS as filler content above 2 vol.%. On the other hand, the transfer film formed by ZnO and SiC filled PPS composites was thick, non-uniform and did not completely cover the counterface. The wear debris was larger with elongated fragments as compared to the one developed with unfilled PPS. Wear resistance was observed to increase as the bond strength of the transfer film-counterface increased.

Publications concerning the effect of transfer films on the tribological behaviour of NFRPCs are limited. The formation of thin uniform transfer films is believed to be one of the feature of natural fibre that makes NFRPCs enhance in tribological properties. The lubrication effect of a cotton film on a steel counterface has been studied by Fervel et al. (2003). The COF of steel rub against steel (ball-on-disc) was lower for experiments with the presence of a cotton film. The COF of steel-steel sliding contacts was high (0.6–0.8) and unstable. In the presence of a cotton film, the COF reduced to about 0.3 under 30 % humid conditions. This showed that cotton film helps reduce the wear rate of the contacting pair materials during the wear process. Hence, it was believed that in suitable sliding conditions, cotton fibre reinforced-polymer composites have the potential to reduce the wear rate of the composites by forming an effective transfer film. El-Tayeb (2008b, 2009) reinforced chopped sugarcane fibres of length 1, 5 and 10 mm in polyester polymers as against glass fibre-filled polyester resin. The wear performance of chopped sugarcane-reinforced polymers was found to be competitive to glass fibre-reinforced polymer composites. The plastic flow of polymer during wear acted as a protective layer in sugarcane-reinforced polymers and improved the wear properties; whereas the broken glass fibre fragments during wear restrained the formation of any protective layer in glass fibre-reinforced composites, thereby decreasing the wear properties. It was thus concluded that sugarcane fibre can be a potential replacement for glass fibre as reinforcement in polymer composites. The lubrication effect of natural fibre may be due to the cellulose, wax or the synergistic effect of the two. In a review study reported by Aldousiri et al. (2013), it was reported that thermoplastic-based composites or matrices will exhibit high tendency in forming a thin transfer film on the metal counterface which assists in reducing the COF. However, the transfer film forming by thermoplastic composites is not stable at high interface temperature which will cause plastic deformation and deterioration of the surface and lead to high wear rate. On the other hand, thermoset-based composite materials are harder to form a thin transfer film on the sliding metal counterface as compared to thermoplastic. But the property of the transfer film form by thermoset composites is harder and can sustain high temperature.

In general, weak fibres are more likely to form fragmentations and transfer films as compared to stronger fibres (Chand and Fahim 2008). However, the formation of the transfer film is not only dependent on the properties of cellulose, but also on the complex external sliding conditions. The ability of the fibre film to adhere to the counterface strongly affects the tribological behaviour of the composite. The presence of specific chemical components within the fibres may promote adhesion and cohesion of fibre fragments, thereby facilitating the formation of transfer films (Fervel et al. 2003).

6 Tribological Behaviour of Hybrid Fibre Reinforced Polymer Composites

In recent years, the development of hybrid polymer composite systems with more than one fibre reinforcement has been of great interest to many researchers. In general, the use of monolithic fibre reinforced-polymer is adequate for property enhancements as compared to unfilled polymer. However, some of the natural fibre reinforced-polymer products are still below par as compared to the synthetic fibre-reinforced polymer ones. Hybrid fibre reinforcement systems can further improve the performance and at the same time reduce the usage of synthetic fibres. Hybrid reinforcement systems involve the incorporation of two or more fibres into a polymer matrix. The low strength of natural fibres can be balanced with the high strength of synthetic fibres to yield strong and biodegradable hybrid composites. For example, jute reinforced-epoxy composites are detrimental to wear at high loads and sliding speeds. Ceramic fillers Al_2O_3 and SiC reinforced-jute hybrid composites demonstrate better wear resistance at high load and speed sliding conditions (Sabeel Ahmed et al. 2012).

Jawaid and Abdul Khalil (2011) have reviewed cellulosic/synthetic fibre reinforced polymer hybrid composites in terms of processing, mechanical, physical, electrical, thermal and dynamic mechanical properties. Some improvement in the mechanical properties of hybrid composites has been reported on several natural-natural and natural-synthetic hybrid systems such as pineapple/sisal/glass (Mishra et al. 2003), kenaf/glass (Makhtar et al. 2012), woven jute/glass (Ahmed et al. 2007), jute/glass (Ahmed and Vijayaragan 2006), banana/sisal (Venkateshwaran et al. 2011), sisal/silk (Khanam et al. 2007), banana/kenaf (Thiruchitrambalam et al. 2009), oil palm/jute (Jawaid et al. 2011), basalt/hemp (Czigány 2006), flax/wood fibre (Wambua et al. 2007), banana/glass (Nayak 2009), kenaf/pineapple (Aji et al. 2011), bamboo/glass (Thwe and Liao 2003), bamboo/cellulose (Okubo et al. 2009) and aramid/sisal (Zhong et al. 2011).

The combination of hybrid natural fibre with synthetic fibre in polymer composites is increasingly attracting attention for tribological applications. The synergy of the two different fibres has been found to be beneficial in improving the tribological behaviour of polymers. Biswas and Xess (2012) reported that the reinforcement of hybrid glass fibre and short bamboo fibre improves the erosive wear characteristics of epoxy. Results revealed that the 15 wt% of bamboo/GF reinforced epoxy exhibited the lowest erosion rate versus impact velocity as compared to other composites. In an attempt to further improve the tribological properties of cotton fibre-polyester composites, hybridisation of cotton fibre reinforced-polyester filled with graphite and UHMWPE was reported by Hashmi et al. (2006, 2007). The specific wear rate of polyester reduced when reinforced with cotton and further reduced after the addition of graphite. The COF of polyester resin increased on cotton reinforcement and reduced significantly after the addition of graphite in the cotton–polyester composite. Graphite is known for its lamellar crystal and layer-lattice structure which acts as a lubricant in sliding contact (Chand and Fahim 2008; Srivastava and Pathak 1996). In addition, the temperature of the contact surface was observed to reduce after the addition of graphite in cotton–polyester composite. Similar findings were observed when cotton fibre reinforced polyester composites were filled with UHMWPE (Hashmi et al. 2006). The UHMWPE provided a lubrication effect under dry sliding wear and further reduced the COF value. An addition of 14.19 vol.% of UHMWPE in cotton-polyester composite reduced the COF by around 50 and 30 % as compared to pure polyester and cotton-polyester composites respectively. The influence of TiO_2 nanoparticles on the tribological behaviour of PTFE-cotton fibre was studied by Zhang et al. (2009). The tribological performance of three different PTFE-cotton hybrid composites i.e. unfilled, filled with TiO_2 nanoparticles and modified TiO_2 nanoparticles were compared. It was reported that the hybrid composites filled with grafted TiO_2 nanoparticles exhibited a lower wear rate due to the disintegration of agglomeration and the improvement of interfacial adhesion between filler/matrix.

7 Summary

It is evident that natural fibre-reinforced polymer or biocomposites are currently in focus to replace conventional synthetic fibre products. The increasing awareness about environmental changes and pollution as well as governmental regulations will continue to boost the demand for green biocomposites. Various methods can be used to produce green biocomposites. Chemical treatments can enhance the property of interface adhesion between the natural fibre and polymer matrix, and also decrease their water absorption capacity. Consequently, this can improve the mechanical and tribological properties of green biocomposites.

The effects of fibre loading, length, treatment, orientation, heat treatment, hybridisation and transfer film formation at various sliding conditions have been reviewed and discussed in this chapter. All these fibre and sliding parameters may control the tribological behaviour of natural fibre-reinforced polymer composites. The addition of natural fibres to either thermoplastic or thermoset will result in enhancing the tribological behaviour due to the surface strengthening effect after reinforcement. An optimum fibre loading and length with proper fibre-matrix surface treatment can effectively reduce the wear rate and COF of NFRPCs. N-O of fibres against sliding direction shows better wear resistance as compared to that in AP-O and P-O for unidirectional fibre-reinforced polymer composites. For fibre mat reinforced-polymer composites, AP-O shows better wear resistance followed by P-O and N-O. The lubricating effect of transfer films during wear process plays an important role in reducing the wear volume loss and COF of NFRPCs. The knowledge on tribo-chemical reactions that occur during wear sliding processes and formation of transfer films needs to be explored further. It has been observed that the combination of natural fibres and traditional fillers i.e. UHMWPE and graphite can further improve the tribological performance of NFRPCs.

8 Future Prospects

The tribological applications of polymer composites have steadily increased. Due to environmental concerns, green biocomposites are likely to replace conventional polymer composites. Based on published literature, there are many researches in process to focus on the tribological behaviour of green biocomposites using natural fibre-reinforced synthetic polymer matrix or resin. However, it has also been noticed that there is a lack of research on the tribological behaviour of completely green biocomposite materials which involve plant fibre-reinforced biodegradable matrix. Most of the polymer matrices used in the studies are synthetic polymers. This is due to their hydrophilic nature, limited mechanical strength and fast degradation rate. Further research on the improvement of tribological properties of completely green biocomposite materials is needed to understand the wear mechanism as compared to that of partially green composite materials.

There are only a limited number of studies on modelling and simulation of the tribological behaviour of sliding wear mechanisms of NFRPCs. Moreover, most of the modelling studies and methods reported are post-modelling based on experiments data to obtain mathematic formulations. Pre-modelling and simulation studies based on the nature of composite materials have not been focused on enough.

As reinforcement elements in polymeric composites, there are still many varieties of natural fibres which have not been explored. The tribological performance on other natural plants can be further explored. Furthermore, there is also lack of work on the aging effects of tribological behaviour of NFRPCs such as natural weathering and ozone attack. This study should be carried out in order to estimate the tribological performance of NFRPCs in outdoor applications.

Finally, NFRPCs hold significant potential to fulfil the concept of 'green tribology'. Green tribology is the science and technology of the tribological aspects of ecological balance and of environmental and biological effects, since tribological problems such as high wear rate, energy dissipated and hazards of chemical lubrication contribute to very high global costs. In future, the designs of engineering materials for tribological applications should follow the principles of green tribology i.e. include minimisation of friction and energy loss or dissipation to increase the efficiency of energy, minimisation of wear, biodegradable lubrication, green coating, self-lubrication, biomimetic and bioinspired approaches. The biomimetic functional surfaces and ability to control surface adhesion like lotus leaves are the areas that need to be explored further in NFRPCs to control tribological responses. It can be envisaged that such developments could lead to completely new avenues in using green biocomposites for tribological applications.

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Development and Characterization of Wood and Non-wood Particle Based Green Composites

Abdul Halip Juliana, Seng Hua Lee, Md Tahir Paridah, Zaidon Ashaari and Wei Chen Lum

Abstract Production of green composites involve a manufacturing process that combining both renewable plant-based particles and green polymers. Characteristics of wood and non-wood particles are one of the main factors that influencing the properties of green composite, particularly particle based composite i.e., particleboard and wood plastic composite (WPC). Characterization of wood and non-wood particles are vital for properties determination of the resulting particleboard and WPC. The present work reviewed some characterization studies of particles including the size (length, width, and thickness, aspect ratio, and slenderness ratio) and geometry of the particles. This paper also highlighted the effects of particle size and geometry of wood and non-wood particle on the mechanical and physical properties of particleboard and WPC. Findings revealed that particle size exerted significant effect on the mechanical and physical properties of both particleboard and WPC. On the other hand, types of materials (wood or non-wood) are crucial factor that affects the performance of particleboard, but not a critical factor on the performance of WPC as it contained lesser amount of particles.

Keywords Particle size · Particle geometry · Wood · Non-wood · Green composites

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1 Introduction

The term of "green composite" are created mostly to achieve the combination of acceptable mechanical and physical properties together with their biodegradable and renewable nature in the composite industry. Green composites are gaining favour and regarding as the next generation of sustainable composite materials. As one of the product in the spectrum of composite materials, particle-based green composite is referred to the composite, particularly particleboard or wood plastic composite (WPC), that contained and manufactured from wood or non-wood particles. Particleboard is a wood-based panel product manufactured from particles of wood or other lignocellulosic materials and bonded using adhesives under pressure and temperature (Nemli and Aydın 2007). WPC are a relatively new modern concept that was developed in Italy in 1970s which combined wood or non-wood materials in flour/particles/fibres form with thermoplastic polymers and pressed under specific heat and pressure (Pritchard 2004). The main constituents of these composites are plant-based natural particles and biodegradable or naturally renewable resin system. They are called green composite mainly due to their composition (plant-based material) which is degradable and sustainable. Bajpai et al. (2014) has classified these green composites into a three categories; (1) Green or fully biodegradable composite where the composite is made of natural particles and biodegradable resin, (2) Partially green/biodegradable composite composed of natural particles and traditional formaldehyde-based resins, and (3) Hybrid green composite that consisted of two or more different natural particles in combination with biodegradable or traditional resins, mainly due to properties customization purpose. The present work reviews the development and characterization of particle-based green composite made from wood and non-wood particles using natural-based adhesives and formaldehyde-based adhesives.

2 Wood and Non-wood Particles

Wood particles are usually used in particleboard and WPC manufacturing. The term *particle* is a generic term applied to all lignocellulosic elements, either wood or non-wood, from which composites are made. The terminology can be referred to various types of particles depending on their applications. For example, the major types of particles used in particleboard manufacturing include wood shavings, flakes, wafers, chips, sawdust, strands, slivers, and wood wool (Moslemi 1974). Meanwhile the major types of particles used in WPC are commonly called fibre, particle, wood flour and sometime sawdust. Wood flour and sawdust are the same product, but in different size where the sawdust is normally having smaller size as compared to the wood flour. As reported by Loss (2013), wood dust covers the range from millimetres down to less than 0.1 μm. Particles larger than about 10 μm do not remain suspended in air for long, however particle with 10 to less than 1 μm sizes are able to enter airways which can eventually cause serious health problems (Loss 2013). In present work, most of the particles used for particleboard and WPC are mostly at larger size with more than 10 μm. These particles can be obtained from wood and non-wood species.

Wood can be categorized into hardwood and softwood, respectively. Botanically, hardwood are woods that come from angiosperms (flowering plants) with vessel element (or pore), and softwoods are those woods that come from gymnosperms (mostly conifers) with lack of vessel element (Wiedenhoeft and Miller 2005). Wood is a major raw material used for particleboard and WPC production, which accounted for 95 % of the lignocellulosic material available (Ghalehno et al. 2011a, b). In tropical countries, particularly in Malaysia, rubberwood is a main raw material for wood composite such as particleboard production (H'ng et al. 2012). While, in temperate countries, pine and poplar wood are favoured species that used in particleboard and WPC manufacturing. As the global supply of wood depleting continually, attention has been shifted to non-wood particles in particleboard production. Non-wood plants consist of dicotyledonous and monocotyledonous plants and can be categorize into various classification. In recent study done by Paridah et al. (2015), they have classified the non-wood plants into two main groups namely conventional plant fibres (cotton, kapok, flax, jute, hemp, ramie, kenaf, sisal, abaca, henequen, coir, and bamboo) and non-conventional plant fibres or agro-based fibre residues (corn stalk, wheat straw, rice straw, rice husks, sugarcane/bagasse, pineapple leaf, banana pseudostem, coconut stem, oil palm fibres). These two materials (wood and non-wood) are gaining attention from researchers and can be processed into particles to produce particle based green composites. A rough inventory of potential fibre resources available in world are done by Rowell (2008). According to the author, wood is a major source of fibre (1750 million dry tonnes), however, the sources of non-wood are also equally important as the combined value of these non-wood materials are greater than wood (2283 million dry tonnes).

3 Green Polymers

Apart from plant-based particles, adhesive is also a main component to determine the nature of green composites (Bajpai et al. 2014). Current wood adhesive market was dominated by formaldehyde-based resins due to their low cost and high reactivity (H'ng et al. 2011). Nevertheless, their non-renewable nature and subsequent emission of formaldehyde has caused high concern about environmental and health issues. As concern grew over the risk to environment and public health, the formaldehyde-based adhesives are gradually replaced by green adhesives in the production of green composite. Green adhesive, or more specific, renewable resources adhesives, is the loose term used to describe polymeric compounds that synthesis from natural materials (Pizzi 1991). These adhesives are environmentally friendly, biodegradable and renewable. Tannin-based adhesives and lignin adhesive are the two main types of these green adhesives (Pizzi 1980; Nimz 1983). Application of the aforementioned adhesives as wood panel adhesives have been studied extensively (Trosa and Pizzi 2001; Pizzi 2006; Ballerini et al. 2005; Pichelin et al. 2006; El Mansouri et al. 2007; Mansouri et al. 2011). In the recent years, several types of natural-based wood adhesives such as soy protein adhesives (Khosravi et al. 2010; Xu et al. 2011; Jang et al. 2011), crop-based starch and sugar adhesives (Tondi et al. 2012; Sulaiman et al. 2013), wheat gluten (Khosravi et al. 2011) and animal protein glue (Konnerth et al. 2009) have also been developed. These adhesives proved feasible to be used as wood adhesive to produce composite with comparable properties to that of conventional formaldehyde-based adhesive, for example, urea formaldehyde (UF) resin. However, despite their good potential as wood adhesive, some modification might be needed to further improve its properties (Huber and BeMiller 2010). For starch-based adhesives, crosslinking agent such as epichlorohydrin could be used to overcome the undesired properties of the native starch (Ackar et al. 2010). Sulaiman et al. (2013) modified oil palm starch with epichlorohydrin and found that the modification has greatly improved the mechanical and physical strength of the particleboard produced from it. Table 1 shows the particleboard produced using different types of lignocellulosic material and adhesive by several researchers worldwide.

For the production of WPC, two major class of polymers are commonly used, namely thermoplastic and thermosetting polymers, which can be differentiated by their response to temperature. Thermosetting polymers polymerize and become irreversibly hard at high temperature. While thermoplastic repeatedly soften and melt with increasing temperature and re-solidify upon cooling. As reported by Wolcott (2003), the primary selection criteria for thermoplastic polymer used in WPCs is the melting and softening temperature that less than the thermal degradation temperature of wood (~210 °C). This including five types of thermoplastic polymers, namely high density polyethylene (HDPE), low density polyethylene (LDPE), polyvinyl chloride (PVC), polypropylene (PP) and polystyrene (PS) are commonly used in the WPC manufacturing. These polymers are considered green because they are recyclable and hence impose fewer burdens to the environment. However, PVC are no longer regarded as a green polymer in the near future for it produces toxic gases during burning (Kaley et al. 2006).

4 Characterizations of Particles

In present study, characterizations of particles including the size (length, width), shape, aspect ratio or slenderness ratio, and adhesion (wettability and buffering capacity) of the particles are discussed. These characteristics are substantially affecting the performance of the manufactured green composites such as particleboard and WPC. The performances of particleboard are frequently influence by the characteristic of the particle due to high particle ratio in particleboard as compared to WPC. In most cases, particleboard is wood-based composite consist of wood

Table 1 The particleboard produced using different types of lignocellulosic material and adhesive

Particle type	Particle	Binder	Composite type	References
Wood	Industrial wood	Crop-based starch and sugar	Green	Tondi et al. (2012)
	Pine	Pine tannin	Green	Valenzuela et al. (2012)
	White birch	Urea formaldehyde resin	Partially green	Pedieu et al. (2009)
	Eucalyptus	Urea formaldehyde resin	Partially green	Colak et al. (2009)
	Rubberwood	Urea formaldehyde resin	Partially green	Lee et al. (2015a)
	Poplar	Urea formaldehyde furfural resin	Partially green	Ghafari et al. (2016)
	Recycled softwood particles	Citric acid and sucrose	Green	Umemura et al. (2015)
	Rhizophora spp.	Gum Arabic	Green	Abuarra et al. (2014)
Non-wood	Date Palm	Urea formaldehyde and Phenol formaldehyde resin	Partially green	Nemli and Kalaycoglu (2001), Amirou et al. (2013)
	Macadamia nut shells	Castor oil derived resin	Green	Wechsler et al. (2013)
	Coconut stem	EMDI isocyanate resin	Partially green	Papadopoulos et al. (2002)
	Cotton stalk	Urea formaldehyde resin	Partially green	Guler and Ozen (2004)
	Bamboo	Urea formaldehyde resin	Partially green	Papadopoulos et al. (2004)
	Oil Palm trunk	Binderless	Green	Boon et al. (2013), Baskaran et al. (2015)
	Bamboo	Citric acid	Green	Widyorini et al. (2016)
	Sweet sorghum bagasse	Citric acid	Green	Kusumah et al. (2016)
	Rice husk	Soybean protein concentrate-based resin	Green	Ciannamea et al. (2010)
	Bagasse	Binderless	Green	Nonaka et al. (2013)
	Kenaf	Binderless	Green	Xu et al. (2004), (2005)
Admixture	Tobacco stalks + Paraserianthes falcataria	Urea formaldehyde	Partially green	Acda and Cabangon (2013)
	Reed + wood	Urea formaldehyde	Partially green	Ghalehno et al. (2011a)

(continued)

Table 1 (continued)

Particle type	Particle	Binder	Composite type	References
	Bagasse + wood	Urea formaldehyde	Partially green	Ghalehno et al. (2011b), Hazrati-Behnagh et al. (2016)
	Beech + Norway spruce	Pine tannin	Green	Sedano-Mendoza et al. (2010)
	Rubberwood + oil palm trunk	Urea formaldehyde	Partially green	Lee et al. (2014), (2015b)
	Sugar cane bagasse + Pine	Phenol-formaldehyde	Partially green	Hein et al. (2011)
	Willow + Pine	Urea formaldehyde	Partially green	Warmbier et al. (2013)
	Apple tree pruning + sunflower stalk	Urea formaldehyde	Partially green	Ghofrani et al. (2015)
	Pine + Spruce	Wheat gluten	Green	Khosravi et al. (2011)

particles (100 % plant particles) of varying shape and size and bonded together with an adhesive and consolidated under heat and pressure. However, in WPC production, the ratio of wood particle is significantly lower. Apart from the polymer, the primary component of WPCs is wood or natural fibre filler, which adds stiffness and strength to the composite when processed with a polymer component. This allowed WPC to exhibits hybrid characteristics of wood and plastic.

4.1 *Effect of Particle Size on the Properties of Particleboard*

In particleboard manufacturing, particle size is one of the main parameters that have been reported to affect the properties of particleboards (Moslemi 1974). A number of studies done by several researchers had stated that particleboards made from larger and longer sized particles were found significantly stronger in bending and bonding strength as compared to the board made from smaller sized particles (Ong 1981; Jamaludin et al. 2001; Juliana et al. 2012). Table 2 tabulates the mean values of the length, width, thickness, aspect ratio and slenderness ratio for some wood and non-wood particles used in particleboard manufacturing. The particle mesh sizes used in particleboard production are ranging from 0.12 to 1.0 mm. However, as shown in Table 2, the lengths of particles are not fully indicated by the mesh size. From observation, the lengths of the particles that passed through the mesh are not influenced by the mesh size. Some particles passed through the same mesh size could have longer length as it was falling vertically through the mesh. As reported by Saffari (2011), the fine (10.68 mm length) Poplar particles resulted in higher mean values than coarse (24.54 mm length) ones for modulus of rupture (MOR), modulus of elasticity (MOE), internal bonding (IB) and linear expansion (LE), with values of 7.76, 1049, 2.48 MPa, and 0.174 %, respectively. Increasing the length of particles and the slenderness ratio (length/thickness) also increases both MOR and MOE, but decreases the IB (Miyamoto et al. 2002).

Apart from wood, effects of particle sizes of non-wood such as date palm frond, oil palm trunk, rice straw, kenaf and bagasse particles on the properties of particleboard also have been carried out by several studies (Hegazy and Ahmed 2015; Juliana et al. 2012; Hashim et al. 2010; Li et al. 2010). As tabulated in Table 2, most of non-wood particles have higher aspect ratio (length/width) and slenderness ratio compared to wood particles. Slenderness and aspect ratios can be used to estimate the behaviour of the composite. As described by Maloney (1993), wood particles with high slenderness ratio can be aligned to increase the board strength. This may anticipate that raw material from non-wood have the potential to be used in the manufacture of green particleboard panels. For instance, palm date frond particle with great aspect ratio and slenderness ratio had the highest strength properties on the panel product. Meanwhile, binderless particleboard made from OPT strand had significantly higher MOR and IB values compared to fine sample,

Table 2 The mean values for the length, width, thickness, aspect ratio and slenderness ratio of some wood and non-wood particles for particleboard manufacture

Material	Mesh size (mm)	Length (mm)	Width (mm)	Thickness (mm)	Aspect ratio	Slenderness ratio	Author(s)
Wood	3.00 1.00	13.70 9.90	2.90 2.10	0.9 0.6	4.7 4.7	15.2 16.5	Papadopoulos et al. (2004)
Rubberwood	1.0–2.0 0.5–1.0	7.04 4.06	0.89 0.54	n/a	8.0 9.0	n/a	Juliana (2013)
Poplar	Large Small	24.54 10.68	6.46 1.60	0.70 0.48	n/a	n/a	Saffari (2011)
Kenaf core	1.0–2.0 0.5–1.0	3.68 1.89	1.18 0.67	n/a	3.0 3.0	n/a	Juliana (2013)
Kenaf bast	1.0–2.0 0.5–1.0	3.89 4.88	0.08 0.09	n/a	52.0 52.0	n/a	Juliana (2013)
Flax	3.00 1.00	18.20 15.40	1.4 1.1	0.5 0.4	13 14	36.4 38.5	Papadopoulos and Hague (2003)
Date palm (Saqui)	0.64–0.25 0.25–0.12	48.60 16.20	1.90 1.30	0.62 0.21	15.6 19.8	58.3 78.9	Hegazy and Ahmed (2015)
Date palm (Barhi)	0.64–0.25 0.25–0.12	45.90 12.80	2.30 1.20	0.83 0.28	20.9 12.4	36.9 54.6	Hegazy and Ahmed (2015)
Date palm (Sukkari)	0.64–0.25 0.25–0.12	42.30 14.80	2.20 1.30	0.53 0.22	20.9 13.4	33.5 48.1	Hegazy and Ahmed (2015)
Bamboo	3.00 1.00	15.60 12.50	2.2 1.5	0.7 0.5	7.0 8.3	22.2 25.0	Papadopoulos et al. (2004)

and met MOR requirement of Japanese Industrial Standard (Hashim et al. 2010). In their study, the OPT strands were produced manually by separating vascular bundles with a length of 3–5 cm from the chip, while the fine particle were processed into fine particles using a hammermill and a wiley mill. Li et al. (2010) fabricated particleboard from six particle sizes of rice straw and found that the performance of green composites was highly dependent on the particle size, whereas the increasing of particle size increased the bending strength but decreased the dimensional stability.

A comparative study of wood and non-wood particleboard done by Juliana et al. (2012) revealed that same flaking process produced slightly different size and geometry of particles. In their study, the highest particle length was given by rubberwood, followed by kenaf bast and kenaf core. Meanwhile, kenaf core particles have the widest dimension, followed by rubberwood and kenaf bast particles. As a result, the analysis of the aspect ratio indicated that the length of kenaf core and kenaf bast particles was 3 and 52 respectively, as compared to a mere 8 for rubberwood. The differentiation on the length and width of particles was due to the different specific gravity of the materials. Other studies revealed that non-wood particles such as bamboo and flax particles were typically longer, thinner and narrower than the wood chips. Therefore, their length to width (aspect ratio) and length to thickness (slenderness ratio) ratios were typically higher than those of the wood chips (Papadopoulos et al. 2004; Papadopoulos and Hague 2003). Nevertheless, properties of the particleboard made from wood species has generally better mechanical and physical properties than the particleboards made from non-wood species.

4.2 *Effect of Particle Size on the Properties of Wood Plastic Composite*

Meanwhile, in WPC manufacturing, particle size also plays an important role on the flexural and tensile strength properties. Based on Ashori (2008), one of the critical parameters that influencing the strength properties of WPCs is the size of the fibres. As illustrated in Table 3, there are lots of studies done using wood and non-wood particles for WPC fabrication. From Table 3, the particle used in WPC are ranging from 0.126 to 10.00 mm length. However, according to Ashori (2008), short and tiny fibres (average particle size 0.24–0.35 mm) should be preferred. Meanwhile, another study done by Clemons (2002) stated that typical particles sizes for WPC production is 10–80 mesh or 0.18–2.0 mm, and the smaller particles were said to yield better performance (Takatani et al. 2000). They provide a higher specific surface area and the fibres are distributed more homogeneously compared to composites with long fibres and so the compatibility of fibre and matrix is improved. With this, swelling decreases and breaks during processing are reduced. Several studies have investigated the effect of particle sizes on the flexural and tensile properties of WPCs made from wood and non-wood (Migneault et al. 2008; Rafighi et al. 2014; Kallakas et al. 2015). Migneault et al. (2008) used three fibre length classes (long; 0.481 mm, medium; 0.304 mm, and short; 0.196 mm) of white birch to evaluate the effect of fibre length on the properties of the composites. In their study, the mechanical properties (flexural, tensile, toughness) of extruded wood-fibre/HDPE composites increased with increasing fibre length, but the physical properties were decreased. From observation, mechanical properties of WPCs are significantly increased with increasing particle length from 0.18 mm to approximately 0.50 mm (Table 3). However, the properties of WPCs are adversely affected when the particle length increased to 0.68 mm and above.

Apart from particle sizes, aspect ratio of the fibres, wood species (hardwood, softwood or non-wood), and mixing ratio of wood and plastic are also the main factors that affected the properties of the resulting WPCs (Takatani et al. 2000; Stark and Rowlands 2003; Chen et al. 2006). Aspect ratio is defined as the ratio of width to height. Therefore, shorter fibres have lower aspect ratios and vice versa. Many studies have revealed that fibre are better reinforcing materials compared to particles as the resulting composites display higher flexural strength (Bledzki and Faruk 2003; Migneault et al. 2009) and lower water sorption rates (Bledzki and Faruk 2003). Nevertheless, Migneault et al. (2009) reported that greater water sorption and volumetric swell were obtained as the fibre aspect ratios increased. Piao et al. (2014) produced WPCs from sawdust and fibre of lodgepole pine and loblolly pine, respectively and their dimensional stability were compared. The study revealed that as the fibre/sawdust ratio increased, the thickness swelling and water absorption of the composites made from loblolly pine increased as well. Conversely, the dimensional stability of the composites made from lodgepole pine were more dimensionally stable as the fibre/sawdust ratio increased. The author attributed the findings to lower aspect-ratio of the loblolly pine fibre which consisted mostly fibre bundles and fractions. Different wood species also played an important role in influencing the properties of the WPCs as they possess different density (Piao et al. 2014). In general, WPCs made from softwood displayed slightly inferior tensile and flexural properties compared to the hardwoods WPC (Stark and Berger 1997).

Generally, properties of the WPCs made from hardwood species such as rubberwood and poplar are better than the WPCs made from softwood species such as pine. As illustrated in Table 3, flexural strength of WPC made from rubberwood are slightly greater than WPC made from radiata pine at a similar particle ratio (60 wt%), PP matrix (40 wt%) and particle size (1.5–2.0 mm). Chen et al. (2006) investigated the effect of mixing ratios and particle sizes on the properties of wood plastic composites. They found that the composite mat with the highest wood:plastic ratio (70:30) required the shortest time for the middle layer to reach targeted temperature and cool down to the targeted temperature as well. The mixing ratio of wood and plastic also affected the moisture content and dimensional stability of the WPC as wood is a hygroscopic material that readily absorb water (Shiue et al. 2001). Therefore, the moisture content and thickness swelling increase along with higher wood particle content. In comparison, between wood and non-wood reinforcing materials, no

Table 3 Properties of some wood and non-wood plastic composites

Type	Material	Particle size (mm)	Matrix	Ratio of particle (%)	Flexural strength, MOR (MPa)	Flexural modulus, MOE (MPa)	Tensile modulus (MPa)	Tensile strength (MPa)	Impact strength (KJ/m^2)	Author(s)
Wood	Radiata pine	2.0	PP	60	13.9	3034	n/a	n/a	n/a	Wechsler et al. (2008)
	Rubberwood	1.5	PP PP PP	40/60 50/50 60/40	23.6 26.5 25.9	2591 2744 2925	n/a n/a n/a	n/a n/a n/a	n/a n/a n/a	Ayrilmis and Jarusombuti (2010)
	Aspen	≤0.126	PP	20/80	23.8	870	n/a	n/a	7.26	Kallakas et al. (2015)
	White birch	0.196 0.304 0.481	HDPE	40	37.8 41.8 43.5	3200 3410 3390	2830 2960 2990	23.4 24.9 28.2	4.71 5.36 5.75	Migneault et al. (2008)
	Birch	0.63 0.63–1.25 1.25–2.00	PP PP PP	35/65 35/65 35/65	28.3 27.1 26.2	2340 2070 1910	n/a n/a n/a	n/a n/a n/a	4.03 4.99 4.67	Kallakas et al. (2015)
	Poplar	0.25	PP	50/50	47.1	5260	5435	28.2	n/a	Ayrilmis et al. (2013)
	Fir	0.425 0.180	HDPE	70/30	13.6 11.4	1349 1152	n/a n/a	6.4 5.1	n/a n/a	Rafighi et al. (2014)
	Beech	0.425 0.180	HDPE	70/30	14.6 12.7	1362 1262	n/a n/a	8.0 7.0	n/a n/a	Rafighi et al. (2014)

(continued)

Table 3 (continued)

Type	Material	Particle size (mm)	Matrix	Ratio of particle (%)	Flexural strength, MOR (MPa)	Flexural modulus, MOE (MPa)	Tensile modulus (MPa)	Tensile strength (MPa)	Impact strength (KJ/m^2)	Author(s)
Non-wood	Kenaf	0.18–0.42	PP	0 40	n/a	n/a	700–800 3200–3300	25–28 44–47	n/a	Mirbagheri et al. (2007)
	Hemp	6.35	PP	30	52–57	3600–3900	n/a	n/a	n/a	Wibowo et al. (2004)
	Jute	n/a	PP	40	24.1	4100	6100	64	n/a	Reddy and Yang (2011)
	Flax	n/a	PP	30	42.9	3900	1659	27.3	n/a	Arbelaiz et al. (2005)
	Oil palm trunk (OPT)	10.0	PP	10 50	14.1 17.4	1650–1750 2648	1800–1900 3300	29.5 25.6	0.027 0.035	Abdul Khalil and Bhat (2010)
	Oil palm empty fruit bunch (EFB)	10.0	PP	10 50	14.3 17.9	1600–1700 2702	1500 2600	28.5 25.0	0.028 0.036	Abdul Khalil and Bhat (2010)
	Bamboo	0.42 0.25	PP	10 30 50	n/a	n/a	906 1070 1314	32.4 31.5 29.6	2.5 2.8 2.5	Lee et al. (2009)

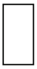
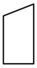
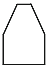
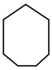
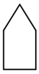
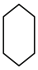
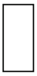
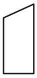
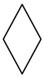
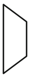
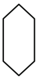
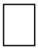
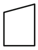
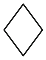
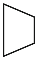
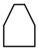
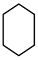
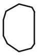
OPT Oil palm trunk; *UF* Urea formaldehyde; *MUF* Melamine urea formaldehyde; *MOR* Modulus of rupture; *MOE* Modulus of elasticity; *IB* Internal bonding; *TS* Thickness swelling; *WA* Water absorption; *F* Face; *M* Middle; *n/a* not available significant difference in term of performance of the resulting composites was observed. This finding implying that types of materials are not a decisive factor that affects the performance of WPCs.

Possibility of using recycled polymers and materials has encouraged the development of wood plastic composites (WPC). However, application of recycled polymers has caused some concerns regarding to the uncontrollable properties of the composites. Fortunately, some studies have successfully proved the feasibility of the application of these recycled plastics. Gozdecki et al. (2015) reported that the WPCs made from recycled polymers such as polypropylene (PP) and high density polyethylene (HDPE) showed only slightly poorer properties compared to that of WPCs made from made from virgin polymers. Recycled HDPE was used by Adhikary et al. (2008) to produced composites with superior dimensional stability and comparable tensile and flexural properties compared to that of virgin HDPE.

4.3 Classifications of Particle Geometry in Green Composite

Particle geometry (shape and size) is one of the most important factors in determining the properties and appearance of particleboard. As shown in Table 4, the classification of particle geometry has been made by studies done by Kruse et al. (2000) and Juliana et al. (2012). Kruse et al. (2000) had defined eight types of wood strand shapes. Meanwhile, Juliana et al. (2012) had classified flaked rubberwood as

Table 4 Defined wood and non-wood particle types with different shapes

Material	Classes									
	1	2	3	4	5	6	7	8	9	10
Wood strand[a] (%)										
Rubberwood[b] (%)	 23	 17	 15	 11	 13	 12	 9			
Kenaf core[b] (%)	 20	 19	 12	 9	 15	 4	 9	 2	 3	 7
Kenaf bast[b] (%)	 25	 13	 15	 11	 11	 10	 15			

Source [a]Kruse et al. (2000), [b]Juliana et al. (2012)

well as flaked kenaf stem into several classes; seven for rubberwood, ten for kenaf core, and seven for kenaf bast. In a study done by Juliana et al. (2012), majority of wood (rubberwood) and non-wood (kenaf core) particles appeared in form of rectangular and nearly rectangular form (Classes 1, 2, 3, 4 and 5). This finding is quite similar to that of reported for wood by previous study who found that the majority of commercial dry wood strands collected from OSB mills were rectangular or nearly rectangular in shape. In their study, the particles generated from the non-wood kenaf core mostly assumed a variant of rectangular shapes. Some of the kenaf core particles were present in a semi circular-end shape (classes 9 and 10) but most of them still retained the rectangular shapes. About 38 % of the kenaf bast particles had curled shapes (classes 1 and 2). In addition, around 36 % of the kenaf particles were kneel-shaped (classes 5, 6, and 7), mostly in the form of bundles of fibres.

5 Limitations

The major drawback for both of these green composites (particleboard and WPC) is the high hygroscopicity of the lignocellulosic materials. Lignocellulosic materials are porous and hygroscopic materials that composed of three hydroxyl containing components including cellulose, hemicelluloses and lignin which attract water through hydrogen bond. Dimensional instability, particularly in particleboard, has limited its potential for exterior application. When exposed to repeated humidity cycles during long-term application, springback and re-expansion occurred and subsequently results in permanent thickness swelling of the composites (Back and Sandstrom 1982). Dimensional changes for the composite in use could affected its performance functionally and visually. WPC, on the other hand, is more stable than particleboard due to the encapsulation by the thermoplastic polymer. Nevertheless, it is impossible to completely rule out the moisture absorption without using chemical modification and costly surface barriers, which at the same time increase the cost of the production (Rowell et al. 1986).

One of the predominant disadvantages of the application of wood and non-wood natural materials for the production of WPC is lower allowable processing temperature (Rowell et al. 1997). Lignocellulosic materials started to degrade at temperature above 200 °C and the degradation could impact on the composite performance. Therefore, types of polymer used with wood and non-wood materials are restricted to commodity thermoplastics such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS). Nonetheless, higher temperatures are still permitted provided that shorter processing period are applied. Another downside of WPC is the inferior compatibility between hydrophilic wood particles and hydrophobic matrix that could adversely affected the properties of the composites (Turku and Karki 2014).

6 Conclusion

The characteristics of plant based particles are very crucial to determine the properties of green composites. Particle size, aspect ratio and geometry play as important factors that influencing the properties of both particleboard and WPC. In addition, mixing ratio and material type (wood and non-wood) also exerted great influence on the particleboard performance, but has less effect on the WPC properties due to its higher ratio of polymer over particles, and therefore exhibits greater extent of plastic-like characteristics and properties.

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Woven Natural Fiber Fabric Reinforced Biodegradable Composite: Processing, Properties and Application

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Abstract In recent years, the use of biodegradable polymers has become more popular due to the increasing awareness of the environmental impacts of petroleum-based plastics. The most feasible way toward having eco-friendly composites is the use of biodegradable polymer composite reinforced with natural fibers such as bamboo, kenaf, jute, sisal, ramie, flax and hemp. The research on natural fiber reinforced composites has generally been focused on the use of short fibers. Woven fabric has been employed in various applications which include aerospace, automotive parts and structural reinforcement due to their high strength and stiffness. Although there is less study being conducted regarding biodegradable polymer composites reinforced with natural fiber woven fabric, natural fibers possess many benefits when used as fabric, for instance, ease in handling of fibers and also the provision of homogenous distribution for the matrix and reinforcing fiber. Thus, this chapter is concerned with the processing, properties and applications of woven natural fiber fabric reinforced biodegradable composites.

Keywords Woven fabric · Natural fiber · Biodegradable polymers · Biocomposites

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1 Introduction

The use of fiber reinforced polymeric composites has become increasingly popular due to growing concerns regarding the impacts of petroleum-based plastics on the environment. Most consumer products are made of non-degradable fibers and resins from petroleum-based plastics which have caused a few environmental problems after being discarded. A few major challenges in the use of material from petroleum-based plastics are the decline of the availability of petrochemical resources, increases in their price and the persistence of these materials in the environment beyond their functional life. For the reasons mentioned above, biodegradable material plays an important role in human life and it has also been triggered by the government regulations which results in the growth of environmental awareness and contributes to a fundamental change towards producing fully 'greener' composites throughout the world.

Presently, the most practical approach to produce environmentally friendly composites is the utilization of natural fibers as reinforcement. Natural fiber composites possess advantages such as having the ease of availability, renewability of raw materials, low density, and high specific strength and stiffness. Most researches are concentrated on the composites reinforced with short natural fibers; however, inadequate works on the natural fiber fabric composites have been published. Natural fiber fabrics have many outstanding properties, such as high tenacity, resistance to bacteria, and high strength and stiffness due to continuous yarns oriented in at least two axes (Liu 2008). Furthermore, in fiber reinforced composites, the interfacial bonding force between the fibers and the polymer matrix will replace the fiber-to-fiber friction created by the yarn twist. Besides, the yarn is only required to withstand the stresses experienced during processing (Miao 2008).

In order to produce totally biodegradable composites, substituting the petroleum-based thermoplastic with a biopolymer has also been heavily investigated. Biopolymers can be defined as polymers produced from renewable natural sources, which is normally biodegradable and nontoxic. "Green composites" with excellent mechanical properties in comparison to non-renewable petroleum based-products can be produced from biopolymers reinforced with woven natural fiber fabric. In this chapter, the processing, properties and applications of woven natural fiber fabric reinforced biodegradable composites will be discussed.

2 Natural Fibres

2.1 Advantages and Disadvantages of Natural Fibres

The rise of global environmental awareness and the concern for environmental stability as well as the new environmental regulations has triggered the effort of searching new products and methods that are environmentally friendly. The utilization of natural fibers as a potential alternative for man-made fibers in composite materials has attracted the interest among researchers throughout the world. Studies with natural fibers have shown that natural fibers have the potential to be an effective reinforcement in thermoplastic and thermosetting materials (Faruk et al. 2014). Natural fibers are abundant in nature, but not adequately utilised.

The growing interest in natural fibers is mainly due to their low specific density, which is typically 1.25–1.50 g/cm^3, compared to glass fibers at about 2.6 g/cm^3, allowing natural fibers to provide s higher specific strength and stiffness in plastic materials (Hariharan 2005). The other key driver for substituting natural fibers for glass is the lower price of natural fibers (200–1000 US$/tonnes) compared to glass (1200–1800 US$/tonnes) (Jawaid 2011). Natural fibers also offer several advantages as they are recyclable, biodegradable, abundant, exhibit good mechanical properties, provide better working conditions and are less abrasive to equipment when compared to common synthetic fibers, which can contribute to significant cost reductions (Faruk et al. 2014). All these characteristics make their use very attractive for the manufacture of polymer matrix composites.

However, researchers who have worked in the area of natural fibers and their composites agree that these renewable sources have some drawbacks, such as poor wettability, incompatibility with some polymeric matrices and high moisture absorption (Duhovic 2008; Faruk et al. 2014). The key differences between natural fibers and glass fibers are shown in Table 1. One of the most important problem of natural fibers is fiber-matrix adhesion. Poor adhesion between hydrophobic polymers and hydrophilic fibers can result in low mechanical properties in the natural fiber reinforced polymer composites. In fiber reinforced composites, the function of matrix is to transfer the load to the stiff fibers through shear stresses at the interface and this process needs a good bond between the matrix and fibers. Poor adhesion at the interface lead to several drawbacks such as the full abilities of the fibers in the composite cannot be exploited and the composite prone to environmental attacks that may weaken it, thus reducing its life span. The composite properties can be

Table 1 Comparison between natural and glass fibres (Wambua et al. 2003)

Properties	Natural fibers	Glass fibers
Density	Low	Twice that of natural fibers
Cost	Low	Low, but higher than NF
Renewability	Yes	No
Recyclability	Yes	No
Energy consumption	Low	High
Distribution	Wide	Wide
CO_2 neutral	Yes	No
Abrasion to machines	No	Yes
Health risk when inhaled	No	Yes
Disposal	Biodegradable	Non-biodegradable

enhanced through physical and chemical treatments (El-Sabbagh 2014; Le Moigne 2014).

The main drawbacks of cellulosic fibers are hydrophilic and absorb moisture. The moisture content of cellulosic fibers can vary between 5 and 10 %, which can lead to dimensional variations and influence the mechanical and physical properties of the composites. Other disadvantages of natural fibers are moisture sensitivity, heterogeneous quality, and low thermal stability. The thermal degradation of natural fibers is a three-stage process. The first stage, from 250 to 300 °C, is attributed to the low molecular weight components such as hemicellulose. The second decomposition process is seen in the temperature range of 300–400 °C and the third one is observed around 450 °C. The second degradation process is associated with the degradation of cellulose whereas the high-temperature process is due to lignin (Lee 2006; Tajvidi 2010). The degradation of natural fibers is a crucial aspect in the development of natural fiber polymer composites and can limit the use of some thermoplastics. Thermal degradation of the fibers can also result in the production of volatiles at processing temperatures above 200 °C. This can lead to porous polymer products with lower densities and inferior mechanical properties (Saheb 1999; Oksman 2002). The key advantages and disadvantages of natural fibers are shown in Table 2. A wide variety of different fibers can be applied as reinforcements or fillers.

2.2 *Categories and Properties of Natural Fibers*

Natural fibers are obtained from plants, animals, and minerals. Natural fibers from plants can be grouped in several classes which are bast, leaf, seed, fruits, stalk and wood fibers. These natural fibers are classified based on its source, for instance,

Table 2 Benefits and limitations of natural fibres (Jawaid and Abdul Khalil 2011; Duhovic et al. 2008; Sreekumar 2008)

Benefits	Limitations
Lower specific weight results in a higher specific strength and stiffness than glass	Lower mechanical properties especially impact resistance
Renewable resource	Heterogeneous quality
Production with low investment at low cost	Moisture sensitivity
Low abrasion, therefore tool wear	Low thermal stability
Non toxic	Low durability
Abundantly available	Poor fire resistance
Biodegradable	Poor fiber-matrix adhesion
Thermal recycling is possible	Price fluctuation by harvest results or agricultural politics

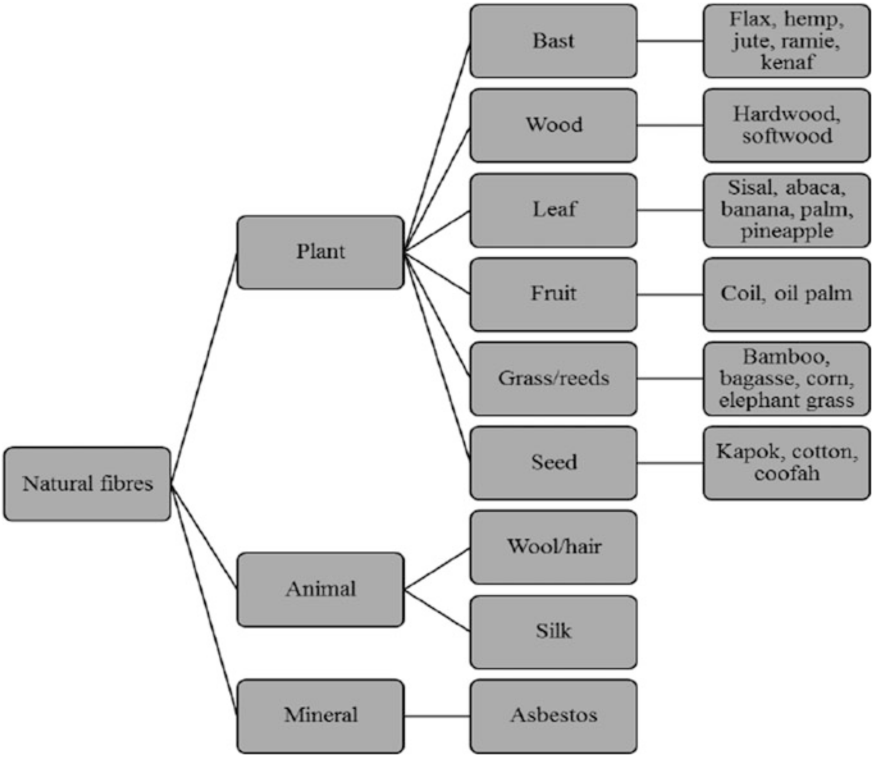

Fig. 1 Categories of natural fibres (Jawaid and Abdul Khalil 2011; Duhovic et al. 2008; Rowell 2008)

natural fibers that are grouped into bast are jute, hemp, kenaf, and flax which obtained from fiber-sheaved of dicoltylic plants or vessel sheaves of monocotylic plants. Three main categories of natural fibers depending on their origins are shown in Fig. 1. Table 3 compares a number of physical and mechanical properties of different natural fibers to those of common synthetic fibers.

3 Woven Fabrics

There are three main categories of fabric structure; woven, knitted, and braided fabric. Normally, woven fabrics demonstrate excellent dimensional stability in the warp and weft directions. Furthermore, due to its load path eccentricity, woven

Table 3 Physical and mechanical properties of natural fibres and glass fibres (Rowell 2008; Olesen and Plackett 1997; Peterson 2006; Jawaid 2011; Abdul Khalil et al. 2012)

Fibers	Length of fiber (mm)	Diameter of fiber (μm)	Density (g/cm^3)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
Bamboo	2.7	14	0.8–1.1	391–1000	48–89	1.9–3.2
Flax	10–65	5–38	1.4–1.5	800–1500	60–80	1.2–1.6
Hemp	5–55	10–51	1.5	550–900	30–70	1.6
Jute	0.8–6	5–25	1.3–1.46	393–700	10–55	1.5–1.8
Sisal	0.8–8	5–25	1.33–1.45	600–700	22–38	2–3
Ramie	40–250	18–80	1.5	400–938	62–128	2–3.8
Kenaf	1.4–11	12–36	1.2	295	21–60	2.7–6.9
Cotton	15–56	12–35	1.5	287–597	6–12.6	3–10
Banana	0.17	13.16	1.35	529–914	27–33.8	5.3
Pineapple	3–9	20–80	1.5	170–1627	60–83	1–3
Oil palm fiber	0.89–0.99	19.1–25	0.7–1.55	248	3.2	2.5
Bagasse	0.8–2.8	10–34	1.2	20–290	19.7–27.1	3–4.7
E-glass	7	13	2.5	2000–3500	70	2.5

fabric has high out-of-plane strength carrying secondary loads. Woven fabric can be identified as a structure in which the warp yarns and the weft yarns are interlaced. The direction parallel to the length of the roll is known as warp direction, while the direction perpendicular to the length of the roll is known as fill or weft direction (Campbell 2010). Interestingly, the tensile strength of a woven fabric is comparable to the sum of the strengths of the yarns oriented along the tensile direction. Nevertheless, there are some concerns related to woven fabric have been recognised (Shah 2013):

1. The stress transfer between fibers within the yarn can be affected by the addition of the twists in yarns. This factor can influences the strength and the fracture mechanism of the yarn.
2. The 'crimp' produced when the twisted yarn are used as reinforcements has an bad effect on the composite properties because of yarn misalignments and the resulting stress concentrations.
3. Yarn permeability and impregnation will be reduced because the twist tightens the yarn structure.

Woven fabric is identified by the linear densities of warp and weft yarns, the weave pattern, the number of warp yarns per unit width (warp count), the number of weft yarns per unit length (weft count), warp and weft yarn crimp, and surface density. The simplest woven fabric structure is the *plain weave* where the warp and weft yarns are interlaced in a regular sequence of one under and one over. Plain

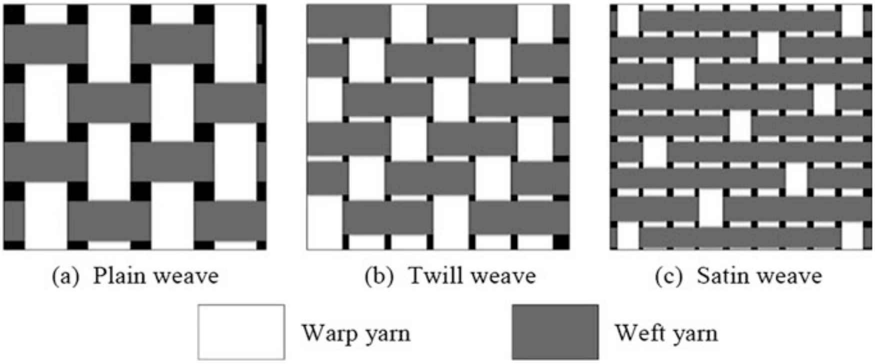
(a) Plain weave (b) Twill weave (c) Satin weave

Fig. 2 Woven fabric terminology

weaves have more interlaces per unit area than any other type of weave, and therefore have the tightest basic fabric design, and are the most resistant to in-plane shear movement (Kawabata 1989). The difference between each types of woven fabric can be seen in Fig. 2.

Twill weave is defined as a fundamental weave with yarns interlaced to produce a pattern of diagonal lines on the surface. *Satin weave* is a fundamental weave characterized by sparse positioning of interlaced yarns, which are arranged with a view to produce a smooth fabric surface devoid of twill lines (diagonal configurations of crossovers).

3.1 Fabric Processing Method

Several different manufacturing processes can be used to convert natural fibers from the plant to the woven fabric, with different effects on the environment. Currently, there are two main manufacturing methods for textiles: mechanical processing (stripping, boiling, and enzyme use) and chemical processing (multi-phase bleaching), which is quite similar to that of the viscose rayon fiber.

(a) Mechanical processing

Mechanical methods, which crush the natural fibers into pulp, are the less harmful but more expensive approach. In this method, the woody parts of the plant will be crushed, followed by the use of natural enzymes to break the walls into a soft form. Then, the natural fibers can be mechanically combed out and spun into a yarn. However, this process is more labour intensive and expensive, thus it is scarcely used in the manufacturing of clothing (Abdul Khalil et al. 2012).

(b) Chemical processing

Most fabrics in the market are smooth-textured that feel similar to rayon; it is, in fact, a form of rayon. Rayon can be defined as a regenerated cellulose fiber, where a natural raw material altered through a chemical process into a fiber that can be categorized between naturals and synthetics. The cellulose can be obtained from wood, jute, cotton fiber, bamboo and etc. The viscous process is an established and widely used process for natural fibers. In chemical process, a strong solvent is used to dissolve the cellulose material to make a thick solution. Then, the thick solution is forced through a spinneret into a quenching solution where strands solidify into fiber. This process is also known as hydrolysis alkalization or solution spinning. The solvent used for this process is carbon disulfide, which is harmful for human reproductive system and pollutes the environment through air emissions and wastewater (Abdul Khalil et al. 2012). The recovery of this solvent is normally around 50 %; the other half goes into the environment. Sodium hydroxide and sulfuric acid are the other hazardous chemicals used in the viscose process (Patagonia 2014). There is an environmentally friendly chemical process known as the closed loop system called lyocell. The only impediment for this method is the high cost in setting up the factories (Mass 2009).

3.2 Natural Fiber Woven Fabric

Nowadays, due to environmental consciousness, government regulations around the world have encouraged scientists to develop eco-friendly and sustainable materials, including for the textile industries. In order to meet the current need of fibers in textiles, there are several natural fibers that are commonly used as fabrics, such as bamboo, hemp, flax, jute and ramie that require low environment impact conditions (Shahid ul et al. 2013). Table 4 indicates the benefits and limitations of some commonly used natural fibers. Table 5 reveals the chemical components of natural fibers; the cellulose content in the natural fibers listed reaches more than 70 % which meets the preliminary requirement for textile applications (Yueping 2010).

4 Biodegradable Polymers

Currently, the utilization of biodegradable polymers has become more popular because of the concerns over the influences of petroleum-based plastics on the environment. Biopolymers can be defined as polymers generated from renewable natural sources. They are normally biodegradable and nontoxic. Biodegradable material is a material that can be degraded by the enzymatic action of living organisms that produce CO_2, H_2O, and biomass under aerobic conditions or hydrocarbons, methane and biomass under anaerobic conditions (Ren 2009; Guo

Table 4 Benefits and limitations of some commonly used natural fibres (Shahid ul et al. 2013; Nurul Fazita 2013; Liu 2008)

Fibers	Benefits	Limitations
Cotton	• Abundant availability • Environmentally friendly • Breathable and soft • Cost-effective • Renewable nature • Agro based	• Large consumption of pesticides and herbicides • High water requirement
Bamboo	• One of the fastest growing plants • Takes up more greenhouse gases and releases more oxygen • Does not need replanting or fertilisers • Use no pesticides • Excellent mechanical properties such as high tensile modulus and low elongation at break • Their specific stiffness and specific strength are comparable to those of glass fibers.	• Bad elasticity • Poor wrinkle recovery • Harsh handle • Low dyeability • Itching when worn next to the skin
Jute	• Agro based • Annually renewable • Biodegradable • Low cost • No residues of pesticides and heavy metals	• Spinning problems
Ramie	• Wrinkle resistance • High strength • Stain resisting ability • Resistant to bacteria, mould and insect attack	• Requires chemical processes to degum the fibre • Brittle and stiff • High cost
Flax	• Low dose of chemical requirement • Environmentally safe	• Quality and consistency problems
Hemp	• No requirement of pesticides • High tensile strength • Hemp textiles feel softer • Environmentally friendly crop • Requires low quantity of water • No waste production	• Cultivation restriction

Table 5 Chemical components of different fibres (Abdul Khalil et al. 2012; Li 2010; Yueping 2010; Kostic et al. 2008; Li et al. 2000; Nam 2006)

Chemical component (%)	Bamboo fiber	Jute fiber	Flax fiber	Ramie fiber	Sisal fiber	Hemp fiber
Aqueous extract	3.16	3.06	5.74	–	–	3.3
Pectin	0.37	1.72	1.81	–	–	1.6
Hemicelluloses	12.49	13.53	11.62	–	10	12.3
Lignin	10.15	13.30	2.78	1–2	8	2.9
Cellulose	73.83	68.39	78.05	65–75	78	76.1

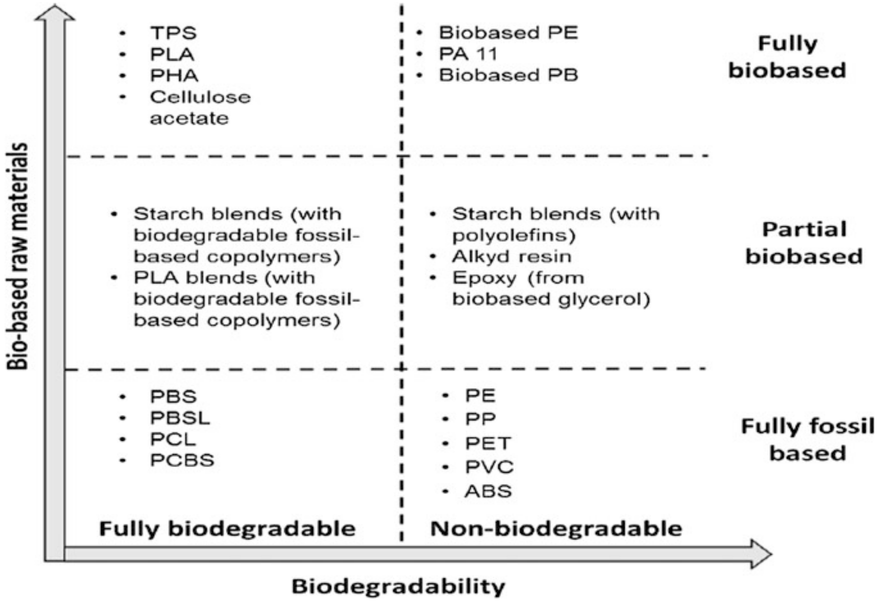

Fig. 3 Schematic representation of the diversity of degradable materials

Table 6 Comparative properties of common biopolymers

Property	PHBV[a]	PCL[a]	PEA[a]	PBSA[a]	PBAT[a]	PLA[a,b,c]
Density (g/cm^3)	1.25	1.11	1.07	1.23	1.21	1.24
Glass transition temperature (T_g), °C	5	−61	−29	−45	−30	70
Melting temperature (T_m) (°C)	153	65	112	114	110–115	175
Tensile strength (MPa)	–	14	14	19	9	49.6–61.6
Tensile modulus (MPa)	900	190	262	249	52	3500
Elongation at break (%)	15	>500	420	>500	>500	6
Water vapour transmission rate (WVTR) at 25 °C (g/m^2/day)	21	177	680	330	550	172

[a] Mousa (2016), [b] Chen (2010), [c] NatureWorks LLC (2011)

et al. 2012). Biopolymers can be manufactured from two different systems. First, from biological systems such as plants, microorganisms, and animals. Second, chemically synthesized from biological materials such as natural fats or oils, sugars, and starch. These raw materials can be produced into biodegradable polymers through two approaches: the first approach is by the extraction of native polymer from plant or animal tissue, and the second approach is through chemical or biotechnological monomer polymerization (Flieger et al. 2003). Figure 3 schematically illustrates the variety of biodegradable plastics. Table 6 displays the properties of commonly used biodegradable polymers.

4.1 Types of Biopolymers

4.1.1 Poly (Lactic) Acid (PLA)

A lot of research has been conducted on the biodegradable polymers, especially on Poly (lactic) acid (PLA) which is made from renewable resources. The fermentation of feedstock from crops such as corn and sugarcane will produce Lactide and lactic acid monomers. The two-step ring-opening polymerization of lactide is the most popular approach to produce the high molecular weight of PLA (greater than 100,000 Da), which has expanded its uses. In 2002, *Cargill Dow* used about 300 million USD to begin mass-producing its new PLA-based plastic under the trade name NatureWorks™ (Flieger et al. 2003).

The production of PLA presents numerous advantages: it is obtained from a renewable agricultural source (corn), its production utilizes carbon dioxide and provides significant energy savings, it is recyclable and compostable (under the right conditions), as well as its physical and mechanical properties can be manipulated through polymer architecture (Auras 2004).

Motivating factors such as the increased availability of PLA and growing petroleum costs have led to the production of PLA-based biocomposites that can compete with the petroleum-based plastics that are available in the market. PLA is a good candidate for packaging applications because of its good mechanical properties, transparency, and biodegradability, resistance to fats and oil and its renewable resources. It resembles polystyrene in some of its properties.

However, it also has some shortcomings: a low heat distortion temperature makes the application for hot food impractical, brittle and has low impact strength, low viscosity, low thermal stability, high moisture sensitivity, medium gas barrier properties, high cost (compared with PE, PP, PS) and a low solvent resistance (e.g., against water) of the pure polymer can render its suitability for many applications. A drawback of processing PLA in the molten state is its tendency to undergo thermal degradation, which influences its process temperature and the residence time in the extruder and hot runner. This affects the recyclability of PLA (Hamad 2011). Several reports have shown that PLA is thermally unstable above its melting temperature. The presence of moisture has a particularly significant effect at higher temperatures as it induces hydrolysis. Thus, care has to be taken to ensure that PLA does not undergo degradation during processing. Drying the samples before use or processing them under nitrogen atmosphere is recommended (Smith 2005).

4.1.2 Polyhydroxyalkanoates (PHA)

Polyhydroxyalkanoates (PHA) can be manufactured by bacterial fermentation from renewable natural sources such as sugar or lipids. Interestingly, the bacterium

Ralstonia eutropha converts sugar directly into PHA plastic (Flieger et al. 2003). PHAs also known as the most attractive and largest groups of biopolyesters. It has more than 150 different types of monomer composition with different properties and functionalities (Chanprateep 2010). Due to its wide range of industrially useful properties, PHA has a potential to be used in both performance and commodity applications.

In terms of the processing method, PHA plastics can be processed using conventional processes, such as extrusion, moulded or coated onto other substrates using conventional processing equipment. Furthermore, the PHA can also be produced in a latex form as well as in dry powders. PHA has been used in many applications such as, such as packaging materials, fast food service ware, disposable diapers, single-use medical devices and paints due to the superior properties of the PHA (Flieger et al. 2003).

Poly-3-hydroxybutyrate (PHB) is the most common type of PHA and it has properties comparable to those of polypropylene. Due to the biocompatibility and nontoxicity of PHB, it can be implanted in the body without causing inflammations. However, PHB has several limitations, including its brittleness, it is stiffer and has narrow thermal processing window, which have limit its used in medical applications. Several properties of PHA and PHB are they can biodegraded in microbially active environments within 5–6 weeks (Flieger et al. 2003). They also can be either thermoplastic or elastomeric materials. Poly (hydroxybutyrate–valerate) (PHBV) is a PHB-like copolymer and *Monsanto Company* is known the sole manufacturer of PHBV under the trade name Biopol™. PHBV has a properties such as less stiff and tougher, and it is normally used for packaging applications.

4.1.3 Poly (Butylene Succinate), (PBS)

Polybutylene succinate (PBS) or also known as polytetramethylene succinate is a thermoplastic resin that is biodegradable from a polyester family with properties that are similar to polypropylene. It comprises of polymerised units of butylene succinate, with repeating $C_8H_{12}O_4$ units. There are two main methods of PBS synthesis. The first one is via the trans-esterification process (from succinate diesters) and the second one is direct esterification process starting from the diacid. However, the most common way to synthesise PBS is via direct esterification of succinic acid with 1,4-butanediol that consists of two steps of a continuous process (Jacquel et al. 2011).

The melting temperature and heat distortion temperature of PBS is about 115 and 97 °C, respectively. The tensile yield strength of unoriented specimens is comparable to that of polypropylene, which is about 30–35 MPa. PBS with Young's Modulus of 300–350 MPa is a flexible material depending on the degree of crystallinity. Sensitivity to water content, the content of residual carboxylic acid terminals and the molecular structure of polymer chains are the factors that influenced the thermal stability of PBS. Thus, PBS pellets normally need to be dried under hot air prior to thermal processing. The drying process can reduce the water content to less than 0.1 % to avoid hydrolysis, which will happen at high temperatures with the trace of water. Furthermore, when the processing temperature of PBS exceeds 200 °C, a significant decrease of shear viscosity can be detected (Xu and Guo 2010).

The molecular weight of PBS mainly affect the suitability of its processing method. For extrusion and injection moulding, PBS with an M_w of less than 100,000 is suitable to be used. However, for the process which required high melt strength, such as film blowing and casting, PBS with higher M_w or long-chain branches is chosen to make sure the process is smooth. In the case of biodegradability, PBS and its copolymers are biodegradable in soil burial, lipase solution, water, compost and activated sludge. There are several factors that affect the biodegradation rate of PBS such as, its chemical structure, the degree of crystallinity, the biodegradation environment and specimen size. The hydrolysis of PBS at neutral pH without enzyme is slower than in enzymatic degradation (Xu and Guo 2010).

4.1.4 Polybutyrate (PBAT)

Polybutyrate (PBAT) or its common name for polybutyrate adipate terephthalate is classified as biodegradable random copolymer owing to its random structure that has a wide absence of structural order. Due to this reason, it cannot crystallize to any significant degree, which results in low modulus, and stiffness as well as large melting point. The drawback of PBAT is it has high toughness and flexibility but it will not be rigid and strong. This property makes it unsuitable to be used for application that requires strong and rigid properties.

However, the flexibility and toughness of PBAT makes it suitable to be blended with other biodegradable polymers that are very brittle but have high modulus and strength (Jiang et al. 2006). Its biodegradability may offer the blended copolymer materials that has a potential to replace the non-biodegradable standard plastics with environmentally friendly plastics that will be biodegraded in short duration of time. As long as it being flexible complements the other polymers and if both copolymers can degrade as well as the blended copolymer, PBAT may preserve biodegradability.

PBAT can be synthesised through the reaction of butylene adipate and dimethyl terephthalate (DMT) with 1,4-butanediol. Initially, the polyester are created by adding1,4-butanediol and adipic acid together. By using an excess of diol in the reaction, the chain lengths are kept low. After that, by using 1,4-butanediol, the polyester of DMT is created. In order to create the copolymer PBAT, the second polymer is used with the first reaction product. Then, using a transesterification catalyst with the over-abundance of 1,4-butanediol, this polyester will be added to the adipic acid polyester. This will results in a copolymer of the two previously prepared polymers. In brief, a catalyst functions to promote the transesterification of the polyesters of adipic acid and DMT to produce the random copolymer PBAT (Zhao et al. 2010).

In the marketing aspect, PBAT is used commercially as a fully biodegradable plastic. BASF's Ecoflex is a commercial PBAT indicated 90 % degradation after 80 days biodegradation. Basically, the main applications of PBAT are compostable plastic bags for gardening, cling wrap for food packaging, water resistant coatings as in paper cups and agricultural use. Due to the high flexibility and biodegradability of PBAT, it is also utilized as an additive that improves the rigidity of biodegradable plastics. By using this additive, it may provide flexibility to the plastics as well as maintaining the biodegradability of the produced blend. The PBAT also can be used as a component in antimicrobial films that can be utilized in food packaging. The advantage of this film is to inhibit bacterial growth to preserve food products safely (Bastarrachea et al. 2010).

4.1.5 Poly (Vinyl Alcohol) (PVA)

Poly (vinyl alcohol) (PVA) is a water-soluble polymer thermoplastic with 1, 2-diol or 1, 3-diol units that are reliant on the hydrolysis of poly (vinyl acetate). The content of 1, 2-diol units is reduced with the temperature reduction of vinyl acetate polymerization. There are several methods used to synthesize PVA, including the polymerization of metal compounds and the polyaldol condensation of acetaldehyde, followed by the saponification process. The polymerization of metal compounds produces PVA with a low molecular weight, while the polyadol condensation of acetyldehyde has only little success until now. However, the most popular method is by the polymerization of vinyl ester or ethers, followed by saponification or esterification.

The factors such as molecular weight and degree of hydrolysis affect the properties of PVA. The properties of PVA such as block and solvent resistance, and tensile strength will be improved with the increase in molecular weight and degree of hydrolysis, while flexibility, water sensitivity and solubility will be decreased. PVA has several advantages such as low cost, good mechanical performance, excellent barrier properties, resistance against organic solvents and water solubility (even in old water), thus it is suitable to be used in many applications, including textile products, food packaging, finishing adhesives, paper coating, and medical devices. The biocompatibility of PVA has also been widely investigated for the food industry and established to be a safe biopolymer product due to its apparent nontoxic characteristic (Mousa 2016).

5 Woven Natural Fibre Fabric Reinforced Biodegradable Composites

Composites consist of natural fiber fabric will directly affect the composite performance. This is because they probably comprise of various fiber types through yarn or fiber blending, have longer fiber length due to the requirements in yarn formation, have better control on the fiber alignment via processing (example: spinning and weaving), and may perhaps control fiber volume via yarn size (Foulk et al. 2006). Though short natural fibers are a potential reinforcement for biopolymers, their properties can differ significantly depending on the type, grade, harvest quality, processing method and age. However, cellulose-based fibers are being considered as a choice for polymer reinforcement due to the sustainability of the fiber source (native cellulose), and they offer a sufficient reproducibility of mechanical and fiber (e.g. diameter, stiffness, tenacity) characteristics (Bledzki 2009). The selection of reinforcing fibers is vital, as the fiber parameters will have a massive influence on the overall composite performance.

5.1 Processing of Woven Natural Fibre Fabric Reinforced Biodegradable Composites

For thermoplastic composites, compression moulding method is the common technique used to process the fabric preforms that are covered with polymer into the final product. The processes for thermoplastic composites have been proven that they can be successfully implemented for biodegradable polymers composites. Figure 4 displays the material routes, preform types and final moulding processes for aligned fiber thermoplastic composites.

For the structure of aligned fiber materials, there are two main classes for the distribution of fiber and matrix (defining the precosolidation level). The first class involved the unconsolidated ‘dry’ mixtures of polymers and reinforcing fibers such as commingled yarn. Commingled yarn is suitable for further processing to convert hybrid yarn into textile structures due to its flexibility. The advantage of this class is the textiles can be draped to a mould surface while cold. And this offers a better handling during isothermal processes. However, the disadvantages for this class are full impregnation and consolidation must take place in the final conversion process as well as an often-considerable material bulk that must be accommodated in the moulding process (Long 2005).

For the second class, it comprises of partially or fully preconsolidated sheet, such as, via film stacking and melt impregnation, which is consequently semi- or fully rigid. For woven natural fiber fabric reinforced biodegradable composites, film stacking (Nurul Fazita 2013, 2014; Porras and Maranon 2012; Lee 2010) and solvent impregnation (Huang and Netravali 2007) methods are commonly used. The film staking method was among the most favorable composite production

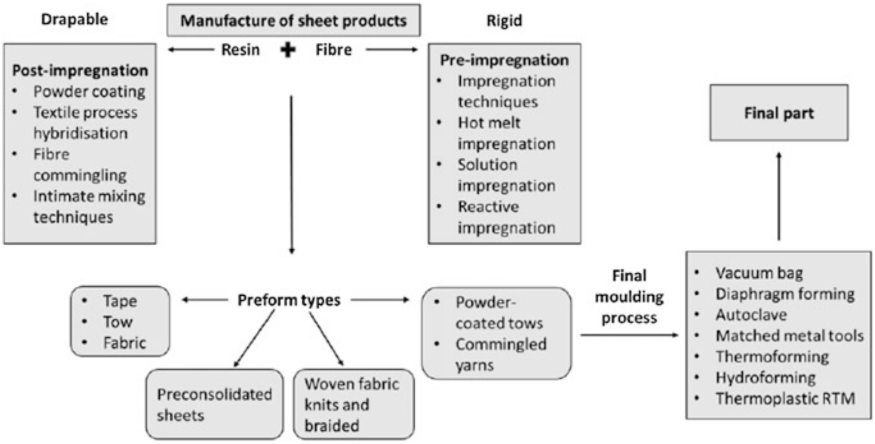

Fig. 4 Material routes, preform types and final moulding processes for aligned fibre biodegradable polymer composites (Long 2005)

technique as it showed a significant improvement of physical properties as compared to other composite fabrication technique. The film stacking method will supports handling for non-isothermal processes where heating happen in the initial step followed by transfer to the cool moulding tool, but hinders the use of isothermal conversion processes because in the cold material state, the material cannot be conformed to the tool (Long 2005).

A reduction in melt viscosity occurs as a biodegradable polymer is heated above the melting temperature. Thus, this allows a wide range of biodegradable polymers to be used as matrix materials in textile composites with different thermal and mechanical properties. Normally, the biopolymers with low melting temperature are easy to process owing to drying and handling issues. Figure 5 shows the techniques that are used to impregnate the reinforcing textile structure with the matrix polymer. Various techniques have been adapted from the conventional thermoplastic to produce intimate fiber–biopolymer combinations, including solution impregnation, hot-melt impregnation, powder coating, reactive impregnation, fiber commingling and textile process hybridization (Long 2005).

In addition, various methods have been studied and employed as the final moulding process in order to prepare biodegradable polymer composites reinforced with fibrous biomass. Among all of the methods available, the compression moulding method is known as a common and economical consolidation technique. Several researches have been done to combine biodegradable polymer films with woven natural fiber fabric into composites by using the compression moulding method (Song 2012; Ben 2007; Lee 2010; Porras and Maranon 2012; Nurul Fazita et al. 2013). It employs one or more hydraulic presses and consolidates the prepreg stack between parallel platens, possibly using a picture frame mould to prevent resin flowing from the edges of the laminate. Compression moulding has several

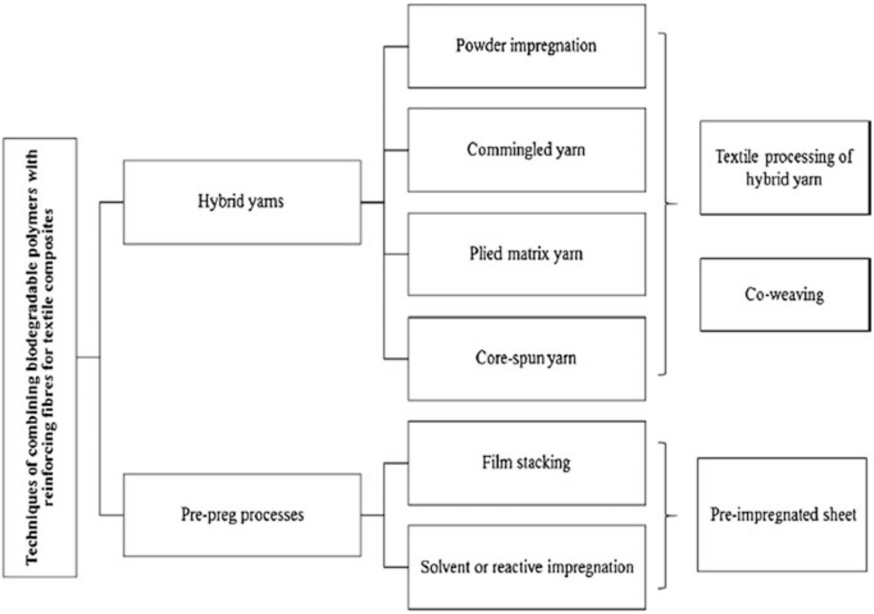

Fig. 5 Techniques of combining biodegradable polymers with reinforcing fibres for textile composites (Long 2005)

advantages, including production and labour costs are low than other manufacturing methods, small amount of material wasted during the manufacturing process, it is relatively low cost, and the most suitable method when dealing with thick sections, larger or more complicated parts, or parts that need a high degree of dimensional stability and accuracy. However, compression moulding may not be an option for delicate joints or more fragile shapes. Cryogenic deflashing may be used for deflashing process when the finished part is very small. Compression moulding is a manufacturing process appropriate to be used for the bulk production from the most simple to the very complicated, and from very small to relatively large parts.

5.2 Properties of Woven Natural Fibre Fabric Reinforced Biodegradable Composites

Woven fabric reinforced composites have several benefits, including more balanced properties in the fabric plane, good stability in jointly orthogonal warp and weft directions, subtle conformability, better impact resistance, higher toughness, exhibit better damage tolerance and easier handling in production (Chabba and Netravalli 2005). In recent years, fully biodegradable green composites composed of biodegradable polymers as a matrix and natural fibers as reinforcement particularly attracts attention due to their fully degradation, lightweight, and aesthetics. Many researchers have investigated natural fiber fabric such as hemp, flax, jute, kenaf, ramie, caraua, bamboo and mischanthus to be reinforced with biopolymers. Table 7 summarizes the natural fiber fabric reinforced biodegradable composites research papers available to date.

5.3 Applications of Woven Natural Fiber Fabric Reinforced Biodegradable Composite

5.3.1 Automotive Applications

The use of short fibres (Zah et al. 2007), nonwoven (Thilagavathi et al. 2010; Holbery and Houston 2006) and woven (Cristaldi et al. 2010; Holbery and Houston 2006; Cengiz and Babalık 2009; Alves et al. 2010) natural fiber fabric in automotive applications have been widely studied. However, previously, most of the studies used petroleum-based polymers, which are not biodegradable as a matrix. Currently, more researches have been conducted to study the utilization of woven natural fiber fabric reinforced biodegradable composites as materials in automotive applications. A study was carried out by Rwawiire et al. (2015) by using biodegradable bark cloth reinforced green epoxy biocomposites for the potential application in interior automotive panels. The produced biocomposites had an average strength higher than the threshold strength required for car instrument or dashboard panels. This makes bark cloth reinforced green epoxy composites a potential material for interior automotive panels. Koronis et al. (2013) reported the utilization of natural fibers in short fibers as well as woven fibers fabric reinforced biopolymers by several main automotive manufacturers, such as BMW, Mercedes-Benz, Audi, Toyota, Mitsubishi and Ford. This is attributable to their effort to reduce the use of expensive carbon, glass and aramid fibers. Besides, owing to the lower density and cost of some natural fibers, the car's body can be lightened considerably. Therefore, natural fibers are widely used as reinforcement in composites for interior and exterior parts for numerous passenger and commercial vehicles.

5.3.2 Construction and Structural Applications

Bodros et al. (2007) has studied the use of flax fiber as a reinforced material in several biopolymers such as Mater-Bi® ZF03U/A, Bionolle PBS, Ecoflex PBAT, PLA, PLLA and PHB for structural applications. The comparison for their tensile properties were made with those of composites made out of polypropylene/natural fiber. The specific tensile properties of the PLLA/flax biocomposite were also compared to those of flax or glass unsaturated polyester composites. They have

Table 7 Mechanical properties of natural fibre fabric-biopolymer composites

Natural fiber fabric	Biopolymers	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	References
Jute fabric	Biopol	–	–	–	–	Mohanty et al. (2000)
Flax fabric	Soy protein resin	54.6	0.99	22.6	0.75	Huang (2007)
Jute fabric	Poly(butylene succinate) (PBS)	–	–	–	–	Liu et al. (2009)
Flax non-woven	polyhydroxybutyrate (PHB) and its copolymer with hydroxyvalerate (HV)	30	7	–	–	Barkoula et al. (2010)
Denim fabric	Poly (lactic) acid (PLA)	75	4.65	–	–	Lee (2010)
Twill and plain weave hemp fabric	Poly (lactic) acid (PLA)	68	3.5	–	–	Song (2012)
Bamboo fabric	Poly (lactic) acid (PLA)	77.58	1.75	149.34	–	Porras and Maranon (2012)
Woven and non-woven jute fabric	Soy resin	37.1	1.04	38.4	1.12	Behera et al. (2012)
Woven hemp fabric	Polyhydroxybutyrate (PHB)	–	–	–	–	Michel and Billington (2012)
Sterculia urens uniaxial fabric	Poly (lactic) acid (PLA)	18.9	2.02	–	–	Jayaramudu (2013)
Bamboo fabric	Poly (lactic) acid (PLA)	80.6	5.92	143	4.50	Nurul Fazita (2013, 2014)
Flax fabric	Polyhydroxybutyrate (PHB)					Kulma (2015)
Bark cloth extracted from *F. natalensis*	Biodegradable epoxy resin	33	3	153	3.1	Rwawiire (2015)

(continued)

Table 7 (continued)

Natural fiber fabric	Biopolymers	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	References
Lyocell-Hemp fabric	Poly (lactic) acid (PLA)	96.01	11.15	140	8.5	Baghaei and Skrifvars (2016)
Lyocell fabric	Poly (lactic) acid (PLA)	101.23	11.42	160	9.72	Baghaei and Skrifvars (2016)
Manicaria Saccifera palm fabric	Poly (lactic) acid (PLA)	68.45	4.89	133	3.94	Porras et al. (2016)
Plain weave flax fabric	Poly(Butylene Adipate-Co-Terephthalate) (PBAT)	30	–	12	–	Phongam et al. (2015)

concluded that PLLA/flax fiber biocomposite is a promising material to substitute a polyester/glass fiber laminate, the materials that are frequently used for structural applications. The other study on the use of natural fibers biodegradable composites was conducted by Dweib et al. (2004). Structural panels and unit beams for housing applications were made from soybean oil based resin and natural fibers such as, flax, cellulose, pulp, recycled paper, chicken feathers using vacuum assisted resin transfer molding (VARTM) technology. Flax and chicken feather were used in the form of nonwoven. The composites showed promising results to be used in building construction. They introduce many benefits such as desired ductility, high strength and stiffness to weight, fatigue resistance, survivability in severe weather conditions, and design flexibility. They also offer an important environmental advantage, which is renewable resources are used as a replacement for petroleum-based materials. Another interesting research on the use of woven natural fiber fabric reinforced biodegradable polymers for construction applications was published by Alm et al. (2009). They have produced an I-shaped beam made from woven jute fabric and soybean oil based resin using vacuum assisted resin transfer moulding (VARTM) method.

5.3.3 Packaging Applications

In the case of packaging applications, Nurul Fazita et al. (2014) has demonstrated the feasibility of bamboo fabric reinforced poly (lactic acid) to be used in packaging applications. Several functional properties related to packaging applications such as heat deflection temperature, impact resistance, thermal properties and water absorption had been tested on the composites. These properties were compared with polypropylene, one of the main materials used in the packaging industry. Another study related to packaging was carried out by Jayaramudu et al. (2013), focusing on the effect of fabric surface-treatments on the mechanical and thermal properties of the biocomposites in order to ascertain whether the PLA and *S. urens* fabric system could effectively be used for making biocomposites suitable for packaging applications. In their study, cellulose fabric *Sterculia urens* reinforced PLA matrix biocomposites were prepared by a two-roll mill. In brief, it was proven that the *S. urens* fabric reinforced biocomposites with excellent engineering properties has been produced and the biocomposites are useful for food packaging.

5.3.4 Biomedical Applications

The use of flax fabric in biomedical applications had been discussed by Kulma et al. (2015). In their work, the effect of modification on phenylpropanoid metabolism and establish the effectiveness of flax products from PHB-overexpressing plants for biomedical applications, mainly for wound dressing production has been studied. This study had been inspired by the development of flax genetics studies that provided a prospect to improve plant/fiber quality production. The common method used in the modern plant biotechnology is generation of transgenic organisms for both scientific and commercial purposes. The improvement in gene technologies and transformation techniques has led to the application of genetic engineering in basic and applied flax breeding research. Production of novel plant fibers, with better qualities such as longer, thinner, soft, resilient, etc. for composite and textile applications is expected with the help of a better knowledge on the advancement of cell wall. One of the advantages of the modification in plant cell wall is extractable fibers can be obtained easily. In this study, they have introduced polyhydroxybutyrate (PHB) synthesis genes into the flax genome. They have reported the positive effect of PHB—cellulose composite fiber-based wound dressings to heal human chronic wounds of venous etiology.

6 Conclusion and Future Perspective

The use of woven natural fiber fabric biodegradable composites in the industrial application provides challenges for researcher around the world to access the processing methods, performance, and quality of natural fiber fabric-biopolymer composites for use as materials in many applications. Natural fiber fabric has excellent mechanical properties compared to short natural fibers, which indicates that it may be a potential material for reinforcement in biodegradable polymers. Woven natural fiber fabric reinforced biodegradable composites are biodegradable, renewable, and recyclable; it may replace or reduce the use of man-made fibers in various applications. However, there are a few aspects that need to be addressed when using totally biodegradable composites, such as biodegradability issues, raw material cost, reproducibility of these composites' properties and their long life cycle, especially when they are utilized in automotive, structural and construction industries. Therefore, a lot of researches need to be carried out in order to assure that these biocomposites can be successfully used for the desired applications. Research areas such as the appropriate processing method and the feasibility of these biocomposites to be converted into anticipated products are essential. This chapter, therefore, focused on the processing and properties of the woven natural fiber fabric reinforced biodegradable composites in various applications. An essential point is whether these materials can be combined in the best way to reach the level of performance of their predecessors.

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Kenaf-Biocomposites: Manufacturing, Characterization, and Applications

Majid Niaz Akhtar, Abu Bakar Sulong, Muhammad Shahid Nazir, Khaliq Majeed, Mohd. Khairul Fadzly Radzi, Nur Farhani Ismail and Muhammad Rafi Raza

Abstract Given the environmental issues faced by the industry, the development of engineering products from natural resources has increased worldwide. The increasing demand for cost and weight reduction can be attained by sustainable manufacturing techniques. Kenaf plants are natural resources, which show high performance compared with other natural fibers. Kenaf fibers can be modified by physical and chemical methods. Kenaf polymer composites are fabricated via processing technologies based on thermoforming, thermoplastics, and thermosets. Thermoplastic processes, such as compression molding, pultrusion, extrusion, and solution blending, have been adapted but are limited to two-dimensional structures based on polymer composites. However, the thermoset processes include sheet molding and resin transfer molding techniques, which were also employed for the fabrication of kenaf polymer composites. Most of the recent work discussed Kenaf-Reinforced Composites (KRCs) prepared by compression molding. However, resin transfer molding has received attention because of its versatility. This chapter aimed to highlight and explore advance research related to the fabrication of kenaf polymer composites by various routes, as well as their physical and mechanical properties. A brief description of KRCs with different additives, fiber loadings, treatment, and polymers is also discussed. Furthermore, these KRCs with versatile mechanical properties may be used for construction, building materials,

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animal beds, corrosion resistance, marine, electrical, transportation, and automotive applications.

Keywords Natural fibers · Injection moulding · Compression moulding · Resin transfer moulding · Physical properties · Mechanical properties · Automation

1 Introduction

The rapid growing market urgently requires manufacturers to fabricate high quality parts, with lower prices and more practical sense for production with high volume and low cost composite systems (Rowell et al. 1997; Akbarzadeh and Sadeghi 2011; Jawaid and Khalil 2011). In recent years, renewable materials have attracted researchers because they are sustainable, economical, green, and abundant in nature. These materials are inexpensive, environmentally friendly, and have been used in various applications. The renewable material resources, also known as biomaterials or green materials, have become a commercial interest with importance. These biodegradable or environmentally satisfactory materials have enhanced interest over the past few decades because of environmental issues derived from the utilization of petroleum-based materials (Liu et al. 2007; Majeed et al. 2013; Majeed et al. 2015). The materials are reinforced from bast and core (Dehbari et al. 2014), as well as fibers of annual fiber crops, such as hemp (Pracella et al. 2006; Panthapulakkal and Sain 2007), flax (Bos et al. 2006; Angelov et al. 2007), jute (Karmaker and Youngquist 1996; Van den Oever and Snijder 2008; Oksman et al. 2009), sisal (Joseph et al. 1999; Fung et al. 2002, 2003), rice (Majeed et al. 2014; Arjmandi et al. 2015; Majeed et al. 2015) ramie (Feng et al. 2011), or kenaf (Rowell et al. 1999; Ismail et al. 2013), with thermoplastic polymers; these reinforced composites are used in a variety of fields such as plastic ware, aerospace, corrosion resistance, and automotive industries.

Natural fibers are mainly classified into three categories, namely, plant, animal, and mineral. Figure 1 shows the classification of plant, animal, and mineral fibers, respectively. Plant fibers include stems, leafs, wood, cereal straw, seed, fruit, and other grass fibers; these fibers are the most popular among the natural fibers. Plant fibers can also be used as reinforcement in fiber-reinforced composites. The structure and chemical composition of plant fibers is fairly complex and more complicated compared with those of other types of fibers. These natural plant fibers, such as jute, kenaf, and hemp, basically consist of cellulose, hemicelluloses, waxes, lignin, and several water-soluble compounds; lignin, cellulose, and hemicelluloses are the major constituents. Table 1 lists the typical properties of natural fibers.

Kenaf plants are composed of bast and core fibers, which have different properties. The bast and core fibers are typically different with respect to their chemical compositions. Table 1 shows the bast and core properties of kenaf plants (Razak et al. 2013). Among these types of natural fibers, kenaf fibers are widely used in various industrial applications because of their versatile properties. Kenaf fibers

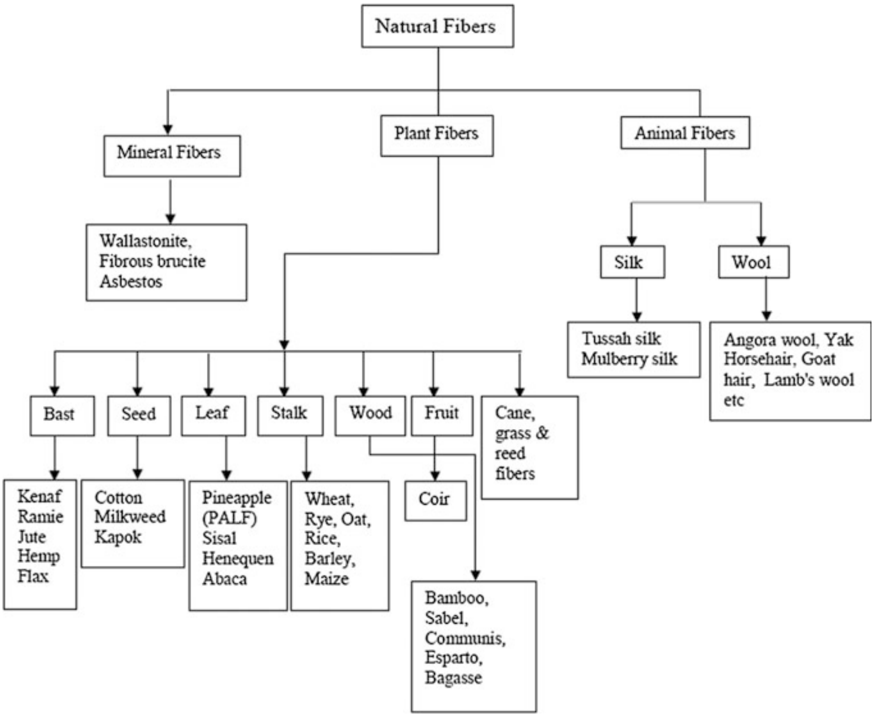


Fig. 1 Classification of plant, animal, and mineral fibers (Akil et al. 2011; Jawaid and Khalil 2011)

Table 1 Typical properties of natural plant fibers (Summerscales et al. 2010; Jawaid and Khalil 2011; Majeed et al. 2013; Mahjoub et al. 2014)

Fiber	Tensile strength (MPa)	Elastic modulus (GPa)	Specific modulus (E/1000 ρ)	Elongation at break (%)	Density (ρ) g/cm^3
Kenaf	240–600	14–38	12–32	1.6	1.45
Flax	500–1500	58	38	2.7–3.2	1.5
Jute	393–773	60	39	1.5–1.8	1.3
Hemp	690	70	46	2.0–4.0	1.47
Cotton	400	5.5–12.6	–	7.0–8.0	1.5–1.6
Carbon	4000	230–240	–	1.4–1.8	1.4
E-glass	3400	71	28	3.4	2.55

have several advantages in terms of their chemical composition, and these fibers have higher cellulose content, as depicted in Table 2. Generally, higher cellulose content can produced excellent mechanical properties of the end-product in terms of the tensile and flexural strength (Sosiati et al. 2014). Moreover, the combination of

Table 2 Chemical composition of kenaf plant (Razak et al. 2013)

Chemical compositions	Kenaf bast (%)	Kenaf core (%)
Cellulose	69	32
Lignin	3	25
Hemicellulose	27	41

higher tensile and flexural strength can make these fibers a better choice for molded, extruded, and non-woven products (Bajpai et al. 2012).

Jute plants are best cultivated in adequate water which exists in tropics and sub-tropics parts. In contrast to kenaf plants can grow inadequate water supply. Therefore, kenaf plants are successfully grown in tropical and subtropical countries such as Malaysia, China, Japan, South America, Mexico and in Europe (Karmakar et al. 2008; Akil et al. 2011). By 2050, the expected production of jute and kenaf should be three to four times higher than the present production rate because of their use in non-traditional diversified products. Researchers have already mentioned and explored various kenaf products; however, researchers also need to exert more effort to improve the quality fibers to strengthen the industry (Paridah et al. 2011).

Major areas in which kenaf fibers are used include the automotive and textile industry (requires both woven and non-woven); in bio-fuel for energy, bio-composites as eco-friendly materials; pulp and paper for packaging materials (Puglia et al. 2005) and also in house hold commodities. Kenaf fibers are compact lignocellulosic composite structure. This composite structure appears as multi cellulose layers fibril which fills the non cellulosic matrix. However, lignin is one of the most important non cellulosic parts of kenaf composite structure whose content will responsible for the change in physical and chemical properties and decide the intended applications (Chen et al. 2005). These characteristics of kenaf invite the researchers to produce diverse properties of fibers (Joshi et al. 2004).

Kenaf fibers have high tensile characteristics (breaking load and extension), high variations in length and diameter, large moisture-regain values, higher lignin and hemicellulose content, and lower cellulose content compared with flax and others fibers. Kenaf has a lower order of amorphous and crystalline regions than other natural fibers (Gindl and Keckes 2005). One of the attractive features of kenaf fibers is its fast growing rate from seed to 3–4 m-tall plants within five to six months. In addition, the fiber content, length, and orientation of kenaf fiber play an important role for suggesting its mechanical properties (Liu et al. 2007). Therefore, the preference of the industries for the use of kenaf compared with other natural fibers has continuously increased (Nimmo 2002). Moreover, polymer composites have been given much attention because of their use in numerous fields. These reinforced composites are inexpensive, light in weight, and can be easily fabricated/molded into the desired shapes.

Various researchers have found that natural fiber reinforced by thermoplastic and thermosetting composites produces better performance. Thus, treated and untreated (UT) fiber, strength of natural fiber in composites, growth condition, and manufacturing process may affect performance (Mehta et al. 2004; Rouison et al. 2004).

Table 3 The properties and characteristics of kenaf stems (Khalil et al. 2010)

Characteristics/properties	Bast	Core	Stem
Dimension (cm)			
Height (range)			1.45–2.50
Diameter		1.52 (0.09)	1.74 (0.212)
Perimeter		5.73 (0.131)	6.60 (0.101)
Proportion (%)			
Cross-section area	21.96 (2.03)	78.04 (2.51)	
Weight proportion	32.2	68.5	
Density (g cm^3)		0.21 (0.038)	0.29 (0.044)
Acidity (pH)	7.13	5.221	5.87

When successful extraction and modification of natural fibers will attained then it will be the best candidate to substitutes the glass fiber in reinforcement polymer composites (Glasser et al. 1999).

It has been reported that E-glass fiber shows the good mechanical properties as compared with natural fibers such as flax, jute, hemp and kenaf. Furthermore, the density of natural fibers at 1.2–1.5 g/cc is comparatively lower than of E-glass fiber at 2.5 g/cc but strength and specific modulus are significantly comparable (Clemons and Caulfield 2005; Mahjoub et al. 2014). A comparison of the typical properties of natural fibers is illustrated in Table 1; these properties include the density, tensile strength, elastic modulus, specific modulus, and elongation.

The reinforcement and orientation of semi-crystalline cellulose microfibrils that are embedded in hemicellulose–lignin matrices can be used to form the cell wall of the lignocellulosic fiber (Jonoobi et al. 2011). The properties and characteristics of kenaf stem are shown in Table 3. Based on the table, the kenaf stem height is 145–250 cm, whereas the core and stem diameters are 1.52 and 1.74 cm, respectively. The perimeters of the core and stem are 5.73 and 6.6 cm, respectively. A kenaf stem consists of the skin and core. However, the proportion of cross-sectional area of the skin is approximately 22 %, whereas that of the core is approximately 78 %. The density of the core and stem is 0.21 and 29 g/cm^3, respectively (Khalil et al. 2010).

2 Techniques for the Preparation of Natural Fiber Composites

Natural fiber-reinforced composites have been produced using conventional methods. These processing methods involve mixing, compounding, extrusion, compression molding, pultrusion, solution blending, filament winding, and resin transfer molding (RTM), injection molding among others.

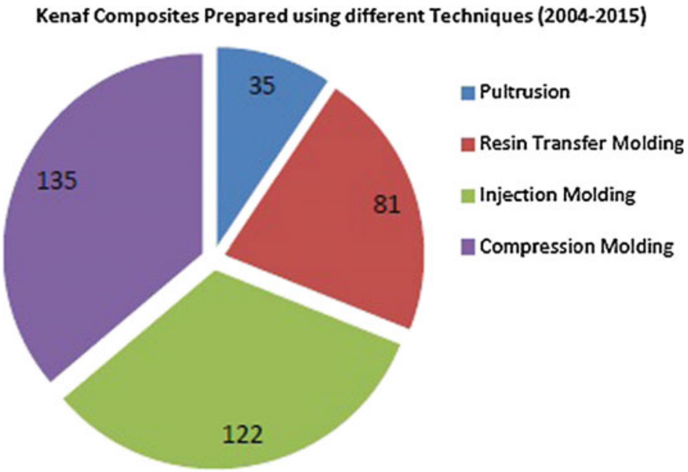


Fig. 2 KRCs prepared using pultrusion, RTM, injection molding, and compression molding (www.sciencedirect.com)

KRCs have been prepared using pultrusion, RTM, injection molding, and compression molding techniques. According to Science Direct sources, compression molding and injection molding techniques are commonly used for the preparation of kenaf-reinforced composites (KRCs). However, RTM is one of the most attractive techniques to date. Figure 2 shows the papers published from 2004 to 2015 about KRCs that used these techniques.

2.1 Processing Technologies for KRCs

Various techniques have been employed for the production of KRCs. Among these manufacturing techniques, compression molding, injection molding, pultrusion, and RTM have attracted researchers because of their improved production efficiency.

In the pultrusion method, fibers are usually pulled in a resin bath and heated. Fiber impregnation depends on the resin content and curing of fibers. Extrusion is the method of producing granules and components with single screws, twin screws, or counter rotators. For excellent mixing, twin screw extruders are used. By contrast, single screw extruders are only used for minimal mixing effects.

Compression and flow compression moldings are two of the most important methods for the production of KRCs. These methods use high pressure, moderate temperature, low cyclic time, and produce large objects that can be cut into the desired forms (Faruk et al. 2012).

The thermoset compression molding process uses kenaf fiber mats for the production of KRCs. Kenaf mats are sprayed in the resin system before compression in a hot press. Injection molding is a versatile method for fabricating complex geometric shapes within a very short time. The process has several advantages over other methods, such as its recyclability and large function integration, as well as less shrinkage and warping with no need for finishing of the end products. RTM is a technique that is used to make components from mat fibers with resin by changing the pressure in a closed vessel system.

Processing technologies for the production of kenaf polymer composites are based on thermoplastic matrices; these processes include compression molding, pultrusion, extrusion, and solution blending. All these processes are only limited to two-dimensional structures. However, thermoforming and thermoset techniques are also used for the fabrication of polymer composites. Thermoset processes, including sheet molding compounds and RTM, were also employed for the fabrication of kenaf polymer composites (Faruk et al. 2012). Moreover, some of these methods use continuous forms of the fibers for the fabrication of composites. The orientation of fibers and the high fiber content are important parameters for the stiffness and high strength of the composites (Nosbi et al. 2010). Kenaf fibers have been used in various fields, such as paper production, woven and non-woven textile industry, socks, and absorbed oil industrial applications (Akil et al. 2011). Kenaf core materials can also be used as animal bedding materials because of their water absorption characteristics (Lips et al. 2009). Kenaf fibers have attracted attention for their utilization in thermoplastic composites as reinforcing agents. Kenaf fibers have better mechanical strength and toughness, with a high aspect ratio. Moreover, a single kenaf fiber has a Young’s modulus of 60 GPa, which shows higher strength compared with other fibers (Karnani et al. 1997; Akil et al. 2011).

Injection molding technique is commonly utilized for the fabrication of different structures from thermoplastics. This well-known and established method is used for the fabrication of natural fiber-reinforced composites. Even distribution of fibers and the tensile properties of the green composite may successfully surge by this adopting method (Mohanty et al. 2004). However, the main concern of this method is the processing parameters, which can significantly affect the physical and mechanical properties of the injection-molded parts during mold filling (Rowell et al. 1997). The major drawback of the process is high fiber attrition and low processing temperature which is required to avoid the burning of fibers otherwise composite properties will may affect badly. Composite fabrication depends on: fiber content, viscosity and flow velocity of the matrix (Karmaker and Youngquist 1996).

Another critical problem concerning the fabrication of fiber-composites is the lack of interaction between fiber (polar) and matrix (non polar) which needs to be addressed. The introduced solutions include the addition of a coupling agent/compatibilizer to enhance the binding force between the polar HO- of cellulose fibers and the non-polar thermoplastic matrix. Where, this interaction may improve the binding and then it may enhance the swelling due to hydrophilic nature of composite, which results in decrease of dimensional stability (Rowell et al. 1999). In addition, alkaline treatment converts the HO-cellulose to NaO-cellulose (Rowell et al. 1986), decrease the permeability of fiber cell wall. Therefore, it may produce good wettability of the composite.

Compression molding is a conventional technique for the production of natural fiber polymer composites. Compression molding has been given much attention in the industry because of the ease and simplicity to produce kenaf-reinforced polymer matrix composites (Zampaloni et al. 2007; Akil et al. 2011). Notably, the orientation of the fibers is very important during the fabrication of kenaf composites. During fabrication, the fibers are very difficult to separate. Therefore, most researchers have changed their source fibers from long fibers to chopped fibers (Avella et al. 2008). KRCs prepared with chopped fibers have better structural, morphological, and mechanical properties compared with sandwiched layers with long fibers. Polypropylene (PP) powder mixed with chopped fibers produced better properties compared with other types of kenaf/PP composites that were produced by dry mixing or sandwiching layers with long and chopped fibers (Zampaloni et al. 2007).

Injection molding is also an important technique for the fabrication of natural fiber composites. KRCs have been fabricated using injection molding technique.

Kenaf/PP composites were fabricated by the carding and needle punching (modified compression molding) method. Thermogravimetric analysis (TGA), differential scanning calorimetry, and dynamic mechanical analysis were employed to investigate the thermal and mechanical behavior of the composites. The kenaf/PP-reinforced composites prepared at 230 °C and 120 s were found to show good correlation in mechanical and acoustic properties (Hao et al. 2013).

Kenaf fiber/high-density polyethylene composites were fabricated and characterized from a rheological and mechanical perspective. The effect of temperature on the fabricated composites was also studied. The loss and storage modulus, as well as the complex viscosity, increased with increasing temperature, whereas the mechanical loss factor decreased (Salleh et al. 2014).

Green composites of kenaf natural fiber were synthesized with the poly(furfuryl alcohol) bio resin. The inter phase and mechanical properties were investigated. With 20 wt% kenaf fiber loading, the green composites showed improved mechanical behaviors, such as the desired storage modulus, tensile strength, and flexural strength. The mechanical properties were also investigated after water absorption (Deka et al. 2013).

Composites reinforced by kenaf fibers with 20 vol.% thermoplastic elastomer were reported. PP, thermoplastic natural rubber (TPNR), and PP/ethylene–propylene–diene–monomer (EPDM) were used as modifiers. Maleic anhydride polypropylene (MAPP) was also used with treated kenaf as coupling agent. PP/TPNR resulted in higher tensile strength than PP/EPDM, whereas MAPP was also found as a significant coupling agent for the improvement of mechanical properties (Anuar and Zuraida 2011).

Kenaf fiber/polylactide (PL) composites were synthesized by the hot pressing method. The effect of the coupling agent silane was also investigated. The coupling agent increased the mechanical properties and decreased the swelling characteristics in the composites. No effects on the thermal properties were observed when these composites were incorporated in the polylactic acid (PLA) base polymer. However, FTIR results confirmed the reaction of silane with kenaf fibers. Therefore, these silane/kenaf PL composites greatly improved the mechanical properties (Lee et al. 2009).

Kenaf/PLA composites for biodegradable application were prepared using compression molding at 160 °C. Thermal analysis was conducted for kenaf fibers, whereas the mechanical properties were determined for kenaf/PLA composites. The tensile and flexural strengths of the kenaf/PLA composites were at 223 and 254 MPa, respectively. However, mechanical properties of the composites increased up to 50 % with increased kenaf fiber content (Ochi 2008).

The kenaf/poly-L-lactic acid (PLLA) composites were prepared and compared with conventional composites. Mechanical properties, such as the Young's modulus and tensile strength, for kenaf/PLLA composites were investigated. At 70 % kenaf fiber loading, the Young's modulus and tensile strength of the kenaf/PLLA composite were higher compared with those of the kenaf sheet or PLLA film. The effects of the orientation of kenaf fibers and molecular weight of PLLA on the mechanical properties were also studied (Nishino et al. 2003).

Kenaf/polyoxymethylene composites were prepared by compression molding and characterized. FTIR and EDAX (EDS mapping) were used to characterize treated and UT kenaf. The non-woven kenaf were chemically treated with the coupling agent zein. Chemically modified kenaf fibers had better visco elastic and mechanical properties. EDAX mapping results revealed surface modification of treated kenaf fibers (John et al. 2010).

Polymer–matrix composites can be produced by RTM (Pearce et al. 1998). RTM consists of four main steps; first, the reinforcement preform is cut and placed in a mold; when the resin has been formed, the catalyst is injected into the mold; after the mold is closed and sealed, the resin is allowed to hardened (Vanegas et al. 2013). RTM can be affected by several factors, such as the design of the mold, filling of the mold, and mold temperature. Composites produced by RTM involve several parameters. From these parameters, the process of filling the mold plays a significant role. The mold-filling process is related to the architecture and permeability of the preform, resin viscosity, injection pressure, resin temperature, location, and configuration of the doors, hole control, and preform placement techniques (Richardson and Zhang 2000).

Rassmann et al. (2011) investigated the mechanical properties and water absorption of non-woven kenaf fiber-reinforced laminates. The materials used in this experiment were kenaf fiber mats, unsaturated polyester resin, and accelerator stitch E. A two-piston apparatus connected to the arm, polyester resin, accelerator, and catalyst stitch E Andonox KP-9 (M-200 catalyst) were separately injected in a ratio of 1.5 % by weight. A static mixer was used to mix the resin and catalyst before pouring the mold. A fiber volume fraction of 15, 22.5, and 30 % was used to produce the layers. The mold temperature was 50–55 °C. The injection pressure was 250 kPa for the 15 and 22.5 % fiber volume fractions, which was increased to 350 kPa for the 30 % fiber volume fraction used to process the RTM (Rassmann et al. 2010).

2.2 Fiber–Matrix Interface

The mechanical properties of the fibers are mainly dependent on the chemical and physical modification of the existing bonds at the fiber ends. However, the interaction of the fiber with the polymer matrix also plays an important role toward improving the physical and mechanical properties of the composites (Summerscales et al. 2010). In addition, the use of coupling agents, such as MAPP, resin, and compatibilizers, can affect the strength of the composites, which can improve their performance. Natural fibers in polymers decrease the desired properties because of the incompatibility and lack of adhesion forces between polymers and fibers. Therefore, the treatment of the fibers and the introduction of a compatibilizer as a coupling agent can enhance the properties of these composites.

3 Properties of Kenaf Fiber-Reinforced Thermoplastic Composites

Some of the natural fiber composites are fabricated using different methods, in which the mechanical strength of the short fiber-reinforced composite mostly depended on the fiber content, fiber aspect ratio (L/D), compatibility of fiber-matrix, and fiber orientation. Feng et al. (2011) revealed that the contributions from (1) the high aspect ratio of the fiber distributed in the polymer matrix and (2) the good compatibility between fiber and polymer by adding a coupling agent or compatibilizer will allow the stress to be effectively transferred from the polymer to the stronger fibers.

Kenaf fibers, for example, have low density, excellent specific properties, a non-abrasive nature, and the ability to act a sustainable reinforcing fillers in plastic composites (Rowell et al. 1997). Several reports have discussed the thermoplastic polymers that are commonly used as a matrix to reinforce this natural fiber; these polymers include polyethylene (PE), PP, and PLA. Table 4 illustrates some parameters related to the thermoplastic polymers with kenaf fibers.

4 General Characterizations of Kenaf Fibers

The characteristics of kenaf fibers and their reinforced composites, such as the structural, mechanical, thermal, and microstructure properties, as well as mechanical testing, have been reported by various researchers. Therefore, an attempt has been made to accumulate their work to understand the properties according to their phase, morphological, and thermal properties. However, the tensile and flexural strength, as well as their corresponding modulus, are investigated to suggest future applications.

Table 4 Different parameters of Kenaf reinforced composites

Fiber/matrix	Method	Conditions	Properties	References
Kenaf/PP	Compression moulding	Kenaf/PP/3 % Epolene wax G-3015P (MAPP)	Highest mechanical (tensile and flexural strength) properties	Zampaloni et al. (2007)
Kenaf/PP	Compression moulding	Kenaf fibre, PP fibre or kenaf/PP blended + Chemically enzymatic treatment	Post treated kenaf fiber has 36 % higher flexural strength and 63 % higher flexural modulus than untreated one	Islam et al. (2011)
Kenaf/PLA/PHB	Compression moulding	40 mass% kenaf fibre-reinforced PLA and PHB	Kenaf PLA/PHB composites have highest flexural modulus, whereas Shore D hardness increased up to 73.1 for kenaf/PHB	Graupner and Müssig (2011)
Kenaf/Epoxy	Closed mould technique associated with vacuum system	48 vol.% kenaf fiber + Epoxy	Kenaf reinforced epoxy fibres composites enhanced the wear and frictional performance	Chin and Yousif (2009)
Kenaf/PP	Press forming	Eighteen layers of kenaf (0.1 mm diameter)	Flexural strength increased with decreased in density and PP fraction	Shibata et al. (2006)
Kenaf/polyester	Pultrusion technique	70 % Kenaf fiber + polyester resin	Diffusion coefficient (D) has highest value and maximum moisture content (Mm) value for sample immersed in distilled water	Nosbi et al. (2010)
Kenaf/PLA	Compression molding	Alkalization treated Kenaf short fiber with PLA	Effect of alkalization on the mechanical and thermal properties were studied	Huda et al. (2008)

4.1 Structural and Thermal Properties

The main factors, such as the composition, microfibril angle of plant contents, moisture contents, length, and diameter of the fibers, are strongly dependent on the chemical and physical properties of kenaf fibers.

XRD, TGA, and FTIR of kenaf fiber composites determined the structural, chemical, and physical properties of the kenaf composites.

XRD was used to visualize the crystallinity and treatment effects on the structure. Kenaf fibers were found to have a semi-crystalline structure; the amorphous and crystalline phases were observed at 16° and 22.5°, respectively. The intensity of the peaks increased from the raw kenaf fiber to the nanofiber, which showed the removal of hemicellulose and lignin. Similarly, FTIR and TGA results verified the removal of hemicellulose and lignin from the raw fibers to the nanofibers (Karimi et al. 2014). Figure 3 shows the XRD patterns of UT and alkali-treated (AT) kenaf fibers. The structures of UT and AT kenaf fibers were examined. The amorphous phase existed between 18° to 21°, whereas crystalline phase was detected at 22.5° (Nitta et al. 2013).

Kenaf core pulp (KCP) was used for the production of cellulose carbamate (CCs). Figure 4 displays the XRD patterns of KCP, the KCP membrane, the CC membranes of K/U with different concentrations: 0.9, 2.8, and 4.5 wt%, respectively. The sharp peaks at 22.2°, 14.7°, and 16.3° confirmed the presence of cellulose I, whereas the peaks at 12.2°, 19.8°, and 20.9° denoted the presence of cellulose II. Raw KCP showed higher crystallinity compared with the other regenerated kenaf samples. Figure 5 shows the FTIR spectra of KCP and K/U-4.5 wt% CCs. In the FTIR spectra, transmission peaks at 2904.19 and 1665.86–1626.12 cm^{-1} were observed, which can be attributed to the stretching of the N-H functional group and the stretching vibration of CO, respectively.

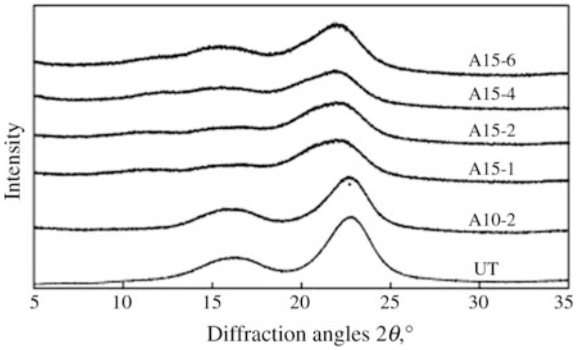


Fig. 3 XRD patterns of untreated (UT) and alkali-treated (AT) kenaf fibers (Nitta et al. 2013)

Fig. 4 XRD patterns of kenaf samples from (*a*) KCP, (*b*) regenerated K/U-4.5 wt%, (*c*) regenerated K/U-2.8 wt%, (*d*) regenerated K/U-0.9 wt%, and (*e*) regenerated KCP (Gan et al. 2014)

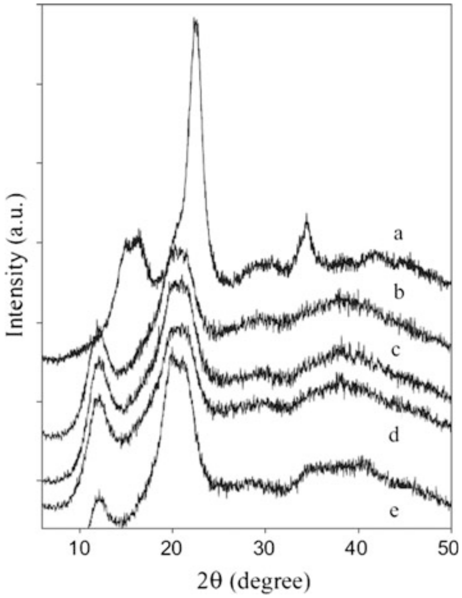
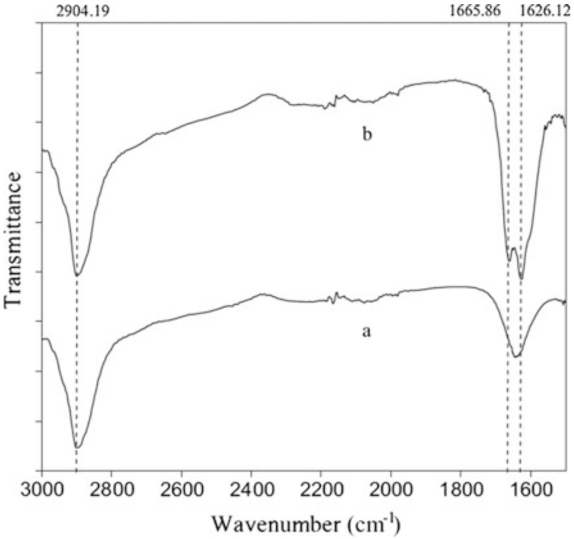


Fig. 5 FTIR spectra of kenaf samples from (*a*) KCP and (*b*) K/U-4.5 wt% CCs (Gan et al. 2014)



4.2 *Morphological Properties of Kenaf Fiber and KRCs*

The morphology, diameter, and length of the fibers affected the physical and mechanical properties. Alkaline and acid treatment of the fibers resulted in modifications that corresponded to the improved properties. The surface morphology of the treated fibers improved compared with that of the UT kenaf fibers. The kenaf fibers with 6 wt% NaOH had better properties than those with 3 wt% NaOH (Edeerozey et al. 2007).

AT and UT kenaf/PP composites were fabricated. Results showed that 5 % AT kenaf fibers were better than the 10 and 15 wt% AT kenaf fibers; this trend was attributed to the absence of any effects on the fiber texture of 5 wt% AT kenaf fibers (Mahjoub et al. 2014). Figure 6 show the SEM micrographs of an UT kenaf fiber and the kenaf fibers treated with 3, 6, and 9 % NaOH.

The kenaf fiber char (KFC) with and without acid treatment has been investigated (Mahmoud et al. 2012). KFC before treatment showed irregular and rough surfaces, whereas a highly heterogeneous honeycomb-like structure was found after acid treatment (Fig. 7) (Mahmoud et al. 2012).

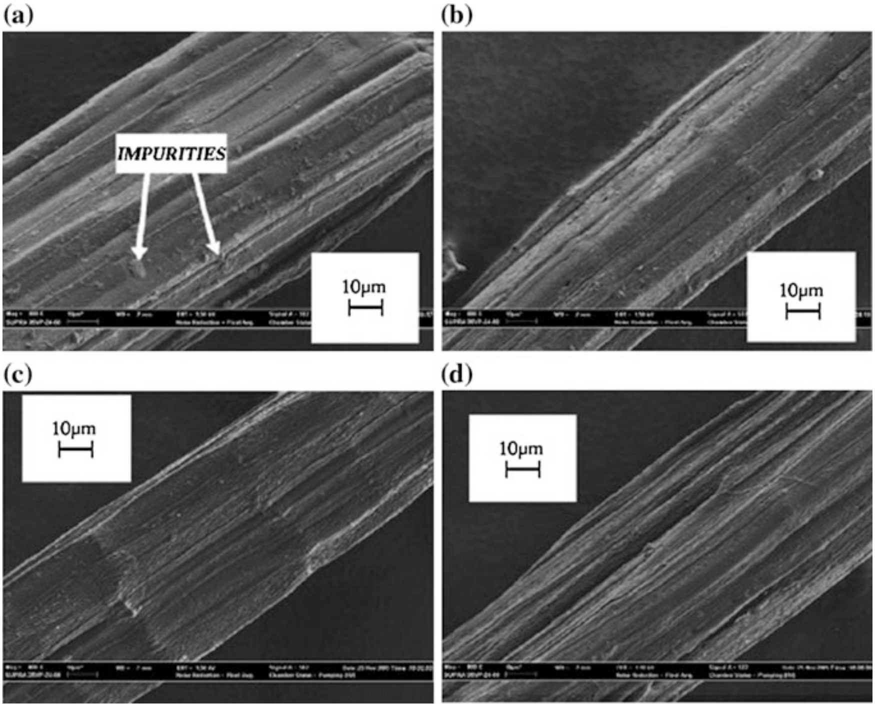


Fig. 6 SEM micrograph of **a** an untreated kenaf fiber and kenaf fibers treated with **b** 3 % **c** 6 %, and **d** 9 %NaOH (Edeerozey et al. 2007)

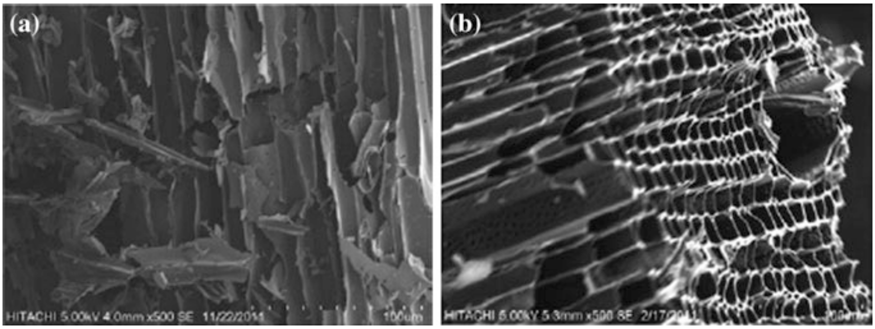


Fig. 7 SEM micrograph of KFC particle **a** before and **b** after treatment (H-KFC) (Mahmoud et al. 2012)

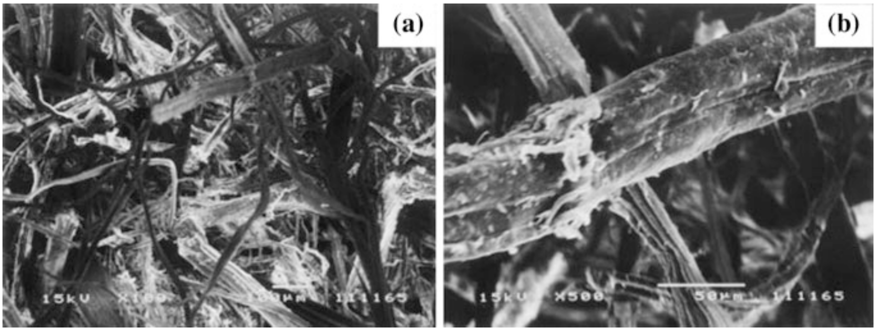


Fig. 8 SEM images of kenaf fibers at **a** 100× and **b** 500× (Pan et al. 2007)

Figure 8 represents the SEM images of kenaf fibers at different resolutions. The diameters of the fibers were found in the range of 5–50 mm. Figure 9 show the pure PLLA and PLLA/KF with different resolutions. The pure PLLA has a rough, fractured, and irregular surface. PLLA/KF composites also show fractured surfaces, which confirmed the brittleness of the composites. The authors explained that micrographs do not show complete information on the dispersion of fibers and their interactions with a polymer (Pan et al. 2007). Moreover, the variations in physical and mechanical properties may be attributed to the microstructures and removal of fibers from the polymer.

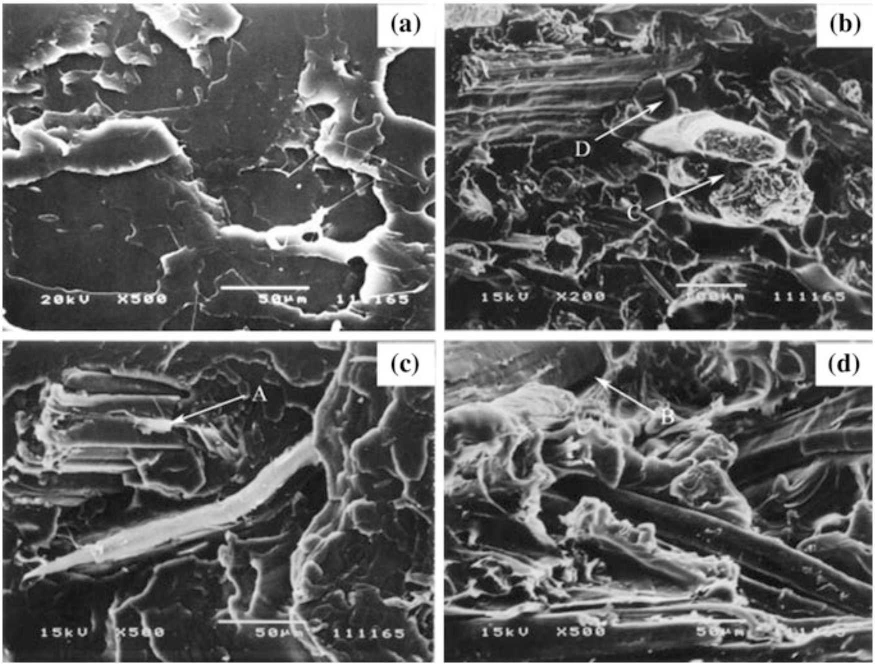


Fig. 9 SEM micrographs of the fracture surface of **a** pure PLLA and the PLLA/KF (70/30) composites: **b** 200×, **c** 500×, and **d** 500× (Pan et al. 2007)

4.3 Mechanical Properties of KRCs

The mechanical properties of the kenaf fiber composites are attractive to researchers and industries because of their applications in various fields. The tensile strength and corresponding modulus of kenaf single fibers are at 11.9 and 60 GPa, respectively (Chen and Porter 1994). To improve these mechanical properties, kenaf fibers were reinforced by various polymers. Thermoplastics such as PP or PE were used, whereas polybenzoxazine and polyester were used as thermosetting resins (Karnani et al. 1997; Aziz et al. 2005).

The proper selection of a processing method plays a major role in the fabrication of the end product. The various processing methods include injection molding, resin transfer molding, compression molding, and thermoforming. Among these methods, compression is commonly used in the fabrication of composite materials because of its low cycle time and high reproducibility. Given its simplicity, compression molding is widely used in the manufacturing of composites. This processing technique is used to fabricate polymer matrix composites under exact pressure and temperature (Groover 2007). In addition, this technique has advantages in terms of speed and fiber attrition. The compression technique can also reduce the changes in the physical properties and without changing the fiber orientation. Therefore, this technique can maintain the isotropic properties of the composites. Basically, the properties of the products are influenced by the molding conditions, such as the molding pressure and temperature. Therefore, the optimum pressure and temperature should be applied in processing to produce good products.

From previous reports it has been concluded that natural fiber composites could be fabricated using variety of ways to gain desire properties. Hossain et al. (2013) studied the flexural properties of epoxy composites fabricated with different processing techniques. Their results showed that the compression-molded composites produced high flexural strength. Therefore, their group concluded that the compression molding process is the best process compared with hand lay-up and vacuum-assisted resin infiltration. Davoodi et al. (2010) compared the tensile properties of kenaf reinforced with PP and epoxy. Their results showed that the epoxy composite has better strength than the PP composites. A study on the mechanical properties of polyurethane composite reinforced with kenaf fiber was conducted by El-Shekeil et al. (2011). Their group demonstrated that different kenaf fiber loading methods contributed different strengths.

Joseph et al. (2002) studied the effect of fiber length and loading on the flexural properties of formaldehyde/banana and formaldehyde/glass compression-molded composites. They found that both composites have increased tensile and flexural strength with increased fiber loading. The influence of fiber length on the impact strength was also investigated. Their group found that increasing the fiber length produced high impact strengths. Du et al. (2010) developed kenaf/polyester composite fibers by compression molding at different molding pressures. The water absorption, density, flexural strength, and impact properties of the composite were evaluated. From the evaluation, the impact, densities, flexural strength, and flexural modulus increased with increasing molding pressure.

The fabrication of kenaf composites with thermoplastic composites was developed by Bernard et al. (2011). Their group encountered the obstacle of having the fibers not uniformly distributed during fabrication. Therefore, their group studied the processing parameters of the compression-molded composite to produce better properties. From the results, the compression molding technique shows a strong bond between the fiber and polymer matrix. The improved properties with compression molding were supported by Liu et al. (2007). Their group also found that kenaf reinforced with polyester composite produced high impact strength compared with injection-molded composites.

The specific strength and corresponding modulus of glass and kenaf composites were investigated. Figure 10 shows the specific strength and specific modulus of kenaf and glass composites, with their respective tensile and flexural strengths. Kenaf composites had a lower specific modulus and strength than glass because glass had higher wettability than kenaf polymer composites. The orientation of fibers and the compatibility between the resin and fibers are the main factors affecting their properties, as suggested by the authors. In addition, the treatment of fibers may lead to better properties for their application in different fields (Westman et al. 2010).

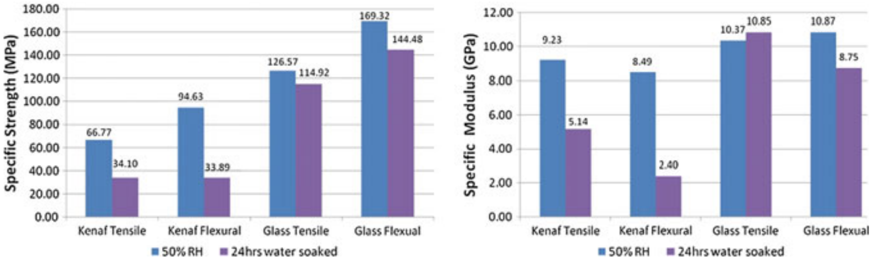


Fig. 10 Specific strength and specific modulus for kenaf and glass composites, with the respective tensile and flexural strength (Westman et al. 2010)

Several researchers have worked on bast fiber-reinforced PP composites by injection molding, but only a few studies presented high mechanical strength (Islam et al. 2012, 2013) as reported in this review. Among the earliest studies, Rowell et al. (1997) blended various types of natural fibers with PP and improved the specific tensile and flexural modulus properties of kenaf/PP composites (50 % by weight), which compared favorably with the glass fiber/PP (40 % by weight) of injection-molded composites. Short ramie fibers were reinforced in PP. Their injection into ramie/PP composites showed that the tensile (67 MPa) and flexural strength (80 MPa) increased when the ramie fiber content was increased up to 30 %. The modulus properties of ramie/PP composites increased significantly compared with those of pure PP as the fiber content increased (Feng et al. 2011). Yang et al. (2011) investigated the effects of different jute fiber contents on the tensile properties of jute/PP composites, and they found that the tensile modulus linearly increases with the increase in the jute fiber content. Meanwhile, the tensile strength initially increased but decreased after the jute content exceeded 30 wt%.

Kenaf bast fibers/thermoplastic polyurethane (TPU) was prepared by the melt-mixing compression molding technique. The influence of the kenaf fiber content was studied, with different loadings in the TPU matrix. Only 30 % of the kenaf fiber loadings showed better tensile and modulus strength compared with other kenaf/TPU composites. By increasing the fiber content in the TPU matrix, the tensile and flexural properties increased. However, the impact strength declined, whereas the hardness increased by the presence of 30 % kenaf fiber content. Furthermore, the tensile and flexural properties decreased in the 40 % kenaf/TPU composites. Figure 11 shows the effect of fiber loading on the tensile and flexural properties of kenaf/TPU composites (El-Shekeil et al. 2012).

KRC was fabricated by RTM. Polyester was used for the preparation of KRC. No fiber treatment was conducted to avoid additional costs. Laminated kenaf composites were fabricated and characterized. The flexural, tensile, and water absorption properties were investigated. The processing conditions exerted minimal effects compared with the pressure effect, which increased the flexural and tensile strength of the composites (Rassmann et al. 2010).

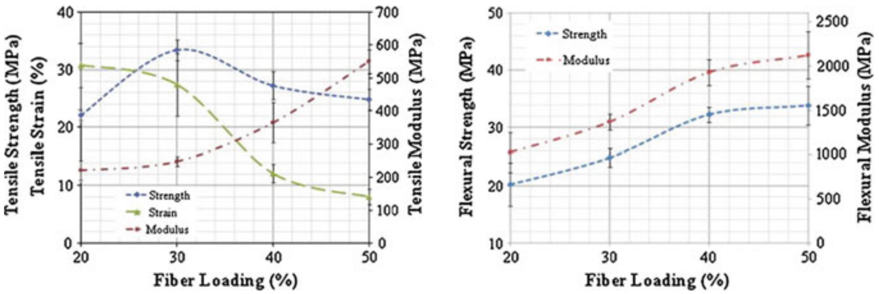


Fig. 11 Effect of fiber loading on the tensile and flexural properties of kenaf/TPU composites (El-Shekeil et al. 2012)

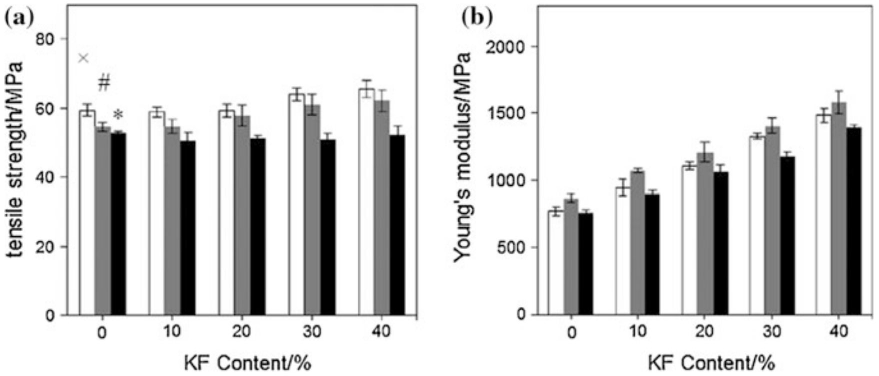


Fig. 12 Tensile properties of KF/PLA composites with (×) 0 %, (#) 5 % (w/w), and (*) 10 % (w/w) thymol. **a** Tensile strength (TS). **b** Young's modulus (E) (Tawakkal et al. 2014)

The major concern of the weak interface or attrition of the fiber matrix is the effect of alkaline treatment on the fiber surface, such as kenaf, abaca, oil palm, and ramie. Upon the removal of the intra-crystalline and inter-crystalline lignin and other surface waxy substances, the mechanical properties and chemical bonding substantially increased (Choi and Lee 2012; El-Shekeil et al. 2012; Meon et al. 2012; Sreenivasan et al. 2014).

Tawakkal et al. (2014) studied the tensile strength of the kenaf/PLA composites with different fiber loadings. Their group found that high fiber content was not fully wetted in the PLA matrix. However, a low fiber content was well distributed into the PLA matrix. They also added 5 and 10 % thymol to the kenaf/PLA composites (Fig. 12). No significant variation was observed in the tensile strength of kenaf/PLA without thymol and 5 % thymol, whereas variations were investigated for 10 % thymol addition in kenaf/PLA composites. This difference may be attributed to the insufficient amount of thymol in the kenaf/PLA composites. Mechanical properties may also decrease with the addition of 10 % thymol. This change was attributed to the influence of the thymol plasticizing effect in kenaf/PLA composites (Tawakkal et al. 2014).

Several researchers introduced MAPP to improve the fiber–matrix adhesion. Fung et al. (2002) showed that PP maleation functions as a coupling agent to improve the tensile strength of interfacial bonding by improving the high strength of the sisal/MAPP composites. Previous work was done on other fibers such as jute. Karmaker and Youngquist (1996) reported the reduction of fiber attrition by the esterification of the anhydride groups of MAPP with the hydroxyl groups from cellulosic fibers.

Anuar et al. (2011) used PLA as polymer matrix for the reinforcement of natural fiber composites. The high affinity of biodegradable thermoplastic has been incorporated with kenaf fibers into the PLA matrix. The tensile strength (74 MPa) of the injected samples was found to increase with up to 20 % kenaf content; this value was higher than that of pure PLA (Anuar et al. 2011). The obtained results were also better than those of flax/PLA (54 MPa at 30 %) and cordenka/PLA (58 MPa at 30 %) as investigated by Khalil et al. (2010), as well as of ramie/PLA (64 MPa–silane treatment, 67 MPa–NaOH treatment; at 30 %) (Islam et al. 2010) and hemp/PLA composites (60 MPa at 30 %) (Hu and Lim 2007). Further studies were performed on the combinations and comparisons regarding the surface treatment of natural fibers. Tran et al. (2014) produced biocomposites from reinforced PLA by treating the husk with alkaline (NaOH) and silane to reduce the resistance of interface bonding; thus, injection molded parts were achieved. Based on their results, when silane and alkaline treatment are combined, the synthesized biocomposites exhibit the highest mechanical properties compared with the absence of silane treatment. In addition, alkali treatment cleans the fiber surface and improves performance.

Sreekumar et al. (2007) fabricated natural fiber composites by RTM. Their group studied the mechanical properties of natural fiber/polyester composites with different fiber contents. As a function of fiber content, the tensile strength of natural fiber/polyester composites with 27 vol.% is 57 MPa, and the flexural strength is 76 MPa (Sreekumar et al. 2007). Rouison et al. (2006) studied the effect of the presence and absence of MEKP with different fiber contents. Their results showed that 1 wt% of MEKP had higher tensile strength and flexural strength compared with 1.5 wt% of MEKP (Table 5). In conclusion, 1.0 wt% MEKP was selected in this experiment. A fiber content of 35 % showed the optimum tensile and flexural strength. A comparative study of fibers with and without MEKP is shown in

Table 5 Mechanical properties of kenaf fibers with and without MEKP

Fiber contents (vol.%)	Additive (wt %)	Tensile strength (MPa)	Flexural strength (MPa)	References
43	Without MEKP	67	84	Sreekumar et al. (2007)
43	With MEKP (1 %)	57	76	Sreekumar et al. (2007)
20.6	Without MEKP	43	71	Rouison et al. (2006)
43	With MEKP (1.5 %)	45	71	Rouison et al. (2006)

Table 5 (Rouison et al. 2006). Table 6 shows a summary of the kenaf bast and core fiber composites prepared by different techniques. Details of the comparison of fiber type, polymer, additive, fiber treatment, fiber loading, and method of preparation are also discussed in Table 6.

5 Applications of KRCs

Renewable and sustainable reinforced composites have generally been applied in various fields, including automotive parts, sports, construction, and mass production industries. Therefore, KRCs with excellent properties can help produce components with various shapes. These KRCs have better physical and mechanical properties and can be used to fulfill the synthetic fiber component requirements in different fields of application and industrial requirements. A summary of applications for KRCs is provided in Table 7. In addition, these natural fibers have the advantage of providing a variety of jobs in urban and rural areas (Pothan et al. 2003; Majeed et al. 2013). Furthermore, the kenaf fiber composites helped to increase fuel efficiency, decrease wastage, and provide positive environmental effects (Faruk and Sain 2014).

6 Future Developments

KRCs have the tendency to show remarkable properties compared with other natural fibers for various reasons, which have been explained in our discussion. However, more investigations are still required to meet future demand and commercialization.

Table 6 Summary of kenaf bast and core fiber composites prepared by different techniques

Fiber type	Polymer matrix	Method preparation	Fibre loading (wt%)	Treatment	Additive	References
Kenaf bast	PLA	Dry blending, compression molding	30	Untreated	APP	Shukor et al. (2014)
Kenaf core (2 mm)	PLA	Compression molding	25	NaOH	APP, PEG	Shukor et al. (2014)
Kenaf core	PE/TPSS	Compression molding	10	Untreated	HNTs	Sarifuddin et al. (2014)
Kenaf core	LDPE/TPSS	Compression molding	40	Untreated	–	Sarifuddin et al. (2013)
Kenaf core	PVC/ENR	Compression molding	20 phr	Untreated	PE-g-MA	Majid et al. (2014)
Kenaf bast non-woven	PP	Compression molding	50	Untreated	–	Hao et al. (2013)
Core (<250 μm)	PLA	Hot press	15, 30, 50.70	Untreated	–	Dehbari et al. (2014)
Kenaf and Sisal	PP	Injection molding	15 and 30	Untreated	MAPP	Phiri et al. (2013)
Kenaf bast and core	PLA	Extrusion	–	NaOH	–	(Jaafar et al. 2013)
Kenaf bast (<500 μm)	PP	Injection molding	20	Untreated	APP	Ismail et al. (2013)
Kenaf core (60–80 mesh)	PP	Hot press	50	Untreated	MAPP	JANI (2012)
Kenaf bast 125–300 μm)	PU	Compression molding	20–50	Untreated	Bast	El-Shekeil et al. (2012)
Kenaf bast (2954 μm)	PLA	Injection molding	0–20	Untreated	–	Anuar et al. (2011)

(continued)

Table 6 (continued)

Fiber type	Polymer matrix	Method preparation	Fibre loading (wt%)	Treatment	Additive	References
Kenaf bast	PP-EPDM	Compression molding	–	Untreated	MAPP	Anuar and Zuraida (2011)
Kenaf chip (150 µm)	PP	Extrusion	40	Untreated	MAPP	Khalina et al. (2011)
Kenaf bast fibers	TPU	Compression molding	2, 4 and 6 %	Untreated	Polymeric methylene diphenyl diisocyanate (pMDI)	El-Shekeil et al. (2012)
Kenaf bast (300 mm)	PP	Compression molding	35.9 g	Untreated	–	Bernard et al. (2011)
Kenaf bast	Recycled PP	Injection molding	10–50	Untreated	MAPP	Ismail et al. (2010)
Kenaf and Wood	PP	Injection molding	0–60	Untreated	MAPP	Clemons and Sanadi (2007)
Kenaf chopped bast	PP	Compression molding	30, 40	Untreated	Epolene	Zampaloni et al. (2007)
Kenaf bast (1 mm)	PP	Injection molding	20–60	Untreated	MAPP	Rowell et al. (1999)
Kenaf bast (500 mm)	PLA	Hot press	0–70	Untreated	–	Ochi (2008)
Kenaf fibers	PP	Compression molding by film stacking method	40	Untreated	–	Wambua et al. (2003)

Table 7 Summary of the applications of Kenaf reinforced composites (KRC's)

Applications	Components	Technique	Description	References
Automotive parts	Seat backs, Armrests, Interior door panels, consoles	Pultruded, injection and compression molded kenaf composites		Faruk and Sain (2014), Akil et al. (2015)
Sports and others	Badminton and squash racket, kenaf mat (acoustic absorber and sound barrier), chairs, sunglasses, animal bedding	Pultruded, injection and compression molded kenaf composites		Akil et al. (2015)
Constructions nd building structures	Roofs, walls, designing https://www.pinterest.com/pin/183099541070956136/	Pultruded, injection and compression, resin transfer molded kenaf composites		Akil et al. (2015)
Marine	Boat, piers, docks, marine and marina structures	Pultruded, injection and compression, resin transfer molded kenaf composites		Akil et al. (2015)

(continued)

Table 7 (continued)

Applications	Components	Technique	Description	References
Electrical	Towers corrosion-resistance applications, cable tray support members and ladders transmission poles and electrical insulating qualities	Pultruded, injection and compression, resin transfer molded kenaf composites		Akil et al. (2015)
Transportation	Exterior paneling window masks, bus luggage racks, seats partitions, structural elements, and cargo containers	Pultruded, injection and compression, resin transfer molded kenaf composites		Akil et al. (2015)
Corrosion resistance	Stairs, ladders, walkways, fencing, drain and staging covers	Pultruded molded kenaf composites		Akil et al. (2015)

7 Conclusions

KRCs have attracted much attention from researchers and industries because of their specific and versatile properties. These composites have been prepared via the different techniques reported in this review. However, compression, injection, and RTM are common techniques used by researchers for the preparation of KRCs. To date, pultrusion is one of the most common methods used by industries for the commercialization of kenaf composites. KRCs have the potential to replace other synthetic fiber composites. In conclusion, KRCs are suitable replacement composite materials for construction, corrosion resistance, marine, electrical, and automotive industrial applications. KRCs are speculated to be suitable for numerous other applications and can fulfill the needs of daily life in the future.

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Mechanical and Thermal Properties of Polypropylene Reinforced with Doum Fiber: Impact of Fibrillization

Hamid Essabir, Mohammad Jawaid, Abou el kacem Qaiss and Rachid Bouhfid

Abstract Natural lignocellulosic materials have an excellent potential as thermoplastic reinforcement. In this study fibrillar doum fibers have been used as a dispersed phase in commodity thermoplastic matrices. Raw fiber was chemically treated with sodium hydroxide solutions and then fibrillated using physical treatments. The specimens were evaluated for structural, morphological, thermal and mechanical properties by infrared spectroscopy, scanning electron, thermogravemetric analysic and dynamical mechanical tests. The obtained results indicated that tensile strengths of the fibrillization treated composites enhanced 16.2 % as compared to 8.5 % for unfibrillar one due to improvement in the interfacial bonding. In addition, for strain at yield, the results are significantly higher than unfibrillar fiber composite, which demonstrated the effectiveness of the fibrillization treatment. At higher fiber content (16 wt%), the glass temperature values of the fibrillar composites are higher (87 °C) than that of unfibrillar composite (86 °C) and for unreinforced PP (78 °C) and it may be attributed to the higher interfacial adhesion in the fibrillar composite. The improvement of mechanical properties achieved, indicates the potential use of composites in many environmentally friendly industrial applications. Fibrillar doum fiber appears to be a good alternative to obtain ecological products.

Keywords Polymer-matrix composites (PMCs) · Mechanical testing · Thermal analysis

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1 Introduction

The composites materials have received extensive attention from both academia research and industry due to environmental issues pertaining to climate change and pollution (Wambua et al.2003; Nekhlaoui et al. 2014, 2015; Essabir et al. 2014, 2015a, b). In this context, the natural fiber reinforced composite has been in considerable demand owing to their lower density, renewability, lower energy requirements and coasts for processing (Nekhlaoui et al. 2014; Väntsi and Kärki 2014; Essabir et al. 2013a; Sahari et al. 2013). In addition, high cellulose component makes them biodegradable and recyclable. Natural fibers such as Coir, hemp, pine cone and Alfa etc. have been identified as the most promising and prospective candidates to replace synthetic fibers, due to their attractive properties such as good specific properties (low densities) (Malha et al. 2013; Santulli et al. 2005). Natural fibres mainly composed of hemicellulose and lignin and the reinforcement is cellulose fibrils. The cellulose fibrils are oriented at an angle named micro fibrillar angle. Generally, in a fiber composite material, the fiber content and fiber orientation determine the mechanical properties. Similarly, natural fibers, the physical properties of fibers depend strongly on the physical and chemical composition of fiber and their structure, percentage of cellulose micro fibril, degree and the section of polymerization (Arrakhiz et al. 2012a). On the other hand, the hydroxyl groups contained in the hemicelluloses, cellulose and lignin builds a large number of hydroxyl groups with the macromolecules of the polymer (Mwaikambo and Ansell 1999). The hydroxyl groups could form new hydrogen bonds with water molecules, which enhance the water absorption, fiber swelling, resulting a debonding of fibers and a poor interface of fiber-matrix (Xiang et al. 2014). To overcome this incompatibility between hydrophilic fibers and hydrophobic polymer matrix, different chemical and physical techniques was employed. Some of them are chemical treatment as: acetylation (Mwaikambo and Ansell 1999), silane treatment (Lee and Wang 2006) or a simple chemical treatment can be used to reduce the hydrophilicity of the fiber by removing non cellulosic compound to promote better interfacial adhesion (Mahjoub et al. 2014; Arrakhiz et al. 2012b). However, it has been reported in many studies that the physical treatments such Stretching (Rongzhi et al. 1997; Botaro et al. 2005), calendaring (Maldas and Kokta 1989) and thermal treatment (Rider and Arnott 2000) may also make the fibers' surface hydrophilic or hydrophobic through changes in surface energy (Rongzhi et al. 1997). Good fiber-matrix adhesion allows an improved load transfer throughout the composite and will largely determine the mechanical efficiency of the composite (Kakou et al. 2014, 2015).

These natural fibers are bundles of individual strands of fibers held together by means of pectin and lignin as matrix (Arrakhiz et al. 2012a; Essabir et al. 2013b). Chemical treatment is done to remove the impurities like waxes, pectin, hemicelluloses and lignin (Arrakhiz et al. 2012c, 2013a, b, c), whilst individualization of the fibrillar strands is done by using mechanical shear force with the help of cryocrushing and high-pressure fibrillization. These micro fibrillar strands could contribute towards producing composite materials of very high strength at a low cost in an environmentally friendly manner suitable for high strength structural applications.

This chapter reports the preparation and characterization Doum fibers reinforced PP composites. Doum fibers are defibrillated and alkali treated. The alkali treatment has been selected as chemical method to purify the fiber's surface which leads to reduction of the hydrophilicity of the fiber in order to improve interfacial bonding between fibers and matrix. Unfibrillar and fibrillar Doum fibers were used as reinforcement phase into polymer (PP), using in each case a fiber content ranging from 2 to 16 wt%. Thus, the objective of this study is to prepare composite materials using unfibrillar and fibrillar treated Doum fiber and polypropylene. The effect of fiber content and fibrillation treatments on the tensile, rheological and thermal properties of materials composites is also reported.

2 Problematic

Most of the polymers are hydrophobic in nature, and thus good adhesion between fiber and polymers is the most important issue in achieving desired properties of the matrix. In addition, interface in composites plays key role in transferring the stress through the fibers to matrix. There are several ways to improve the interfacial adhesion between fibers and matrix (Qaiss et al. 2014, 2015a, b). For example, fibers surface can be treated with different functionalized monomers that act as coupling agents to matrix, or functionalized polymer matrix can also be used (El mechtali et al. 2015; Qaiss et al. 2014, 2015a, b). In addition to the surface treatment of fibers, the use of a compatibilizer or coupling agents can also improve the effective stress transfer across the interface (El mechtali et al. 2015; Qaiss et al. 2014, 2015a, b; Essabir et al. 2016; Kakou et al. 2014, 2015).

3 Doum Fibers

Currently natural fibers are highly appraised, as being cheap, renewable, abundant and simply recyclable (Qaiss et al. 2014, 2015a, b) substitutes of other non recyclable fibers replaced by such as Coco fiber (Essabir et al. 2016), hemp (Elkhaoulani et al. 2013), and Alfa fibers (Arrakhiz et al. 2012b). Among them doum palm (Chamaerops humilis, belongs to the family of monocots) a viable cellulosic source, economically viable and ecologically friendly fast-growing plant requiring only few treatments during growth. The doum palm (Chamaerops humilis) belongs to the family of monocots, such as date palm, Musaceae (banana), grasses. The used fibers are extracted from the petioles doum palm. The sheet is made up of petiole attached to the trunk which grows on the leaflet. Fiber Size obtained (length, diameter) depends on the type of shape, age and tree (Malha et al.

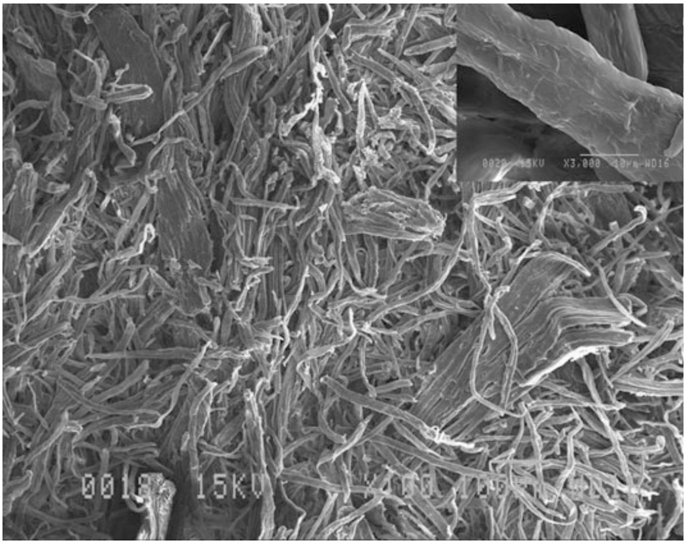


Fig. 1 Micro fibrillar doum morphology

2013). Fiber length obtained depends on the type of tree, shape, and age. The Moroccan Doum fibers are traditionally used in making ropes, canvas,

pulp, paper and lately for insulation and mats (Malha et al. 2013). Raw Doum fibers were gathered from rural areas of Morocco. The length of the doum fiber used was around 25 cm, and the diameter was around 2 cm (Malha et al. 2013). The individualization of the fibrillar strands was done by using mechanical shear force by cryocrushing and calendaring. Before further use doum fibers (Unfibrillar and micro fibrillar) were grinded using a precision grinder (FRITSCH Pulverisette 19) equipped with a 1 mm sieve size. Figure 1 shows the morphology, of the grinded fibrillar strands.

4 Doum Fibers Preparation

4.1 Physical Fibrillization

The technique used to fibrillization of doum fibers consists to individualization of the doum fibrillar strands using mechanical shear force by calendaring process (cryocrushing and high-pressure fibrillization). The calendaring system can be designed and constructed at the laboratory scale (Fig. 2). The system consists of two parallel cylinders with adjustable inter-axis and conjugated movement (Fig. 2). Adjusting the inter-axis and the crushing pressure of the fibers Doum is using system described in Fig. 2. The action of the pressure screw on the axis of the roller

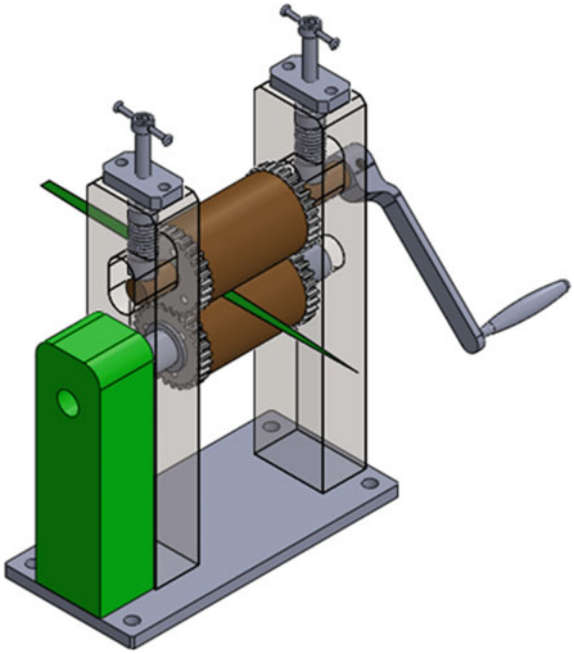


Fig. 2 The calendaring system

is made through the compression spring trapped between the two pads; it provides both the spacing and the adjustment of the fibers rolling pressure. Figure 1, shows the morphology of the fibrillar strands, the diameter distribution of the used fibers is based on 50 dimensioned measures.

4.2 Chemical Treatment

One of the most important problems with natural lingo cellulosic composites is the hydrophilic nature of these fibers, which is incompatible with the hydrophobic polymer matrix. By conducting a chemical treatment, the fiber/matrix adhesion may be enhanced, to remove a certain amount of lignin, waxes and oils that cover the external surface of fibers (Arrakhiz et al. 2012c). All fibers were alkali treated to clean their surface (Arrakhiz et al. 2012c). Crushed fibers are washed completely with water then immersed for 48 h in a 1.6 mol/l sodium hydroxide aqueous solution (Arrakhiz et al. 2012c). The fibers are then neutralized with acetic acid (100 ml), after fibers were dried in an oven at 100 °C to remove moisture.

Chemicals treatment used were sodium hydroxide (NaOH, 98 %) from Sigma-Aldrich (France) and Acetic acid (CH_3COOH, 99–100 %) which is from Riedel-de Haën.

4.3 Composites Processing

Compounding of green composites can be done via extrusion or mixing. Extrusion is a continuous process while mixing is a batch process. Among extrusion techniques, co-rotating twin screw extruders are commonly used for better compounding of green composites (Qaiss et al. 2014, 2015a, b).

Dried treated doum fibers (Unfibrillar and micro fibrillar) were initially compounded thoroughly with neat polypropylene granules at 2, 5, 10 and 16 wt% each. The composites were prepared using a twin screw extruder Leistritz ZSE-18 Twin screw extruder (LEISTRITZ EXTRUSIONSTECHNIK GMBH, Germany) with angular speed of at 125 rpm for polymer and 40 rpm for the fibers (Essabir et al. 2013b). The extruder barrel was heated from the hopper to the die respectively at 200, 200, 200, 200, 180, 180, 180, and 180 °C (Essabir et al. 2013b; Arrakhiz et al. 2013b). The extruded strands composites were cooled in a water bath and pelletized (Thermo Fisher, Stone, UK) into 2–3 mm long small pieces. Engel e-Victory injection molding machine was used to mold the specimens for tensile and rheological tests. The temperature from the barrel to the nozzle was set at 200, 200, 200 and 180 while the temperature mold was set at 45 °C (Arrakhiz et al. 2013b).

The polypropylene (thermoplastic polymer), used as a matrix material, was supplied by Exxon Mobil Chemical, with melting temperature of 165–171 °C and density of 0.9 g/cm^3, and melting temperature of 165–171 °C.

5 Doum Fibers Polypropylene Composites

5.1 Morphological Properties

For morphological characterization, all composites specimens were analyzed with scanning electron microscopy. To obtain clean and precise fracture faces, all composites samples were cryofractured under liquid nitrogen. (SEM) was used illustrate the fibrillar morphology of fibers and to investigate the fibers dispersion/distribution, degree of adhesion between polymer matrix.

The fibrillar-diameter distribution was determined microscopically at 50× magnification on Leica microscope supported with Leica QWin V3 analysis software. Approximately 50 measurements of the fiber diameter were taken. To investigate the interface of fibers and polymeric matrix after cryo-fracture in liquid nitrogen, the SEM was used. The SEM observations of the fractured surface of fibrillar doum/PP composites are presented in Fig. 3. These figures show a good interfacial adhesion between micro fiber and PP matrix by absence of fibers pull-outs. Figure 3 shows that the micro fibers were covered by the PP to a larger extent. The micro fibrillar stands average diameter were also examined, it was found that the diameter of these micro fibrils is only 5.38 μm (Fig. 3).

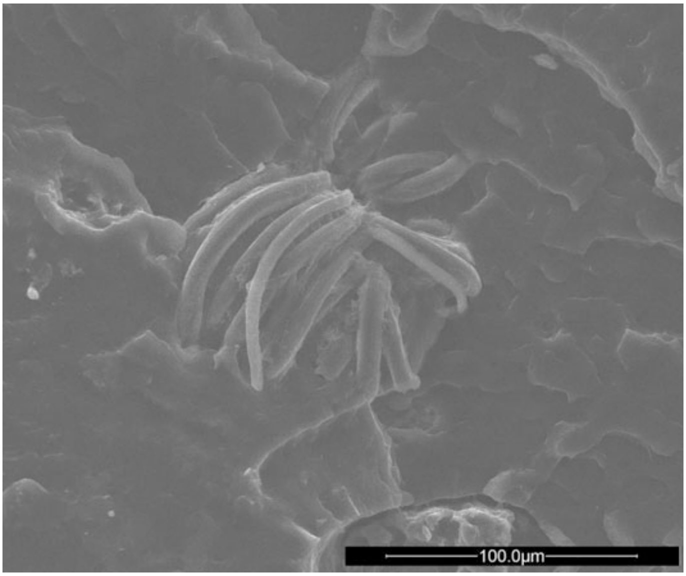


Fig. 3 SEM micrographs of PP/doum composite

5.2 Structural Characteristics of the Fibers

Fourier Transform-Infrared spectra were recorded on an *ABB Bomem FTLA 2000-102* spectrometer (ATR: SPECAC GOLDEN GATE). The spectra were obtained with an accumulation of 16 scans and with a resolution of 4 cm^{-1}. The transmittance range of the scan used was 500–4000 cm^{-1}.

The IR spectrum of untreated doum fibers indicates the absorption band of—OH stretching near 3479 cm^{-1} and C-H stretching vibration from CH and CH_2 in cellulose and hemicelluloses components at 2918–2840 cm^{-1} (Essabir et al. 2013a, b). The absorption band at 1730 cm^{-1} is attributed to carbonyl C=O stretching vibration of linkage of carboxylic acid in lignin or ester group in hemicelluloses (Essabir et al. 2013b). The band observed at 1380 cm^{-1} in the spectrum indicates the bending vibration of C-H and C-O groups of the aromatic ring in polysaccharides (Essabir et al. 2013c). The peaks at 1160 cm^{-1} correspond to the carbohydrate backbone of cellulose (Arrakhiz et al. 2013a) and the C–C ring breathing. The small peak showed at 720 cm^{-1} can be attributed to the presence of lignin (Arrakhiz et al. 2013a).

The alkali treatment of doum removed non cellulosic component from the fibers surface (Arrakhiz et al. 2013a) such as: pectin, amorphous materials, waxes. Also, during the fibrillization process it there an amount of non cellulosic compound removed at the micro fibrillar fibers, of the fact that, the natural fibers are composed of a plurality of micro fibrillar stands based on cellulose connected by lignin and hemicelluloses. The Fourier transforms infrared (FTIR) spectroscopic analysis of the untreated and treated doum (Fig. 3) confirms that, after alkali treatment it was shown a disappearance of the non cellulosic compound peaks (1730, 1463 and 720 cm^{-1}), also, the peak at 1027 cm^{-1} was increased after alkali treatment, this peak is assigned to the C-O and O-H groups stretching vibration which corresponds to polysaccharide in cellulose (Essabir et al. 2013c).

5.3 Thermal Stability

Thermogravimetric analysis (TGA) is the main tools that determine the thermal properties of natural fibre-reinforced polymer composites. The thermal degradation of PP, fibers and their composites was analyzed using TGA Q500 instrument from TA Instruments. Approximately 20 mg of each sample was placed in a platinum pan and heated under air from room temperature to 600 °C at a heating rate of 10 °C/min to yield the onset temperature of decomposition. The TGA results (Table 1) of unfibrillar fibers show two main degradation temperatures. The first peak is related to the degradation of hemicelluloses, pectin (250–320 °C) and cellulose (320–410 °C) (Essabir et al. 2013c), while the second degradation peak is observed beyond 410 °C and cold be due to the lignin degradation (Essabir et al. 2013b; Garside and Wyeth 2003). However, for fibrillar fiber the first peak at 326 °C is attributed to the hemicelluloses and pectin degradation, whilst the second at 405 °C is associated to the cellulose degradation. It was found absence of the lignin degradation peak in fibrillar fiber. The TGA results shows that the fibrillation process lowers the fibers thermal stability, by removing the remainder lignin between the micro fibrillar (in the fibrillar strands), which is less subject to thermal degradation by reason of its complex structure (Essabir et al. 2013c).

In the other hand, the maximum degradation temperature for neat PP was observed at 351 °C (Table 1). It was found in other study (Essabir et al. 2013b) that the use of unfibrillar Alkali doum fiber in polypropylene matrix enhance the thermal stability of PP and has reach 360, 367, and 380 °C when fibers were added into the polymer matrix at 10, 20 and 30 wt% content, respectively. From this results it can conclude that the use of fibrillar fiber can also enhanced the thermal stability of polypropylene.

Table 1 Comparative DTG results for the three systems: neat PP, unfibrillar and fibrillar alkali doum fibers

	Neat PP	Unfibrillar fiber	Fibrillar fiber
Temperature (°C)	351	320/420	324/405

5.4 Tensile Properties

Mechanical properties of natural fiber-reinforced polymer composites are commonly characterized using tensile, flexural, impact, and hardness tests. Those properties of various natural fiber polymer composites are described below.

Tensile tests were carried to measure the force necessary to break a sample. The tensile properties of each composites system were performed, using a universal testing machine INSTRON 8821S (Instron, USA). The tests were performed at a crosshead speed of 5 mm/min using a *5kN* load cell. The Young's modulus was calculated from stress-strain curve (linear region from the strain of 0.0005–0.0025 mm/mm ISO 527–1). The standard dimension was normalized according the norm ISO 527–1. For each composite system five specimens were tested and the average value was reported.

The ultimate Young's modulus, tensile strength and strain at yield are the main three properties evaluated during the tensile test. Those three properties of various natural fibre reinforced polymer composites are illustrated in the Fig. 4. Figure 4a shows the effect of fibrillization on the tensile strength of composite at various fiber content. From this figure it is shown that for two type of fiber, the tensile strength increased with fiber content from 2 to 16 wt%, compared to neat PP. It is noted that for two used fibers, the optimum tensile strength gains was observed in composites at 16 wt% fibers content. This increase can be explained by the high fiber-matrix adhesion. After alkali treatment non cellulosic compound, impurities and waxy substances from the fiber surface are removed, also the content of hemi-cellulose and lignin decreased, which lead to the increase in the effectiveness of orientated cellulose fibers and creation of a rougher topography at fiber surface (Bachtiar et al. 2008). These changes in the fiber surface lead to better interaction with matrix. On other side, from Fig. 4a it was observed that fibrillar doum fibers composite exhibit a higher tensile strength values than unifibrillar doum composites. The gain in term

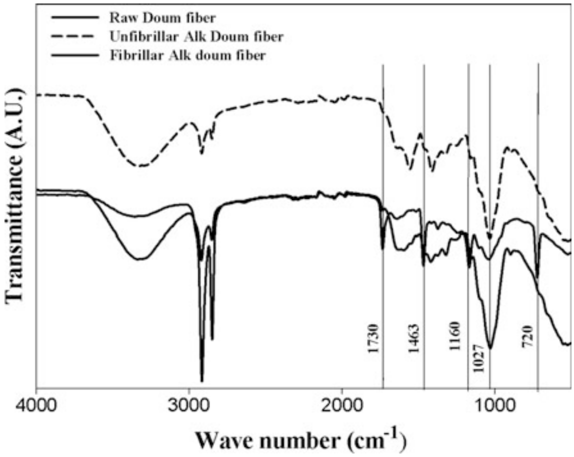


Fig. 4 FT-IR spectra of raw, unfibrillar alkali treated and fibrillar alkali treated doum fibers

of tensile strength is 16 % for the fibrillar doum/PP composite and 9 % for the unifibrillar doum/PP composite. After fibrillation the size of fiber becomes smaller (Fig. 1), thereby the aspect ratio and surface area of fibers increases, which led to the development of a rough surface that resulted in better interfacial bonding (the transfer of the load from matrix to fibers (Liu et al. 2004)).

Young's modulus corresponds to the degree of rigidity of the material. Figure 4b illustrates the effects of fibrillization and of fiber content on the young's modulus. Addition of fibers to matrix, yield an improvement in Young's modulus compared to neat PP. For all type of fibers, it was observed a linear increase in Young's modulus with addition of fiber content. This could be interpreted by the high stiffness of fibers. Another works (Essabir et al. 2013b; Boujmal et al. 2014) have found that the use of fibers as reinforcement improve significantly the mechanical properties, they considered that fibers mainly play an attractive role to enhance the stiffness of the prepared material by supporting the applied load (Arrakhiz et al. 2013a). From Fig. 4b, the young's modulus increased from a value of 1034 MPa for neat matrix to an optimum value of 1488 and 1386 MPa for fibrillar and unifibrillar fiber composites at 16 wt%, respectively. This corresponds to a gain of 44 and 34 % increase in young's modulus, respectively. These results can be explained by increase of fiber-matrix adhesion and specific surface.

Figure 4c shows a study of the ductility of composites during tensile tests from starting tests to elongation at break. For both composites it was seen that a linear decrease in the strain at yield from neat PP to 16wt% fiber content, which is normal that at higher fiber content, the composites become stiffer (higher young's modulus) and less ductile (lower plastic energy absorbed). These results are in agreement with other research (Essabir et al. 2013b).

5.5 Dynamic Mechanical Analysis

The dynamic mechanical tests properties were measured by using a Rheometer Solid Analysis (RSA), and due to the stiffness of the studies material a dual cantilever configuration was used as a fixture of RSA machine (Essabir et al. 2013b). The strain sweep test was performed at a frequency of 1 Hz. The frequency sweep test was ranged from 0.15 to 15 Hz, with a strain rate set at 0.0001 (taken from the linear region of the plot Modulus versus strain).

Dynamic mechanical analysis is a widely used tool for understanding the viscoelastic properties of the composite materials. The viscoelastic properties depend strongly on fiber-matrix adhesion, physicochemical properties of fiber and matrix, the distribution, dispersion, of fiber into matrix. Even a small change in these parameters for a given fiber or matrix can cause significant changes in the dynamic mechanical properties of global composites.

The dynamic mechanical properties are expressed as complex modulus (E*) and loss factor (tanδ). Figure 5 shows the effect o fiber content and applied frequency on complex modulus (E*) and loss factor (tanδ) of both composite. The complex

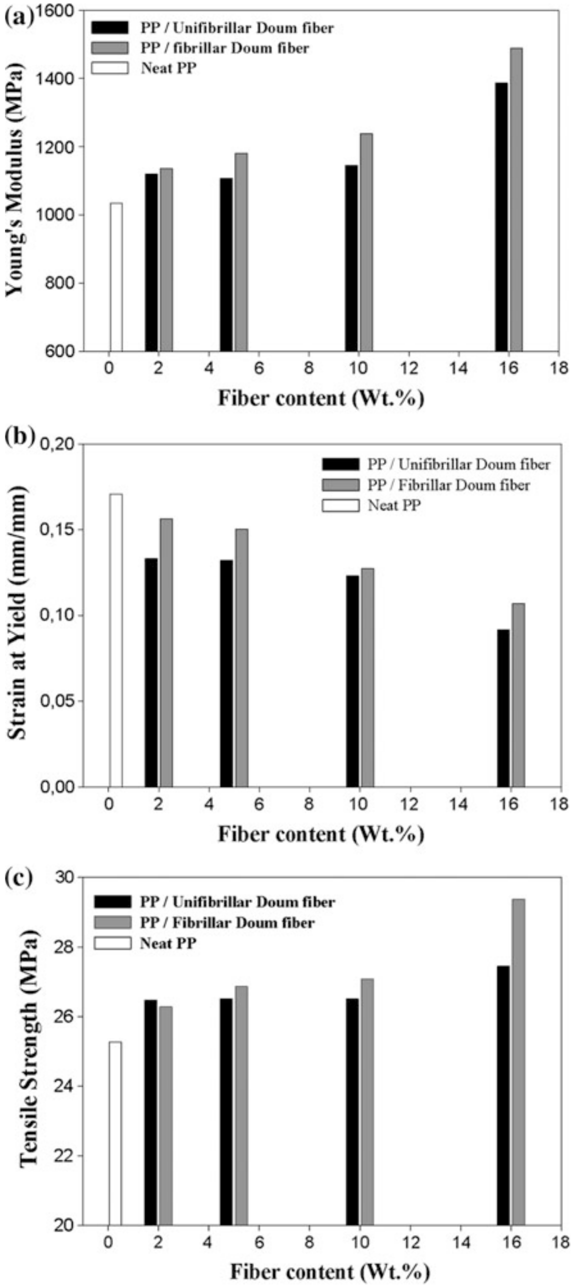


Fig. 5 PP/fibrillar doum and PP/unfibrillar doum composites **a** Young's modulus, **b** tensile strength, and **c** strain at yield

modulus values are found to be increased with increase in fiber content and in frequency. The increase in complex modulus with fiber incorporation indicates that PP matrix gets stiffened. This can be interpreted by the combination of the hydrodynamic and mechanical restraint effects of the fibers incorporated, at high concentrations, in the viscoelastic medium (matrix), which reduce the deformability of the matrix and the mobility of polymer chains (Sudhir et al. 2011). In the other hand, with increase in frequency, there is molecular rearrangement within the interface region and however, the increase of complex modulus values. The measurements performed over a short time (high frequency) result in higher values, whereas measurements performed over long times (low frequency) result in lower values as observed in Fig. 5a. The material undergoes molecular rearrangements in an attempt to minimize the localized stresses (Sudhir et al. 2011). At high frequencies the polymer chains have not enough time to relax; hence at lower frequency the polymer molecules chains will get enough time to attend permanent deformation (Essabir et al. 2013b, c). Figure 5b shows the variation of tanδ as function of fiber content and frequency. A change in the tanδ indicates a relaxation process and it is associated with the movement of small groups and chains of molecules within the polymer structure (Essabir et al. 2013b, c).

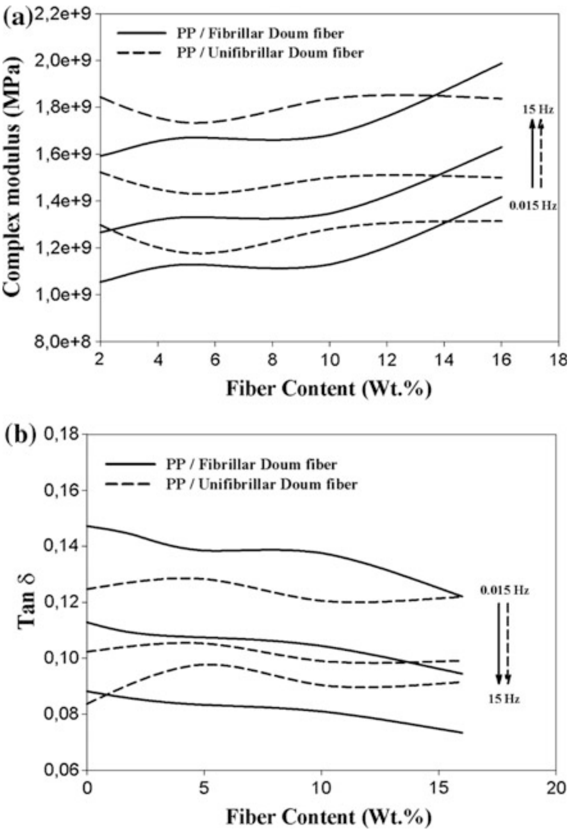
It was observed (Fig. 5b) that the loss factor (tanδ) of both composite systems decreased by incorporation of fibers and by increasing frequency. The addition of fibers in polymer matrix affects the damping behavior of composite.

This is mainly due to the formed stress between stiffer fibers and viscoelastic matrix, which lead to reduction in the additional power dissipation in the matrix material. At higher frequency it was found that the elastic character of the material prevails over a viscous behavior (Essabir et al. 2013b, c), however when the polymer molecules chains will get enough time to attend permanent deformation the viscous behavior prevails the elastic character of material.

The damping behavior of composites in the transition region depend strongly on mechanical polymer chain relaxation and fiber content, the fiber/matrix interface adhesion, fiber loading and fiber shape factor (Manikandan et al. 2001). The temperature at which the tanδ peak occurs is commonly known as the glass transition temperature (T*g*). At temperatures around T*g*, the polymer molecular chains have high flexibility, however the damping behavior of the composite is due primarily to the viscolelastic behavior of matrix (Manikandan et al. 2001). Tg temperature was evaluated from the derivative curves of tanδ versus temperature. The effect of fibers incorporation and fiber treatment on the T*g* is also indicated in Fig. 6. It was observed a shift of T*g* value of unfibrillar and fibrillar composite systems at 16 wt% fiber content (86 and 87 °C, respectively) compared to neat PP (78 °C). This is the fact of having more continuous domains (interface fiber-matrix) with the use of fibers.

The values of T*g* are found closely the same for unfibrillar composites compared to fibrillar one investigated in other work (Essabir et al. 2013b). The increase in T*g* is taken as a measure of the interfacial interaction. The fibrillar composite exhibits higher adhesion between fiber and matrix than unfibrillar composites. The high adhesion of fibrillar composite is in accordance with the tensile properties

Fig. 6 PP/fibrillar doum and PP/unfibrillar doum composites **a** complex modulus (E*) versus frequency and of fibers content, and **b** loss factor (tanδ) versus frequency and of fibers content



presented in Fig. 6. It is well known that the glass transition temperature is combined with conformational crank shafting movements of the main polymeric chain. So if a good distribution of fiber in matrix is occurred, the glass transition temperature increases and the mobility of polymeric chains decreases, which lead to an enhancement in the thermal stability of composites (Essabir et al. 2013b).

6 Conclusion

The composites were successfully prepared with different amounts of doum fibers (2, 4, 10, 16 wt%) by using an extrusion and injection process. Doum fibers were chemically (alkali) treated and defibrillated to obtain micro febrile fibers. Experimental studies have been conducted on the effect of fiber content and physical treatment (unfibrillar and fibrillar) on morphological, thermal, tensile properties and viscoelastic behavior of doum fiber reinforced polymer composites. From this study, it is noted that the tensile properties of polypropylene with the addition of improved fibers, particularly in the case of fibrillar fibers, this was due to the notable intrinsic interfacial adhesion between fiber and matrix. Fiber incorporation also increased the thermal stability of both composites system. The results from the dynamic mechanical analysis show that the incorporation of fibers improved both the complex modulus and glass temperature of composites. The results point to the composites potential in wider industrial applications. In recent years, there has been increasing number of green composite products in the market. It is expected that green composite market will continue to progress as long as tighter government environmental regulation around the world continues to influence corporate goals toward the use of more sustainable and environmentally friendly materials in their new product designs.

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Oil Palm Empty Fruit Bunch Fibres and Biopolymer Composites: Possible Effects of Moisture on the Elasticity, Fracture Properties and Reliability

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Abstract Oil palm (*Elaeis guineensis*) is a widely cultivated tropical tree from which the mesocarp (reddish pulp), a part of the fruit of the tree, is processed to yield edible vegetable oil. However, the process generates a significant amount of oil palm empty fruit bunch (OPEFB), which is regarded as a biowaste. Since the OPEFB contain a lot of fibres, this has led to several studies to investigate its properties for reinforcing engineering materials. Designating OPEFB fibres for fibre reinforced composite applications makes good economic sense because these fibres are renewable, biodegradable and cheaper than man-made fibres. This chapter discusses the mechanics of oil palm fibres based on findings from recent studies carried out by the authors as well as from the literature. The focus is on the effects of moisture on the mechanical properties of the fibres. The findings are applied to establish arguments for designing OPEFB fibre reinforced biopolymer composites such as starch-based composites.

Keywords Oil palm fibres · Biopolymers · Composites · Moisture content · Fracture properties · Reliability

1 Introduction

Oil palm (*Elaeis guineensis*) is grown in over 42 countries, on tens of millions of hectares of land (Tan et al. 2013). Each hectare of the oil palm plantation is estimated to yield a few tonnes of oil from the fruits. The fruits are removed from

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the fruit bunch by the application of steam treatment at high pressures (e.g. 294 kPa) over a period of time, e.g. 1 h (Raju et al. 2008). Consequently, this results in several tonnes of fibrous waste mass—known commonly as oil palm empty fruit bunch (OPEFB)—per hectare of the plantation (Tan et al. 2013). When the waste materials are inappropriately disposed (e.g. left in fields) they could pose severe environmental problems such as fouling as well as attracting pests (Sreekala et al. 1997). Thus it is environmentally and economically interesting to find new ways of recycling and using the OPEFB in added value products and particularly the fibres that are found on the OPEFB. OPEFB fibres are extracted from the empty fruit bunches by the process of water retting (Raju et al. 2008). The retting process involves micro-organisms and moisture for dissolving the cellular tissues and pectin impregnated bast-fibre bundles (Raju et al. 2008). Typically OPEFB yields about 70 % fibres (Wirjosentono et al. 2004).

Although these fibres may be used as fuel (Bakar et al. 2006), there is a growing demand for using these fibres for reinforcing materials, such as biopolymer (e.g. starch) and synthetic polymer (e.g. polytetrafluoroethylene, polyester, epoxy and polypropylene). There are many advantages of using OPEFB fibres for composite applications. The fibres are renewable, biodegradable, have a reduced carbon footprint and significantly cheaper than man-made ones (Mahjoub et al. 2013). OPEFB fibres also possess good thermal and insulation properties (Hariharan and Abdul Khalil 2005); they are non-toxic, flexible in usability and possess high specific strength (Yousif and El-Tayeb 2008). For the latest examples of the engineering applications of OPEFB fibres reinforced polymer composites see www.jecomposites.com. Advantages and disadvantages of OPEFB fibres are listed in Table 1.

Owing to the hydrophilic nature of OPEFB fibres (Dittenber and Gangarao 2012), one important consideration for using OPEFB fibres for reinforcing composites is their susceptibility to water absorption (Selzer and Friedrich 1995), The effect of moisture in polymer applications should be taken into account because the humidity in the atmosphere is likely to encourage the transfer of moisture into the composite and influence the mechanical properties and performance (Haque et al. 1991). Since polymer matrices are hydrophobic, it follows that during the processing of OPEFB fibre composites the fibres absorb water, resulting in fibre aggregation in the blend (Dittenber and Gangarao 2012). Consequently, the non-uniform dispersion of the fibres reduces the capacity of the fibres to provide reinforcement to the composite material. Indeed, natural fibre reinforced polymer-based composites that are used as building materials have failed in wet conditions, leading to surface roughening owing to fibre swelling or delamination. When natural fibre reinforced polymer-based composites are immersed in water, this leads to the diminution of the mechanical properties of the composite material, resulting in decreased stiffness and tensile strength (Sreekala et al. 2001; Sreekala and Thomas 2003; Ku et al. 2011; Dittenber and Gangarao 2012; Ho et al. 2012; Hosseinaei et al. 2012). However, not all the mechanical properties exhibit decreased magnitude—the fracture strain of the moisture-treated fibres yields somewhat higher magnitude than the untreated fibres (Sreekala et al. 2001; Sreekala

Table 1 Some advantages and disadvantages of OPEFB fibre (Sreekala et al. 1997; Bakar et al. 2006; Buana et al. 2013; Mahjoub et al. 2013; Tan et al. 2013)

Advantages	Disadvantages
Physical properties	
• Low specific weight • High specific strength and stiffness • Good electrical, thermal and heat insulation	• Low impact strength • Low fibre/matrix interfacial strength • Overall physical quality varies depending on environmental factors like weather (see Tables 2 and 3)
Sustainability	
• Renewable resource • Production consumes little energy and low CO_2 emissions	• Low durability • Flammable, poor fire resistance
Profitability	
• Production requires low investment and low cost	• Price fluctuation is dependent on harvest results or agricultural politics
Manufacturability	
• Friendly processing, no wear and tear of tools and skin irritation	• Limited maximum processing temperature • Poor fibre/matrix adhesion • Poor moisture and water resistance, causes swelling in fibres
Life cycle	
• Biodegradable • Thermal recycling possible	

and Thomas 2003). Unfortunately, the significance of these changes is not clear because the conclusions from most studies were reached without using a robust statistical analysis.

This chapter is concerned with the structural and mechanical properties of single OPEFB fibres in the hydrated state. The subject is discussed with reference to findings from a recent experimental study carried out by the authors. Briefly, in this study, OPEFB fibres (Changkat Asa Estate, Selangor, Malaysia) were stretched to rupture using an in-house developed horizontal microtensile test rig (Buana et al. 2013), mounted on an inverted microscope to provide real-time microscopic observation of the process of rupture. The advantage of a horizontal test rig is that the fibres could be hydrated continuously in a petri-dish (which formed part of the rig) during testing. In this study, a statistical analysis was used to assess the significance of the changes in the mechanical properties due to moisture treatment, to facilitate new insights in the underlying effects of moisture on the mechanical properties and to present some novel arguments for composite design considerations of OPEFB fibre reinforced biopolymer composite material. From a manufacturer's perspective, this is important for implementing effective optimisation of the manufacturing processes of polymer-based composites reinforce by natural fibres. Currently, there are many studies on OPEFB fibres, investigating the structural perspective (from the molecular level to the whole fibre), biological perspective (from the genetic to biochemistry), and engineering applications (such as composites for automotive and marine). More important, these studies have provided many insights concerning the mechanisms regulating the physical properties of OPEFB fibre but to cover all of them for possible connections to the underlying causes of the changes in the fibre mechanical properties due to moisture effects would not be possible in this discussion. Instead, a few important arguments to lend support to our findings of the moisture effects will be presented and where appropriate highlights the relevant literature to the reader for further details.

2 Structure, Biochemical Composition and Hydrophilicity

2.1 Structure

Figure 1a shows a schematic of the structure of OPEFB fibre. Plant fibres such as OPEFB fibres are biological examples of fibre reinforced composites comprising helically wound cellulose microfibrils (subunits of the fibre), bound together by an amorphous lignin matrix. Cellulose contributes to the mechanical properties of the fibre analogous to how the mechanical properties of connective tissues such as tendons and ligaments in animals are regulated by collagen (Goh et al. 2014).

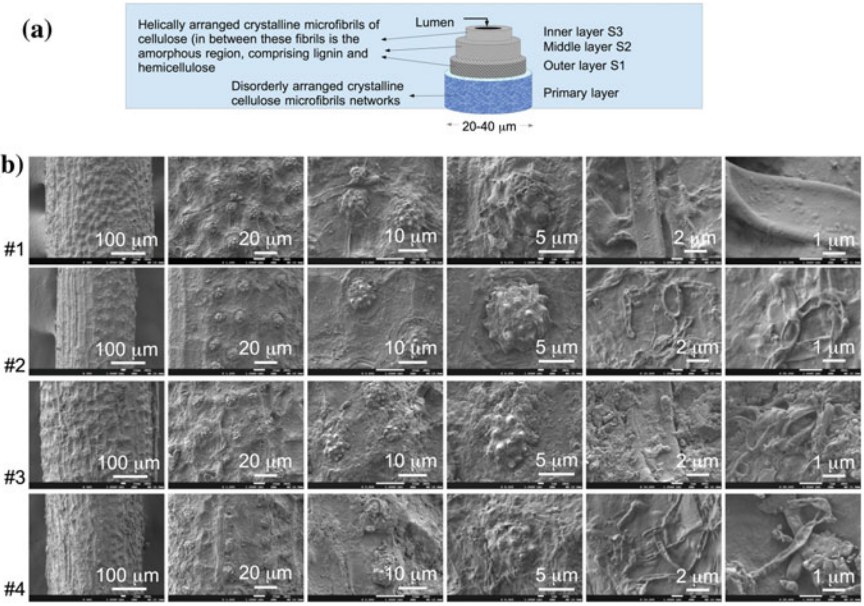


Fig. 1 OPEFB fibre structure. **a** Schematic of the different layers of a OPEFB fibre. **b** The primary cell wall as illustrated by 4 specimens; the images are shown at different magnification under a scanning electron microscope (JEOL JSM-7600F)

Table 2 Structural properties of OPEFB as reported in the literature

Property	Range	Literatures
Length, fibre	0.89–0.99 mm	Jawaid and Khalil (2011)
Diameter, fibre	150–500 μm	Sreekala and Thomas (2003)
Microfibrillar angle	46°	Sreekala and Thomas (2003), Kalam et al. (2005), Khalil et al. (2007), Rao and Rao (2007)
Density	0.7–1.55 g/cm^3	Sreekala and Thomas (2003), Kalam et al. (2005), Khalil et al. (2007), Rao and Rao (2007)

Structurally, the fibre features cell walls composed of distinct layers which have been identified as primary and secondary (Gibson 2012). The primary wall is composed of a disordered arrangement of cellulose microfibrils (Gibson 2012). Figure 1b–d shows the primary cell wall at various magnifications under a scanning electron microscope (SEM). The secondary wall is made up of three layers; the thick layer is the middle layer—the middle layer contributes to the mechanical properties of the fibre (Gibson 2012). The middle layer consists of a series of helically wound cellular microfibrils formed from long-chain cellulose molecules. The angle between the fiber axis and the microfibrils (known as the microfibrillar angle) varies from one fibre to another (Gibson 2012).

The structural properties of OPEFB fibres are summarised in Table 2. The table of composition for the respective constituents was compiled from several references for fibre length, fibre diameter, microfibrillar angle and fibre density. The diameter of the microfibrils are about 3–4 order of magnitude smaller, ranging 10–30 nm (Gibson 2012) than the OPEFB fibre (diameter 150–500 μm).

2.2 *Biochemical Composition*

To be precise, OPEFB fibres comprise cellulose ($C_6H_{10}O_5$), hemicellulose, lignin, and ash content. The percentage composition (by weight) of these constituents in OPEFB fibres are listed in Table 3. The table of composition for the respective constituents was compiled from several references for cellulose, lignin, hemicellulose and ash content. Of note, cellulose contributes significantly to the mechanical properties of the OPEFB; the Young's modulus of cellulose ranges 120–140 GPa; the tensile strength of cellulose ranges 0.75–1.08 GPa. Cellulose is predominantly crystalline (Gibson 2012; Mishra et al. 2012) and coalesces to form microfibrils.

Lignin features a non-crystalline structure comprising phenylpropane, an amorphous polymer of alcohols known as monolignols (Boerjan et al. 2003). Lignin has a Young's modulus of approximately 2.5–3.7 GPa (lower than cellulose), a density of 1200–1250 kg/m^3 and tensile strength of about 25–75 MPa (Gibson 2012). Lignin is known to be insoluble in water or alcohol but soluble in lower concentrations of alkaline solutions (Gibson 2012).

Table 3 Composition of oil palm empty fruit bunch fibres

Constituents	Composition (%)	Literatures
Cellulose	42.7–65	Sreekala et al. (1997), Hill and Abdul Khalil (2000), Abdul Khalil et al. (2008)
Lignin	13.2–25.31	Ismail et al. (1997), Sreekala et al. (1997), Wirjosentono et al. (2004), Bakar et al. (2006), Khalil et al. (2007), Hill and Abdul Khalil (2000)
Hemicellulose	17.1–33.5	Hill and Abdul Khalil (2000), Khalil et al. (2007), Khalil et al. (2008)
Ash content	1.3–6.04	Ismail et al. (1997), Sreekala et al. (1997), Abdul Khalil et al. (2008)

Hemicelluloses are polysaccharides (i.e. carbohydrates whose molecules are made of numerous sugar molecules bonded together and in shorter chains than cellulose). Hemicelluloses make up 20–30 % of all plant cell walls. Hemicellulose has a Young's Modulus of 5–8 GPa (Gibson 2012) (i.e. lower than cellulose)—they provide the cross-linking in microfibrils. Hemicellulose molecules have small side chains consisting of 500–3000 monomer units with acidic groups (Zdunek et al. 2014).

Ash content refers to the remnant of a heat treatment process applied to the fibre during the extraction of OPEFB fibres (Udoetok 2012). Ash content is rich in calcium and potassium, but the exact constitution of the fibres varies according to the fibre extraction methods (Udoetok 2012).

2.3 Hydrophilicity

The OPEFB fibres are hydrophilic owing to the presence of the hydroxyl groups (OH) in the constituents of the fibre (Kalia et al. 2011). We have assessed the microstructure of OPEFB fibres for moisture-treated versus untreated specimens. Micrographs of the primary wall and subsequent layers in are shown in Fig. 2a–c. Distinct (almost-white) inner region (secondary wall) and black outer region (primary wall) are observed in the untreated specimens (Fig. 2a). The inner region appears to be more fibrous, with numerous gaps, while the primary wall appears more homogeneous, reflecting the underlying differences in the orientation of the microfibrils for both layers as well as the differences in the respective constituents. The cross-section of the treated specimen reveals no distinguishable layers, indicating that the pores within the fibre have enlarged significantly and the inner layers have become undistinguishable from the primary wall. Of note, the untreated specimens (Fig. 2a) featured a distinct crystalline black and white colour cross-section. The features of untreated specimen are somewhat similar to those reported elsewhere (Gunawan et al. 2009). Following the procedures reported in the literature (Gunawan et al. 2009), i.e. cleaning and washing with fresh or distilled

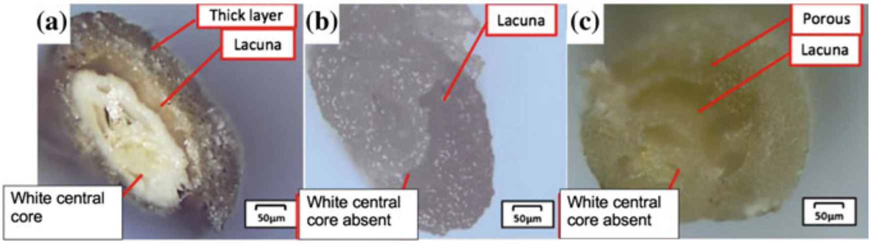


Fig. 2 Cross-sections of OPEFB fibre, shown for the **a** control specimen (from the processing plant), **b** moisture-treated specimen (wet) and **c** moisture-treated specimen (after drying it for 3 days)

water and drying. Figure 2b shows the cross-section of a moisture-treated fibre and Fig. 2c shows the cross-section of a fibre after moisture-treated and dried for 3 days. The moisture-treated specimens exhibited a translucent light brown cross-section. Surprisingly, when the moisture-treated fibres were left to dry for 3 days, the features of the dried fibres were very different from the untreated ones. While the underlying causes of the differences are not known, it suggests that repeating the drying process could irreversibly alter the microstructure of the fibre.

Further analysis of the moisture-treated fibres reveals that the fibres yield an appreciable increase in cross-sectional area, weight and density as shown in Table 4. These changes are clearly attributed to water penetration through the pores of the tubular structures of the fibre. The tendency of water molecules to bond with OPEFB fibres, and the ability to enter the pores and lacuna of OPEFB fibres, characterise the hydrophilicity of OPEFB fibres (Kalia et al. 2011; Hosseinaei et al. 2012). The hydration effects occurs at different length scale, e.g. at the whole fibre (physical) level, and at the molecular level (Kalia et al. 2011; Hosseinaei et al. 2012). To illustrate the molecular level effects, Fig. 3b shows a schematic of the molecular interaction with water. As the water molecule is small, it can diffuse into the spaces between the cellulose and lignin groups. Thereafter, the hydrogen ends of the water molecule facilitate the formation of strong (hydrogen bonds) interactions with the hydroxyl groups within cellulose and lignin groups in OPEFB fibres. Two possible types of hydrogen bonds with OPEFB fibres are shown in Fig. 3c. Of note, the cross-sectional area of the untreated OPEFB fibre correspond to a mean diameter that is numerically equal to 220 ± 158 µm; this falls within the values reported in the literature (Table 4). Although the cross-sectional area of the moisture-treated OPEFB fibre is larger than that of the untreated fibre, and corresponds to a mean diameter that is numerically equal to 309 ± 202 µm, this value falls within the range of values reported in the literature (Table 4).

To justify the hydration effects at the whole fibre level, it is straight-forward to apply the principle of capillary action to help explain how water penetrates OPEFB fibres (Fig. 3c). Here, the OPEFB fibres are considered as narrow tubular structures with permeable walls due to the cohesive forces between the surface of the structure and water (Sreekala et al. 2001; Hassan et al. 2010). Additionally, the diameter of

Table 4 Structural parameters of OPEFB fibres from the authors' present study

	Untreated	Moisture-treated
Cross-sectional area (mm^2)*	0.152 ± 0.078	0.300 ± 0.128
Weight (mg)*	1.171 ± 0.661	11.250 ± 0.541
Density (kg/m^3)*	200 ± 159	792 ± 329

Values shown are mean ± SD. *Indicates significant differences ($P < 0.05$)

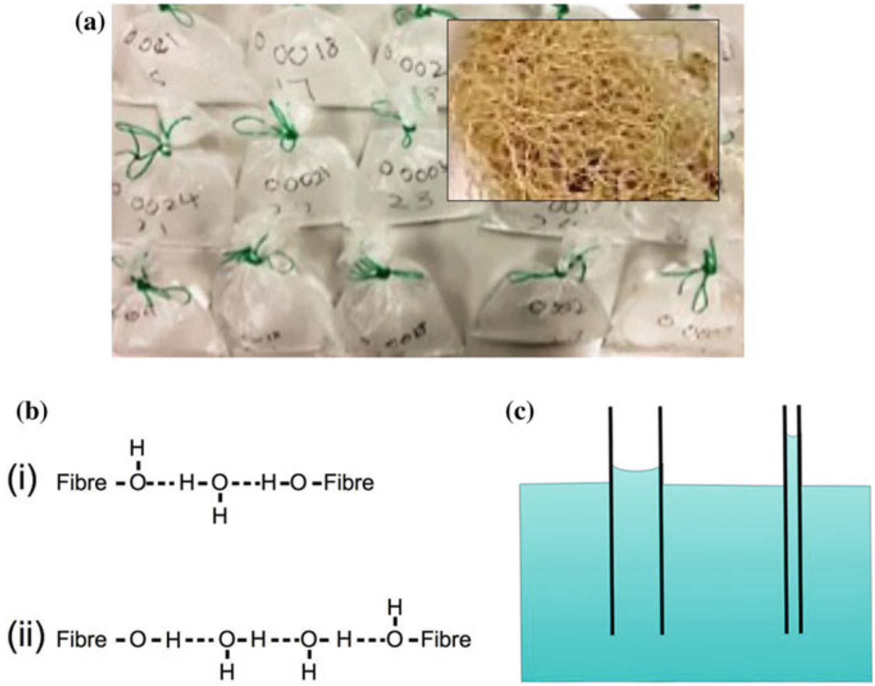


Fig. 3 Hydration. **a** Moisture-treatment of OPEFB fibres for investigating the effects of water on the mechanical properties and structure of OPEFB. **b** Interaction of water with fibre. **c** Schematic of capillary action

the structure and gravitational forces influences the amount of water transported into the OPEFB (Sreekala et al. 2001; Hassan et al. 2010). Since the cross-section of the OPEFB fibre is porous, capillary action takes place at the two ends of the OPEFB fibre, leading to an expansion and enlargement of the porous structure at the surface of the fibres (Sreekala et al. 2001; Hassan et al. 2010). Thus, as water advances into the porous tubular structures in the OPEFB fibre, the portion of water behind the advancing front generates pressure and causes the tubular structures to stretch radially until an equilibrium of forces is reached between the pressure from the water and the reactive stresses in the wall (Sreekala et al. 2001; Hassan et al. 2010). Consequently, this leads to significant increases in the cross-sectional area, weight and density. From a structural perspective, both the increase in weight and cross-sectional area contribute to the increase in the specimen density.

3 Mechanical Properties

3.1 Fracture Morphology

Given the uncertainty surrounding structural changes in the moisture-treated specimens that were subsequently dried for 3 days (Sect. 2.1), for simplicity this chapter shall focus on the findings of the mechanical properties of moisture-treated specimens—hydrated during mechanical testing—versus untreated specimens. As pointed out in Sect. 1, an in-house developed horizontal microtensile test rig (Buana et al. 2013), mounted on an inverted microscope was used to provide real-time microscopic observation of the process of rupture (Fig. 4a). The fracture morphology of untreated and moisture-treated specimens are shown in Fig. 4b. We have observed that the untreated specimens fractured by a combination of mode 1 (rupture planes are perpendicular to the tensile load) and mode 2 (shear rupture in the planes where the load lies) (Fig. 4b, left panel). The mode 2 fracture caused possibly from the delamination of an inner layer (S1, S2 or S3; Fig. 1a) of the fibre. This suggests that the weakest links within the OPEFB fibre are at the interface between the layers. That two modes of fracture occur (instead of one) suggests that the fibre is tough because more energy has to be absorbed to create the rupture surfaces at the sites of mode 1 and mode 2. The basis underlying these fractures is attributed to the breaking of the strong covalent cross-links (arising from pectin and glycoproteins) within the microfibrils. From a fracture perspective, this indicates that the microfibrils are capable of sustaining high stress when the fibre is loaded. Clearly, the mode 1 and 2 fractures in OPEFB fibres will have implications on how the fibres may be used for reinforcing polymeric composites. On the other hand, pull-out of microfibrils in the moisture-treated fibres was observed (Fig. 4b, right panel) particularly from the inner layers of the fibre. Based on the principles of fibre composite concerning fibre pull-out (Ng et al. 2010), it is clear that these microfibrils are pulled out because the moisture treatment causes a diminution of the interfacial adhesion between the microfibrils and the matrix. Since only microfibrils from the inner layers are pulled out, this suggests that the mechanical response of the outer wall is quite different from the inner layers. From a fracture perspective, this indicates that the microfibrils in the outer wall are capable of sustaining high stress but those of the inner walls are not as effective—instead the bulk of the stress is transferred to the interface between the matrix and the microfibril.

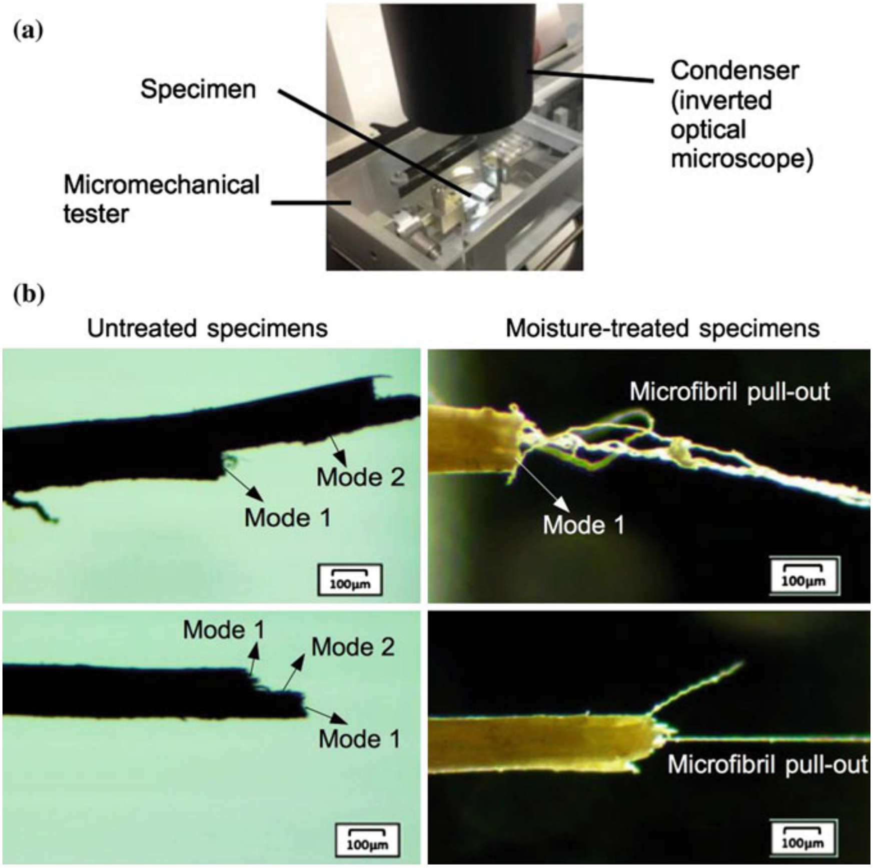


Fig. 4 Simultaneous mechanical testing and optical microscopy. **a** Setup of the micromechanical tester on the stage of an inverted (optical) microscope. **b** Comparison of the fracture morphology of untreated (*left panel*) and moisture-treated (*right panel*) OPEFB fibres

3.2 Stiffness, Fracture Strength and Strain

Figure 5a shows typical stress versus strain curves derived from an untreated specimen and a moisture-treated specimen. The gradient of the stress-strain curve from the untreated specimen at a given strain point is somewhat larger than that of the treated specimen, throughout the loading regime. However, while the untreated specimen fails at a higher stress than the treated specimen, the latter exhibits higher extensibility (i.e. fracture strain) than the former.

The mechanical properties of OPEFB fibres are summarized in Table 5. The statistical analysis (T-test) reveals significant difference in the respective mechanical parameters, namely stiffness ($P < 0.05$; Fig. 5) and fracture strength ($P < 0.05$; Fig. 5) between the untreated and treated specimens. However, no significant

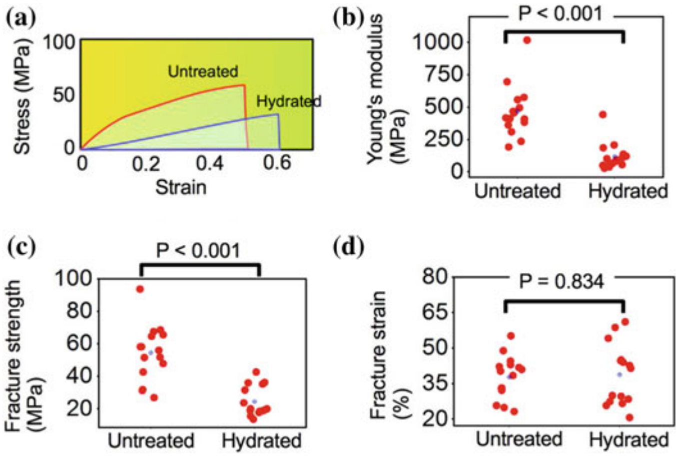


Fig. 5 Mechanical properties of OPEFB fibres from untreated and treated specimens: **a** Typical stress versus strain curves, **b** Young's modulus (otherwise known as 'stiffness'), **c** Fracture strength and **d** Fracture strain (otherwise known as 'extensibility')

Table 5 Results of the mechanical properties of OPEFB from the authors' present study for hydrated fibre versus untreated fibres

	Present study, untreated	Present study, hydrated	Literature
Young's modulus (MPa)*	467.5 ± 200.3	119.0 ± 104.0	1000–6700
Fracture strength (MPa)*	54.5 ± 9.2	24.7 ± 17.3	35–800
Fracture strain (%)	37.9 ± 9.1	38.8 ± 12.8	14–63

The range of values of the respective mechanical properties from the literature (Sreekala and Thomas 2003; Hassan et al. 2010; Buana et al. 2013) are estimates based on data given as mean values and mean ± SD values. The symbol * indicates significant differences between the untreated and hydrated specimens of the present study ($P < 0.05$)

difference was observed for the extensibility parameter (Fig. 5). Thus the findings suggest that the stiffness and strength of the untreated fibres are, respectively, 5 and 2 times larger than the moisture-treated fibres; these trends are consistent with findings from other studies (Sreekala et al. 2001; Zhu et al. 2013). Although the results of the fracture strength and fracture strain fall within those reported in the literature, the mean stiffness of the OPEFB fibres were appreciably lower than those reported in the literature (Table 5).

3.3 Reliability Analysis Using the Weibull Distribution

The variability of the fracture strength of OPEFB fibres suggests that it may be modelled in a statistical sense to help us address the overall reliability of the fibres for reinforcing composites. To order of magnitude, estimate of the statistical variation of strength of the fibres may be described using a Weibull distribution (Weibull 1951; Moser et al. 2003), assuming that the fracture strength is not appreciably dependent on the rate of loading. According to the Weibull formulation, the cumulative failure probability, Pr, of a population of the OPEFB fibres is related to the stress, σ, applied as

$$\mathrm{Pr}(\sigma) = 1 - \exp(-[\sigma/\sigma_0]^{\beta}), \tag{1}$$

where β and σ_0 are the Weibull modulus and the characteristic strength, respectively. The cumulative failure probability of a population of fibres of number N_0 where N_0 is large could be thought of as the number of fibres ($N_0 - N$) having a breaking strength less than or equal to σ/N_0, so

$$\mathrm{Pr}(\sigma) \approx \frac{N_0 - N}{N_0} = 1 - \frac{N}{N_0}, \tag{2}$$

Consider a bundle containing initially N_0 fibres, all of the same length, loaded only from the ends of the fibres. The fibres possess identical load-elongation behaviour (differing only in the strengths as well as elongations to break of the respective fibres), then the load F borne by the bundle is given by

$$F = \sigma AN, \tag{3}$$

where N is the number of unbroken fibres all of cross-sectional area A and all bearing the same stress σ. If a fibre breaks, it no longer bears any load, so Eqs. (1), (2) and (3) then say that the number of fibres surviving application of the F to the bundle satisfies

$$N/N_0 = \exp\left(-\left[\frac{F}{N_0\sigma_0' A}\right]^{\beta}\left\{\frac{N_0}{N}\right\}^{\beta}\right), \tag{4}$$

where: σ'_0 stands for $\sigma_0/L^{1/\beta}$ (which is the statistical mode of the strength distribution for fibres of small dispersion in strength). The maximum load which can be sustained by a bundle is obtained from Eq. (3), as the maximum value of the product σN, and since $N = N_0(1 - \mathrm{Pr}(\sigma))$ for any distribution, Weibull or not, the maximum load is determined by the maximum value of the quantity $\sigma[1 - \mathrm{Pr}(\sigma)]$. For the Weibull distribution, this is obtained by differentiating Eq. (4) and equating to zero to obtain

$$F_{\text{bun}} = N_0 \sigma_0' A e^{-1/\beta} \beta^{-1/\beta}. \tag{5}$$

The 'ultimate tensile strength' of the bundle, σ_{bun}, i.e. the maximum load divided by the initial area of cross section, is then $F_{\text{bun}}/(N_0 A)$, i.e.

$$\sigma_{\text{bun}} = F_{\text{bun}}/\{N_0 A\} = \sigma_0' e^{-1/\beta} \beta^{-1/\beta}. \tag{6}$$

The stress in the remaining fibres (not broken) is $\sigma'_0/\beta^{1/\beta}$ and there are $N_0/\exp(1/\beta)$ of these. Thus the load, $F/\{N_0\sigma'_0 A\}$, supported by the bundle increases linearly with increase in stress on a fibre, σ/σ'_0, for a given m. Beyond a critical σ/σ'_0, increasing σ/σ'_0 leads to a less rapid, but non-linear, increase in $F/\{N_0\sigma'_0 A\}$ (= $\{\sigma/\sigma'_0\}\exp(-[\sigma/\sigma'_0]^\beta)$); a peak value is reached beyond which the $F/\{N_0\sigma'_0 A\}$ decreases with increase in σ/σ'_0.

3.4 Rule of Mixture Models for Predicting Mechanical Properties

In this section, a simple mathematical model that leads to order-of-magnitude predictions for the stiffness and fracture strength of OPEFB fibre reinforced biopolymer composites in the presence of moisture is presented. Since polymer materials are hydrophobic, blending the hydrophilic OPEFB fibres into a polymer matrix could potentially lower the strength of the interfacial adhesion, leading to poorer mechanical properties of the polymer composite. As an example, the application of OPEFB fibres reinforcing starch composite was considered (Lu et al. 2009; Bergeret and Benezet 2011). Starch granules provide an insoluble, biodegradable storage system for plants. This balance of mechanical stability with degradability arises somehow from the starch compositional chemical structure of the amylose and amylopectin, and from the arrangement of amorphous and crystalline zones within the granules (Calvert 1997). One of the motivations for the section is to develop mathematical descriptions for such a biopolymer-based composite in a consistent manner to allow comparison of the composition of the OPEFB fibre in the composite. Another motivation is to establish the bounds in which the design of these composites can be considered.

Let us begin by estimating the stiffness of the starch-based composite. Consider the hand lay-up approach whereby the composite is reinforced by dispersing short OPEFB fibres randomly (oriented and spaced) throughout the matrix phase. The fibres are considered short with respect to the overall length of the composite. The composite elastic modulus E is related to the elastic moduli of the OPEFB fibre, E_f, and PTFE matrix, E_m, and the OPEFB fibre volume fraction, V_f, given by

$$E = \eta_{oE}\eta_{fE}E_f V_f + E_m(1 - V_f) \tag{7}$$

where, η_{oE} is the OPEFB fibre orientation factor and η_{fE} is the OPEFB fiber length efficiency factor (Tucker and Liang 1999; Liang 2012). For OPEFB fibers of length L, the η_{fE} is given by

$$\eta_{fE} = \frac{\tanh(bL/2)}{\beta L/2}, \tag{8}$$

where

$$b = \frac{1}{r_f}\sqrt{\frac{2G_m/E_f}{\ln(R/r_f)}} \tag{9}$$

(Tucker and Liang 1999; Andersons et al. 2006; Liang 2012). We next estimate the strength of the composite. One then finds that the fracture strength, σ_U, of OPEFB fibres reinforcing starch composite can be expressed as

$$\sigma_U = \eta_{fS}\sigma_{Uf}V_f + \sigma_{Um}(1 - V_f), \tag{10}$$

where σ_{Uf} is the fiber strength, σ_{Um} the stress in the matrix at the fibre failure strain, η_{fS} the fibre efficiency which is given by

$$\eta_{fS} = \eta_{oS}\eta_{LS}, \tag{11}$$

where η_{LS} is the fiber length efficiency factor and η_{oS} the fibre orientation factor. For linear elastic constituents,

$$\sigma_{Um} = \sigma_{Uf}E_m/E_f \tag{12}$$

(Tucker and Liang 1999; Andersons et al. 2006; Liang 2012). The η_{fS} is identified with

$$\eta_{fS} = \begin{cases} 1 - L_c/(2L) & L \geq L_c \\ L/(2L_c) & L < L_c \end{cases}, \tag{13}$$

where L and L_c are the OPEFB fibre length and critical length, respectively (Andersons et al. 2006). Of note,

$$L_c = \sigma_U r_f/\tau, \tag{14}$$

where r_f is the OPEFB fibre radius and τ the interfacial shear strength (Kelly and Macmillan 1986; Goh et al. 2008). Thus, L_c depends on the nature of the interface between the fibre and the starch biopolymer and this is expected to vary for different polymeric matrices. The notion of a critical length for OPEFB fibre suggests that when short OPEFB fibres are used there is an optimal length below which the fibre is not effective for taking up high stress (Goh et al. 2008; Shalwan and Yousif 2013).

3.5 Predictions

There are two key practical issues for consideration when modelling the biopolymer composite reinforced by OPEFB fibres using Eqs. (7) and (10): fibre orientation and fibre length. In practice, both increase in fibre length (given all things being equal) and decrease in fibre orientation angle with respect to the direction of the applied load have positive effects on the stiffness and strength of polymer composite (Shalwan and Yousif 2013). Thus, we would expect that for short fibres with random orientation, the $\eta_{oE}\eta_{fE}$ and η_{fS} are $\ll 1$. For this reason, it is not useful to employ short OPEFB fibres because the stiffness and the strength of the PTFE would predominate those of the OPEFB fibres, i.e. $\eta_{oE}\eta_{fE}E_f V_f < E_m(1 - V_f)$ and $\eta_{fS}\sigma_{Uf}V_f < \sigma_{Um}(1 - V_f)$, except at very large V_f values. For simplicity, we shall consider PTFE composites reinforced by unidirectional OPEFB fibres (where applied loads act in the direction of the fibres) with lengths comparable to that of the overall composite. It follows that the E of Eq. (7) can be estimated to order of magnitude by replacing the fibre orientation factor, η_{oE}, by unity and by replacing and the fibre efficiency factor, η_{fE}, by unity. One then finds that,

$$E = E_f V_f + E_m(1 - V_f). \tag{15}$$

Similarly, the σ_U (Eq. 10) of the composite material can be estimated to order of magnitude by replacing the fibre orientation factor, η_{fS}, by unity. Then it was found that,

$$\sigma_U = \sigma_{Uf}V_f + \sigma_{Um}(1 - V_f). \tag{16}$$

For the mechanical properties of starch (Table 6), we estimate the stiffness of the starch matrix as E_m = 15 MPa (lower limit) (Torres et al. 2011) and 770 (upper limit) (Acosta et al. 2013) and the strength of the starch matrix as σ_{Um} = 2 MPa (lower limit) (Torres et al. 2011) and 13.0 MPa (upper limit) (Acosta et al. 2013). To further our arguments of the prediction of the extreme values of the composite stiffness and strength, we evaluated the extremes of the variability of the elastic modulus of the OPEFB fibres which we have expressed in terms of mean ± SD. Accordingly, we argue that the value of E_f that establishes the lower bound of Eq. (15) is numerically equal to 267.2 MPa (dry fibres) and 15 MPa (wet fibres); similarly the value of E_f that establishes the upper bound of this expression is found by setting E_f = 667.8 MPa (dry fibres) and 223.0 MPa (wet fibres). Similar argument applies for the fracture strength of the composite, giving the value of

σ_{Uf} = 45.3.6 MPa (dry) and 7.4 MPa (wet) for the lower bounds and 63.7 MPa (dry) and 42.0 MPa (wet) for the upper bounds.

When these values, i.e. E_f and E_m, were substituted into Eq. (15) [NB: for σ_{Uf} and σ_{Um}, we substitute the values back into in Eq. (16)], and considering V_f from 0.0 to 0.70 (Ku et al. 2011; Zhu et al. 2013), the results as shown in Fig. 6a were obtained. The composite elastic moduli contributed by the untreated fibres versus the hydrated fibres appear to overlap at low V_f, suggesting that moisture has little effects on the composite stiffness. At high V_f, the overlap region appears to decrease with increasing V_f. Overall, the general trend reveals that the elastic modulus of the composite with untreated fibres is higher than that of the composite with hydrated fibres at high V_f. Thus, as the fibre content in the composite increases, the composite becomes more sensitive to the effects of moisture.

As for the fracture strength of the composite, the composite fracture strength contributed by the untreated fibres versus the hydrated fibres appear to overlap at low V_f, suggesting that moisture has little effects on the composite fracture strength (Fig. 6b). At high V_f, the fracture strength of both untreated and hydrated fibre reinforced composite increases with increasing V_f. The general trend reveals that the composite fracture strength of the composite with untreated fibres is higher than that of the composite with hydrated fibres at high V_f.

With regards to the mechanical reliability, it is observed that the untreated and hydrated fibres yield β = 3.33 and 2.94, respectively. Thus, the β of the untreated fibres is higher than that of the hydrated fibre. The σ_0 of the untreated and hydrated fibres are found to be 60.85 and 27.71, respectively. This analysis predicts that the σ_0 of the untreated fibres is two times higher than that of the hydrated fibre.

Table 6 Mechanical properties of starch and starch-based composites from the literature

	Stiffness, (MPa)	Fracture strength (MPa)	Fracture strain (%)	Literatures
Starch, 1 week after preparation	131 ± 31	4.1 ± 0.7	4.5 ± 09	Acosta et al. (2013)
Starch, 5 weeks after preparation	770 ± 171	13.0 ± 2.0	1.9 ± 0.6	Acosta et al. (2013)
Starch, from white carrot (Andes crops)	15.00 ± 1.14	1.99 ± 0.58	22.60 ± 4.95	Torres et al. (2011)
Starch, from Oca (Andes crops)	17.25 ± 3.43	5.91 ± 2.12	54.86 ± 18.10	Torres et al. (2011)
Corn starch, blended with montmorillonite	7.5	2.0	73.3	Majdzadeh-ardakani et al. (2010)
Potato starch, blended with montmorillonite	187.5	28.1	57.3 %	Majdzadeh-ardakani et al. (2010)
Starch, blended with 2 % montmorillonite	29.6 ± 12.1	3.1 ± 0.4	55.1 ± 17.2	Cyras et al. (2008)
Starch, blended with 5 % montmorillonite	195.6 ± 38.6	5.2 ± 0.8	46.8 ± 19.2	Cyras et al. (2008)

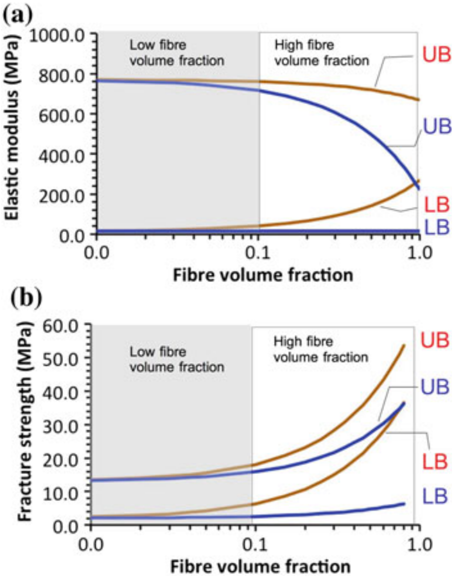


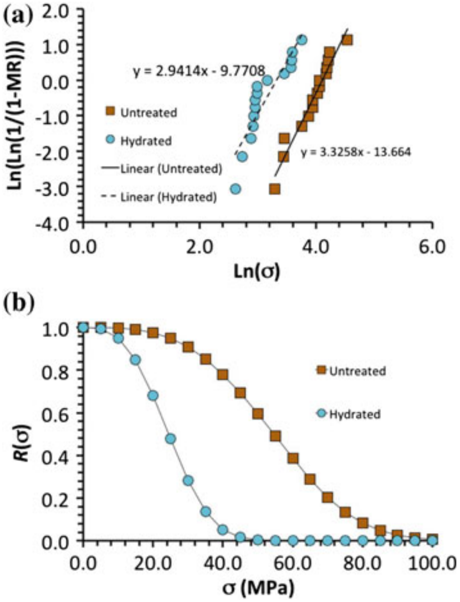
Fig. 6 Predictions of **a** elastic modulus and **b** fracture strength versus fibre volume fraction of OPEFB fibre reinforced biopolymer composite. The biopolymer of concern is starch. The *blue* (*red*) regions enclosed by the pair of *blue* (*red*) *lines* indicate the possible values of the mechanical properties from the composite with wet (dry) fibres (Color figure online)

Figure 7 illustrates how these parameters influence the reliability of the fibres using a plot of the reliability function, $R(\sigma)$, versus fracture stress in the fibre, σ, for the untreated versus the hydrated fibres. Thus the form (parameterized by β) of the curves corresponding to hydrated fibres levels features a very narrow spreads of strength variability as compared to the untreated fibres. Correspondingly, the σ_0 for the untreated fibres is larger than that associated with the hydrated fibres. Assuming that the fibres from OPEFB are of order of 0.5 m long, we let $L = 0.5$ m (see Eq. 6). It follows that order of magnitude estimates of the bundle strength, σ_{bun} (see Eq. 6), for untreated and hydrated fibre bundles embedded in starch matrix yield values of 70.5 and 34.2 MPa, respectively, which conveniently reflect the upper limits of the estimates derived from the rule-of-mixture model, Eq. (16). In conclusion, analysis of the reliability of these fibres reveals that the variability of the strength decreases (in other words the β increases) for fibres that are subjected to hydration treatment as compared to untreated fibres. One possible reason contributing to the wider variability in the strength of the untreated fibre could be the varying conditions in which each fibre experiences as the OPEFB is isolated at the plant.

3.6 Limitations

Thus, Eqs. (15) and (16) provides estimates of the range of possible values of the stiffness and strength of an oil palm fibre reinforced biopolymer composite with varying volume fraction of the fibre. Additionally, it also reveals the sensitivity of the stiffness and strength of the composite to moisture as depicted by the extent of

Fig. 7 Predictions of the mechanical reliability of the OPEFB fibres reinforcing biopolymer composite. The biopolymer of concern is starch. **a** Plot of Ln(Ln(1/[1 − MR]) versus Ln (strength) where MR = $[i - 0.3]/\{N + 0.4\}$, $i = 1, 2, \ldots N$ (i.e. N, the number of specimens for each treatment)



the regions of overlap from the biopolymer composite containing wet versus dry fibres. It must be emphasized the results in Fig. 6 are based on simple order of magnitudes approach. In reality the relationships between the respective mechanical properties and the fibre volume fraction (or otherwise measured in weight percent) depart somewhat from linearity as shown in studies carried out by experiments not only with flax fibre reinforced PP composites (Ku et al. 2011) but also with other types of composites, such as coir fibre reinforced polyester composite (Monteiro et al. 2008), banana fibre reinforced epoxy composite (Venkateshwaran et al. 2012). A review by Shalwan and Yousif (2013) on a wide range of natural fibre reinforced polymer composites, such as coir/PP, palm/PP, Kenaf/PP, palm/rubber, suggests that while it is possible to increase the volume fraction to achieve high composite strength, there exists a critical volume fraction which will result in an optimal composite strength but beyond the critical volume fraction, the strength decreases. It was found that the critical fibre volume fraction varies with different composites but appear to range from 5 to 50 % (Shalwan and Yousif 2013). It is speculated that beyond the critical fibre volume fraction, the fibres tend to aggregate in the composite during the blending process; this results in reduced fibre-matrix interfacial area and encourages fibre pull-out instead of fibre fracture.

4 Conclusion and Future Perspective

Moisture in the OPEFB fibre has a significant influence on the mechanical performance of the fibres. Dry OPEFB fibres exhibit mode 1 and 2 fracture. Moisture-treated OPEFB fibres exhibit mode 1 fracture and defibrillation leading to microfibril pull-out. These variation in the fracture morphology underscore the differences in the mechanical properties of the wet and dry OPEFB fibres. In particular, the stiffness and strength of the dry fibres are, respectively, 4 and 2 times higher than moisture-treated fibres. However, there is no difference in the extensibility of dry and moisture-treated fibres. Simple mathematical models that lead to order-of-magnitude predictions for the stiffness and fracture strength of OPEFB fibre reinforced PTFE composites show that the stiffness and strength of the OPEFB fibre are sensitive to moisture, as depicted by the extent of the regions of overlap from PTFE composite containing wet versus dry fibres. These discussions offer a simple methodology for engineering OPEFB fibre reinforced polymer composites with mechanical properties tailored for the intended purpose.

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Potentiality of Luffa Fiber Used as Reinforcement in Polymer Composites

Sudhir Kumar Saw, Joyjeet Ghose and Gautam Sarkhel

Abstract Recently, natural fiber based composites have received widespread attention due to their application in car bodies, sporting goods, building panels, industrial, and other commercial markets. In the present study, various chemical treatments of native luffa fiber (*Luffa cylindrica)* surfaces using alkalization (2 h agitation with 5 % KOH) and furfurylation (graft furfuryl alcohol followed by oxidation with $K_2Cr_2O_7$ (1N) is discussed and compared. The purpose of chemical treatments is to improve the fiber-matrix compatibility, interfacial strength, physical, mechanical and thermal properties, etc. The grafting of furfuryl alcohol followed by oxidation-generated quinines showed better results than alkaline treatments with respect to enhancement of surface area, compatibility and hydrophobicity together with removal of waxes, lignin and hemicelluloses. The treated surface was characterized by ultraviolet-visible spectroscopy and dynamic contact angle measurements. DSC, TGA, SEM, water absorption and mechanical tests were performed to determine the thermal, morphological and mechanical properties of untreated and chemically treated luffa fiber.

Keywords Luffa fiber · Surface treatments · Ultraviolet-visible spectroscopy · Thermal properties · Mechanical properties · KOH treatment · Furfuryl alcohol · Scanning electron microscopy

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1 Introduction

A combined properties of natural fibers such as active surface, light weight, cheaper, worldwide distribution, renewability, biodegradability, ease of preparation, lower energy consumption and relative non-abrasiveness over conventional man-made fibers has evoked interest in manufacturing using these fibers (Asasutjarit et al. 2009; Bledzki et al. 2010; Khalil et al. 2007). Their soft nature and flexibility is also an advantage in relationship to the common man-made fibers like glass fibers. Moreover, natural fibers are eco-friendly and non-polluting substance, i.e. neutral with respect to the carbon dioxide emissions. These composite materials are used in various applications such as automotive, aeronautic, and building industries (Medina et al. 2008). Although, the main bottlenecks of natural fibers in composites are the poor compatibility between fiber and matrix due to hydrophilic properties and non-homogeneity of fiber surface in most of characteristics. Therefore, chemical modifications are considered in modifying the fiber surface properties including mercerization, silanization, acetylation, benzoylation, acrylation, maleated coupling agents, isocyanates, permanganates and others are reviewed. The objective of chemical treatment is to improve the interaction between fiber and matrix and to increase fiber strength. Moisture absorption properties of fibers are reduced and their mechanical strength are improved (Edeerozey and Hazizan 2007; Weyenberg et al. 2003).

Luffa fiber (*Luffa cylindrica*) is one of the earliest known cultivated crops having been for centuries used in foods, furniture, bath or kitchen sponge and medicine. Luffa production has been steadily increasing in the past 20 years to fulfill the demand for renewable-biodegradable fiber sources. It is found in plenty of tropical and subtropical countries of Asia (India, China, Pakistan and Indonesia), Africa and South America. It has a ligneous fibrous vascular system (hierarchical structure) in which the fibrous cords are disposed in a multidirectional array, forming a natural mat. It is obtained from the fruit of two cultivated species of the genus Luffa in cucurbitaceous family, *Luffa cylindrica* (smooth fruit) and *Luffa acutangula or acgyptiaca* (angled fruit). The young and greenish fruit is eaten as a vegetable all over the world. The ripe and dried fruit is the source of *Luffa cylindrica* or luffa fiber or vegetable sponge or sponge gourd as an industrial fiber (Demir et al. 2006; Seki et al. 2011).

The functional surface of luffa fiber contains many alcoholic groups, acid carboxyl groups, reducing aldehyde groups and phenol groups that provide a large scope for chemical interaction. Surface treatments of luffa fibers aimed at improving the interfacial adhesion with reduced water absorption character. Modified fibers might lead to composites with enhanced properties and much better durability as described in our previous report (Saw et al. 2013). Interestingly, in this context, attempts have been made to modify the luffa fibers through graft furfuryl alcohol induced by oxidation-generated quinines and potassium hydroxide solution with fixed concentration and reaction time, and a comparative study of the modified fibers have been reported. Presently, from the results of research work carried out on this wonder crop, furfurylation showed the best properties. The goal of work is to show the potentialities of this natural plant that is virtually distributed around the world.

2 Experimental

2.1 *Materials*

Luffa fiber (*Luffa cylindrica*) was collected from local resources of Jharkhand region, India. The inherent physical properties and chemical composition of luffa fiber are given in Table 1. The chemicals and solvents such as potassium hydroxide, furfuryl alcohol, potassium dichromate, acetone and other reagents were obtained as analytical grade of Central Drug Houses (CDH) Pvt. Ltd. New Delhi, India and used without further purification.

2.2 *Surface Treatments of* Luffa cylindrica *Fibers*

2.2.1 Alkali treatment of luffa fiber: Prior to alkali treatment, the luffa fibers were washed thoroughly with fresh water. The washed fibers were then dipped in 5 % KOH solution and ultrasonicated for 2 h at 50 °C in a sonifier (Ultrasonicator, model—UD80SH2L) of M/s—Analytical Instruments Consortium, Kolkata, India. Then the alkali solution was drained out and the fibers were washed with fresh water to remove any KOH sticking to fiber surface. Finally the fibers were washed with distilled water containing a little dilute acetic acid and pH of 7 was maintained. The fibers were then air dried for 48 h followed by air oven drying at 80 °C for 5 h as shown in Eq. (1).

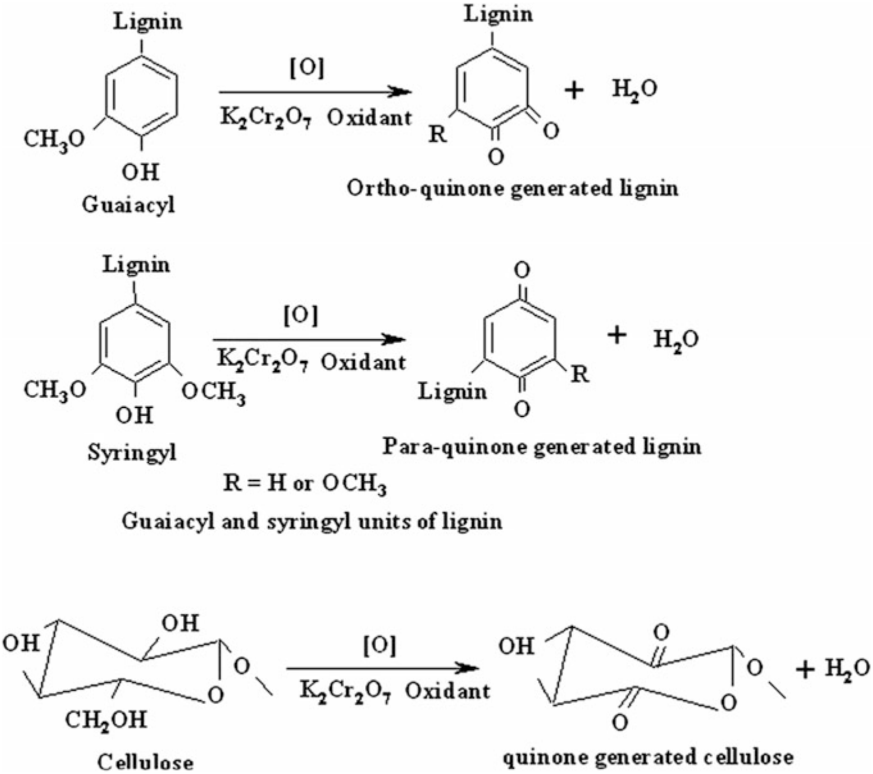
$$\mathbf{Luffa\,fiber\ -OH + KOH \rightarrow Luffa\,fiber\ -O^{-}K^{+} + H_2O + Surface\,impurities} \tag{1}$$

Table 1 Physical properties of luffa fiber

Chemical constituents (%)		Physical properties of luffa fiber	
Cellulose	63.00 ± 2.5	Density (gm/cc)	0.92 ± 0.10
Lignin	11.69 ± 1.2	Diameter (µm)	270 ± 20
Hemicelluloses	20.88 ± 1.4	Aspect ratio	340 ± 5
Ash	0.4 ± 0.10	Microfibrillar angle (°)	12 ± 2

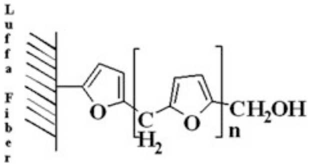
2.2.2 Dewaxing of luffa fiber: The luffa fiber were dewaxed by a soxhlet apparatus with acetone over a period of 48 h, to extract low molecular weight substances (e.g. waxes, therpenes like natural impurities), and then with water for 24 h, to extract inorganic contaminants. The removal of these impurities was confirmed by gravimetrically after drying in a circulating air oven (60 °C).

2.2.3 Oxidation of luffa fibers: The dewaxed fibers (2 g) were oxidized with an aqueous potassium dichromate ($Cr_2O_7^-$) solution, which was prepared by reactions between potassium dichromate (5 mmol) and acetic acid in aqueous medium (100 ml, pH ≈ 2). The most important method for oxidation of lignocelluloses materials are acid catalyzed reaction between lignocellulosic polymer and potassium dichromate oxidant. It has been observed by visual inspection that during the oxidation reaction, the colour of fiber changed from white to reddish yellow. The reddish yellow coloured fibers were washed with deionized water until neutrality. The plausible oxidation reaction of lignin and cellulose macromolecule on luffa fiber surface is shown in Scheme 1.



Scheme 1 The oxidation reactions of lignin and cellulose macromolecule in untreated luffa fiber

Scheme 2 The grafting of furfuryl alcohol chain onto oxidized luffa surfaces



2.2.4 Grafting of furfuryl alcohol on oxidized luffa fiber: The oxidized luffa fiber (2 g) impregnated with furfuryl alcohol (11.35 g) was heated at 100 °C for 2 h in presence of N_2 flow. The excess of furfuryl alcohol was removed by washing using ethanol. Then, the fibers were dried at 50 °C for 24 h. The fiber was named as FA grafted luffa fiber. The weight gain was observed 13.97 % gravimetrically. The grafting of FA chain structure onto luffa fiber is shown in Scheme 2.

3 Instruments and Measurements

3.1 Ultraviolet-Visible Spectroscopy

Ultraviolet-visible absorption spectra were recorded in the full range of wavelength 200–1000 nm on a Perkin-Elmer (model-Lambda 25) spectrometer. The oven-dried untreated and various treated *Luffa cylindrica* fiber were ground into fine powder of particle size 2 μm or less and then dissolved in 1,4-dioxan-water (9:1, v/v) mixture having concentration 1×10^{-3} mol/l. The solution obtained after dissolving the lignocelluloses moieties of the fibers in the solvent mixture was used for this analysis.

3.2 Dynamic Contact Angle and Surface Energy Measurements

The contact angles of untreated, alkali treated, and FA grafted luffa fibers were measured with a DCAT-21 Tensiometer (Data Physics, Germany) using four different probe liquids: water, glycerol, ethylene glycol, and 1-bromo naphthalene. The contact angle values are listed in Table 2. The data reported did changing their position of fiber make averages of at least five measurements. The surface energies of these liquids are listed in Table 2 (Gassan et al. 2000). The polar and dispersed components of the fiber surface energy were estimated from the contact angle measurements using the method of Owens-Wendt-Rabel-Kaelbe (OWRK) (Owens and Wendt 2003) shown in Eq. (2).

Table 2 Surface parameters of probe liquids

Probe liquid	Grade	γ^d (mJ/m^2)	γ^p (mJ/m^2)	γ_T (mJ/m^2)
Water	Busscher et al.	19.90	52.20	72.10
Glycerol	Busscher et al.	21.20	41.50	62.70
Ethylene glycol	Erbil	29.0	19	48.00
1-Bromonaphthalene	Janczuk et al.	43.7	0.90	44.60

γ^d dispersive component of liquid; γ^p polar component of liquid; γ_T total surface energy of liquid

$$-\frac{(1+\cos\theta)\gamma_L}{2\sqrt{\gamma_L^d}} = \sqrt{\gamma_S^p}\sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + \sqrt{\gamma_S^d} \tag{2}$$

where, θ is the contact angle of the sample with the probe liquid (L); $\gamma^d L$, $\gamma^d L$, and γ_L are disperse, polar and total surface energy of the probe liquid; and $\gamma^d S$, $\gamma^p S$ are disperse and polar components of the surface energy of the tested sample.

3.3 Differential Scanning Calorimetry (DSC) Analysis

The calorimetric measurements were taken from TA instruments, USA, model DSC Q_{10} analyzer in nitrogen atmosphere (gas flow rate—50 ml/min) and at constant heating rate of 10 °C/min from 0 to 450 °C in aluminum pan crimped with a pinhole. Fiber samples of approximately 7.3–8.7 mg were placed. The instrument is calibrated for baseline slope, cell constant and temperature by using standard indium metal. DSC has been used to study the variations in transition temperature on the fiber surface.

3.4 Thermo Gravimetric Analysis (TGA)

Dynamic TGA of untreated, alkali treated and FA grafted luffa fiber was executed in the DTG-60 (Schimadzu, Japan) from 30 to 700 °C in platinum pan at a heating rate of 10 °C/min under dynamic nitrogen atmosphere (30 ml/min) to find out the decomposition, thermal stability and % char residue. For each scan 8–10 mg of fiber sample was taken.

3.5 Mechanical Properties

The tensile properties of untreated, alkali treated and FA grafted luffa fiber were determined using a universal tensile machine (Instron, model—3366, UK) at a strain rate of 1 mm/min and a gripping length of 50 mm at 23 °C ± 1 °C and 58 % relative humidity. The tensile strength was measured according to ASTM D 638.

3.6 Stereo Optical Microscopy (SOM)

The image analysis of untreated, alkali treated and FA grafted luffa fibers were measured by Leica Optical Stereo Microscope (Model: Leica FW4000) by capturing photographs with the help of digital camera (Leica stereo zone ×3.2).

3.7 Scanning Electron Microscopy (SEM)

To study the morphological features of untreated, alkali treated and FA grafted luffa fiber, the tensile test samples were fractured in liquid nitrogen after 15–20 min of freezing in liquid nitrogen. The fractured surfaces were coated with a thin layer of metallic gold in an automatic sputter coater (JEOL JFC-1600) to make the surface conducting and analyzed by a scanning electron microscope (Model—JEOL JSM 6390 LV). The SEM image was captured at the following specifications: accelerating voltage, 20 kV; image mode, secondary electron image; working distance, 20 mm and magnification, 500×.

3.8 Water Absorption Test

Water absorption studies were performed following the ASTM D 570-98 standard. The untreated, alkali treated and FA-grafted luffa fiber bundle was cut into 5 cm in length and weighed near about 0.2 g. The samples were oven dried at 80 °C until a constant weight was obtained. Two samples of each untreated and various treated fibers were submerged in distilled water at different temperatures, 25 and 60 °C. The samples were removed from water after certain period of time and weighed in a high precision balance and then submerged again in water. The content of water was calculated by the weight difference. When the content of water remained invariable in the samples, they were removed and curve were drawned in order to determine the water absorption character followed by mechanical properties.

4 Results and Discussion

4.1 *Effect of Chemical Treatment of Fiber Surface*

To enhance interfacial bonding with matrix material and to reduce moisture absorption, surface treatments (alkalization and furfurylation) of the luffa fibers were performed. Chemical treatments may activate the functional groups of lignocellulosic components of fiber polymer or can introduce new moieties that can effectively interlock with the matrix. An important point to consider is that the reagents used in chemical treatment cannot be too expensive, and ideally, the treatments must involve a minimum number of compounds obtained from nonrenewable sources.

Alkalization increased a number of possible reactive sites and allows better fiber wetting. Alkalization has an effect on chemical composition of the luffa fibers, degree of polymerization and molecular orientation of the cellulose crystallites due to removal of cementing substances like lignin and hemicellulose. As a result, it had a long-lasting effect on the mechanical properties of luffa fibers, mainly on fiber strength and stiffness (Demir et al. 2006; Seki et al. 2011). The dispersion of KOH on fiber surface was examined using ultraviolet-visible spectroscopy, thermomechanical and wetting analysis. The weight changes of the fibers after alkali treatments were determined gravimetrically and a loss of weight was observed near 2 %.

The fiber dewaxing allows removal of waxes and some other low molecular weight species from fiber surfaces, preventing weakening of the interactions at the interface of fiber/matrix. As consequences of acetone and then water extraction, a loss of weight was observed near 1.5 %. Furfuryl alcohol (FA) was chosen as reagents because these alcohols can be obtained from renewable sources. The untreated luffa fiber was selected for grafting furfuryl alcohol followed by oxidation with potassium dichromate generating *ortho*- and *para*-quinones on its surface. By visual inspection, it was observed that the fibers had turned reddish-yellow after oxidation reaction. It was then washed with water until neutrality. In this modification, the effects of the polymeric coating layer as coupling agent onto luffa fiber were concluded. The reaction with dichromate ($Cr_2O_7^-$) solution and furfuryl alcohol was studied (Saw et al. 2013) and percent graft yield for luffa fiber was found to be 13.97 % using the following Eq. (3):

$$\%\,\text{Graft Yield} = \frac{\text{Dry weight FA grafted luffa} - \text{Dry weight untreated luffa}}{\text{Dry weigh untreated luffa}} \tag{3}$$

In our continuous interest to elaborate composites based on epoxy resins and various modified natural fibers, we here present results obtained with chemically modified luffa fibers. The aim of study was to submit the luffa fibers to suitable chemical process conditions than those used in the bagasse and coir fibers, aiming to improve both fiber/matrix interactions at the interface and the composites properties as described in our previous report (Saw and Datta 2009; Saw et al. 2012).

4.2 Analysis of Fiber Surface Modification by Ultraviolet-Visible Spectroscopy

The ultraviolet-visible absorption measurements of untreated and chemically treated luffa fiber were carried out using dioxane-water mixture (9:1, v/v). This solvent mixture dissolves the lignocellulose, but limits the wavelength range to above 240 nm, due to dioxane absorption. Ultraviolet-visible spectra of the untreated and chemically treated luffa fiber are shown in Fig. 1. It has been observed that the ultraviolet spectrum of the untreated fiber had absorption maxima only at less than 300 nm, while $Cr_2O_7^-$ oxidized fibers showed two absorption peaks, one at 355 nm and other at below 300 nm. The absorption maximum at 355 nm is known to be caused by π–π^* transition of quinones in the lignocellulose (Lin and Dence 1992). Observation of this absorption maximum is in accordance with the expected formation of *ortho*- and *para*-quinones. The ultraviolet-visible spectrum of the FA-grafted luffa fibers exhibit intense absorption in the visible region (>400 nm), which is indicative of formation of complex quinonoid structures, as expected from Diels-Alder reactions between quinones and conjugated dienes (i.e., furfuryl alcohol) (Nair and Kumar 1996). The absorption spectra of alkali treated fibers also observed in visible region due to the formation of potassium compounds or ethoxide of lignocelluloses materials.

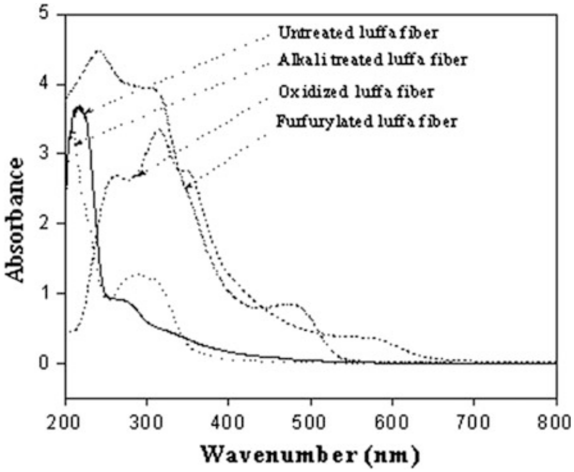


Fig. 1 The ultraviolet-visible spectra of untreated and chemically treated luffa fibers

Table 3 Contact angle (°) and surface energy values (mJ/m^2) of the untreated, alkali treated and FA-grafted luffa fibers

Luffa fibers	Contact angle				γ^p	γ^d	γ_T	χ_p
	Water	Glycerol	EG	1-Br Npth				
Untreated	71.4	58.3	52.8	38.3	14.98	21.77	36.75	0.40
Alkali treated	76.2	55.4	49.1	35.7	11.60	22.64	34.24	0.33
FA-grafted	86.7	45.7	44.2	30.7	13.28	24.83	38.11	0.34

γ^d surface energy of dispersive component of fiber; γ^p surface energy of polar component of fiber; γ_T total surface energy of fiber; χ_p polarity of fiber surface; *EG* ethylene Glycol; 1-Br *Npth* 1-bromo naphthalene

4.3 Determination of Surface Energy by Contact Angle Measurement

The values of the dynamic contact angle measured with the different probe liquids and those of the different components of the surface energy (polar γ^p, dispersive γ^d and total γ_T) are shown in Table 3. As seen in Table 3, both alkali treatment and FA modifications increase the water contact angle of luffa fibers but, decrease the contact angle with other low polar liquids like glycerol, ethylene glycol and 1-bromo naphthalene, indicating the reduction of hydrophilic tendency of the chemically treated fibers. The decrease of hydrophilic character could be explained by the diminution of polar groups such as hydroxyl groups during alkalization and the introduction of aromatic benzene ring as a thin polymeric coating at the surface of the FA-grafted fibers. The data of Table 3 shows the total surface energy is increased after furfurylation of the fibers. This increase is mainly due to increase of the dispersive component of the free energy (γ^d) of the grafted fibers. Introduction of FA polymeric layer on the fiber surface through grafting could increase the γ^d value (Megiatto et al. 2007). Moreover, the FA-grafting leading to low values of γ^p is an indication of the lower availability of the polar hydroxyl groups on the fiber surfaces led to a decreasing of the polar characteristics of the fiber surface. The variations observed on surface free energy for untreated and chemically treated luffa fibers are comparable with values reported by other authors with natural fibers such as jute, flax or sisal get values in the range from 30 to 50 mJ/m^2 (Mohanty et al. 2000; Aranberri-Askargorta et al. 2003).

4.4 Effect of Surface Treatment on the Thermal Energy of Luffa Fiber

Figure 2 shows the DSC curves of untreated, alkali treated and FA-grafted luffa fibers. Some differences could be noted between the curves of chemically treated

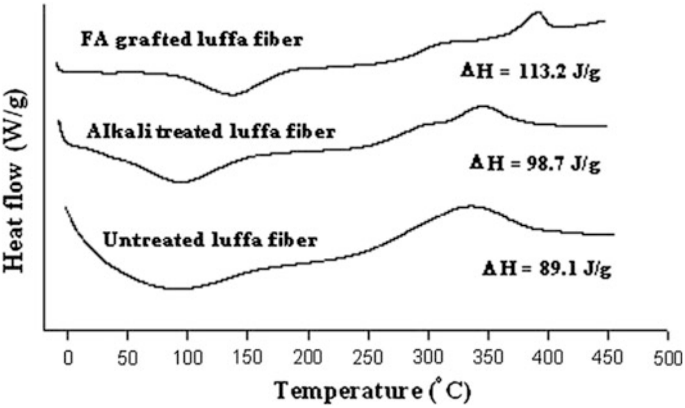


Fig. 2 The DSC curves of untreated and chemically treated luffa fibers

fibers and those of untreated fibers. In Fig. 2, the untreated fibers show an endothermic peak near 97 °C, which is shifted to 115 and 127 °C for alkali treated and FA-grafted luffa fibers, respectively. These endothermic peaks could be related to the release of water and other volatiles. However, these peaks could also be attributed to changes in heat capacity of fiber polymer when the polymer reaches its glass transition temperature (T_g) (Rials and Glasser 1984). The shifting of these endothermic peaks after chemical modification confirms the successive modification of the fiber surface. The DSC curves in Fig. 2 shows an exothermic peak at around 350 °C for the untreated and treated luffa fibers, probably due to the decomposition of celluloses fragment. These peaks are shifted at higher temperature after successive modification of luffa fibers. There is another exothermic peak observed in FA grafted fiber at above 400 °C are corresponding to the decomposition of lignin component as well as related to the decomposition of furan rings of that macromolecule.

4.5 *Effect of Surface Treatment on the Thermal Stability of Luffa Fiber*

TGA of chemically treated and untreated luffa fiber have been studied as a function of % weight loss, thermal stability and char residue versus temperature as shown in Fig. 3 and Table 4. Cellulosic constituents in fiber polymer degrade by dehydration, glycogen formation, and depolymerization. In the case of luffa fiber, two-stage decomposition has been found. The former stage is attributed to loss by dehydration and volatilization processes, whereas the latter stage is attributed to loss by depolymerization, delignification, and oxidation of the char (Kaith et al. 2009). The chemically treated fiber showed two-stage decomposition. The first stage refers to

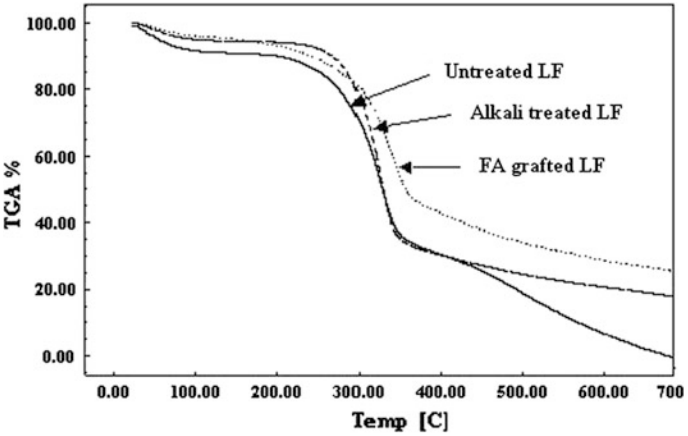


Fig. 3 The TGA thermograms of untreated and chemically treated luffa fibers

Table 4 Thermogravimetric analysis of untreated and chemically treated luffa fibers

Fiber sample	$^{a}T_{o}$ (°C)	$^{b}T_{max}$ (°C)	$^{c}T_{f}$ (°C)	% residue
Untreated luffa fiber	234.21	252.34	700	0.5
Alkali treated luffa fiber	273.54	284.37	700	25.12
FA grafted luffa fiber	304.73	337.48	700	32.33

[a]onset degradation temperature, [b]temperature of maximum rate of mass loss, [c]final degradation temperature

loss of moisture, decarboxylation, and chain scissions while the second stage pertains to breaking up of crystallites and covalent bonds that have raised the final degradation temperature. Thus, it is evident from the TGA data that FA grafted fiber is thermally more stable than untreated fibers. This may be due to the incorporation of FA chains on the backbone polymer, either through covalent bonds or mechanically, confirming the additional strength of the fiber (Princi et al. 2005; Salam 2005).

4.6 Effect of Surface Treatment on the Mechanical Properties of Luffa Fiber

The tensile properties like the tensile strength, tensile modulus and extension at break of untreated, alkali treated and FA-grafted luffa fibers are shown in Table 5. For each type of fiber, a minimum of 10 fibers is tested and the average values are determined. The chemically treated fibers show an appreciable increase in tensile properties when compared to untreated fiber. The chemical treatment done by potassium hydroxide (KOH) solution is the disruption of hydrogen bonding in the

Table 5 Effect of surface modification on tensile properties of luffa fibers

Fiber sample	Tensile strength (MPa)	Tensile modulus (MPa)	% extension
Untreated luffa	178.2	4198.59	3.12
Alkali treated luffa	192.7	5173.63	1.93
FA grafted luffa	226.4	5866.72	1.74

network structure, thereby increasing surface roughness. This treatment removes a certain amount of lignin, wax, and hemicelluloses of fiber cell wall, depolymerizes cellulose, and exposes the short-length cellulose fibril. The ionization of hydroxyl groups of fibers into alkoxide increases the fiber strength and stiffness and hence, an increase in tensile properties (Paul et al. 2010). The SEM observation reveals the fact. However, grafting of FA brings about an increase in the stress value and modulus (226.4 and 5866.72 MPa). About 27 % increase in maximum stress at break and 40 % increase in modulus are observed for FA-grafted fibers. The reason for the increase in the strength and modulus after grafting FA may be due to orderly arrangement of grafted units onto fiber surface and hence degree of crystallinity. It was found that the extension at break (%) value decreases more by 44.23 % with FA-grafted fibers. This may be due to the large increase in the brittleness of the fiber by grafting with FA (Trindade et al. 2005).

4.7 Optical Image Analysis

The optical view of surface morphology for untreated, alkali treated and FA grafted luffa fibers were shown in Fig. 4(a–c, respectively). The physical appearance of the fibers before and after surface treatments gives an idea about wettability of fiber with resin. After alkali treatment, the fiber surface becomes rough and reduces its diameter. In Fig. 4c, clearly were seen the grafting of FA around the fiber surface extending the capabilities of fiber with resin. It may due to loss of natural protecting wax layer, lignin and hemicellulose.

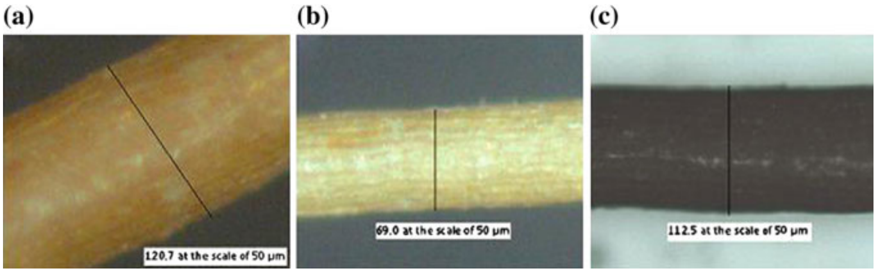


Fig. 4 The optical micrographs of **a** untreated, **b** alkali treated, and **c** FA grafted luffa fiber

Figure 4 shows the effect of chemical treatments on the diameter of both alkali treated and FA grafted fibers with improved fineness. Surface treatment reduces the average diameters of alkali treated fibers from 121 to 69 µm. This is due to the dissolution and leaching of alcohols, lignin component, wax, hemicellulose, and oils (Paul et al. 2010). The alkali treatment decreased the fiber weight by 2 % and the diameter was reduced by 35 % as shown in Fig. 4b. The weight and the diameter of fiber was increased by 14 and 50 %, respectively as well as color of fiber turned to yellow during oxidation and to brown on grafting furfuryl alcohol as observed visually in Fig. 4c.

4.8 Morphological Studies of Treated and Untreated Tensile Fractured Fiber Surfaces

SEM provides an excellent technique for examination of fiber surface morphology. The physical appearance of the fibers before and after surface modification gives an idea about wettability of fiber with resin. Figure 5 (micrographs a–c, respectively) shows the SEM micrographs of untreated, alkali treated and FA grafted luffa fiber. The shape of fiber seems long strips and has not a flat surface. A large number of grooves or channels run more or less parallel along with the longitudinal direction of fibers. There are waxes, oils and small particles providing a protective layer on fiber surface as observed in Fig. 5a. Figure 5b shows a larger number of surfaces cracks and separation of fiber bundle, compared to Fig. 5a. Very interestingly, the intercellular gaps are clearly distinguished and the unit cells are partially exposed which was not obvious in the untreated luffa fiber. These features might result from the partial removal of wax and oily substances and loss of cementing materials such as lignin and hemicelluloses during treatment with potassium hydroxide. In Fig. 5c, clearly there were seen the grafting of furfuryl alcohol around the fiber surface extending the capabilities of fiber with resin. After furfurylation, the fiber surface

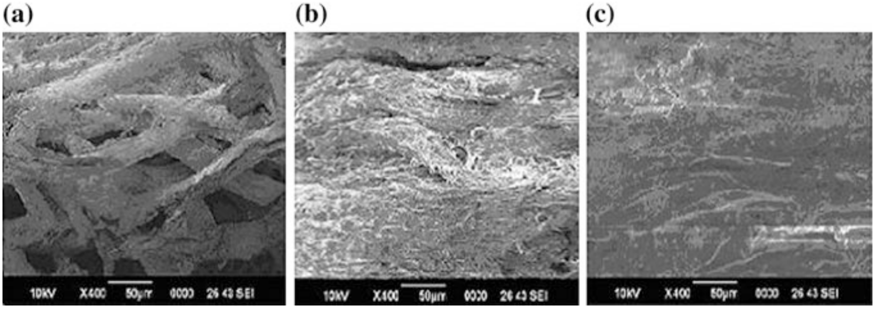


Fig. 5 The SEM micrographs of **a** untreated, **b** alkali treated and **c** FA-grafted luffa fibers

becomes smooth and uniform reduces its diameter. It may be due to loss of natural protecting wax layer, lignin and hemicelluloses (Rout et al. 2002).

4.9 Effect of Fiber Surface Treatment on Water Absorption Properties

Several factors are to be considered in the manufacture of natural fibers reinforced polymer composites. The most significant factor is the degradation study of the composites under atmospheric conditions such as humidity, sunlight or microorganisms. The poor resistance of the fibers to water absorption can have undesirable effects on the composites. Therefore, it is important to study in detail the water absorption behavior in order to estimate not only the consequences that the water absorbed may have, but also how this water uptake can be minimized in some way (Thwe and Liao 2002).

Natural fibers absorb more water compared to synthetic fibers, wood and polymers. Water uptake leads to degradation of the fibers. The effect of this absorbed moisture is to degrade the properties such as tensile strength. The difference in mechanical properties due to treated and untreated fibers are reported elsewhere. Based on experiments on water uptake and assuming one-dimensional diffusion based on Fick's law, several researchers have talked about characteristics of water absorption. When absorption follows Fick's law, it is referred to as "Fickian" diffusion and when it deviates from the Fick's law, it is referred to as "non-Fickian" or anomalous diffusion. Water diffusion in natural fibers has been shown to be Fickian as well as non-Fickian in character. In general, water diffusion in natural fiber depends on factors such as fraction of fibers, inherent absorption properties of the fibers, structural composition, humidity, and on environmental conditions such as temperature.

Water absorption of untreated, alkali treated and FA grafted luffa fibers were monitored at 25 and 60 °C in a static water bath at various time intervals. Figure 6 shows the variation of water absorption with increasing time for all treated and untreated fibers at different temperatures. A similar behavior of water uptake was observed for all the fibers. A greatly reduced relative water absorption occurred after fiber surface treatments. It can be observed from this figure that the water absorption in the fibers sharply increased with time up to 30 h followed by gradual approaching a saturation point (or equilibrium sorption), beyond which no more water was absorbed till 120 h. The water absorption of the FA-grafted fibers reaches to equilibrium point immediately after 30 h, while the untreated fiber still continues to soak water slowly (Fig. 6). The rate and amount of water absorption decreased in order of untreated being the highest, followed by alkali treated, followed by FA-grafted being the lowest. The untreated fibers showed the highest water absorption of about 16 and 20 % at 25 and 60 °C, respectively. The higher bonding between hydrophilic sites and water molecules in untreated fiber leads to

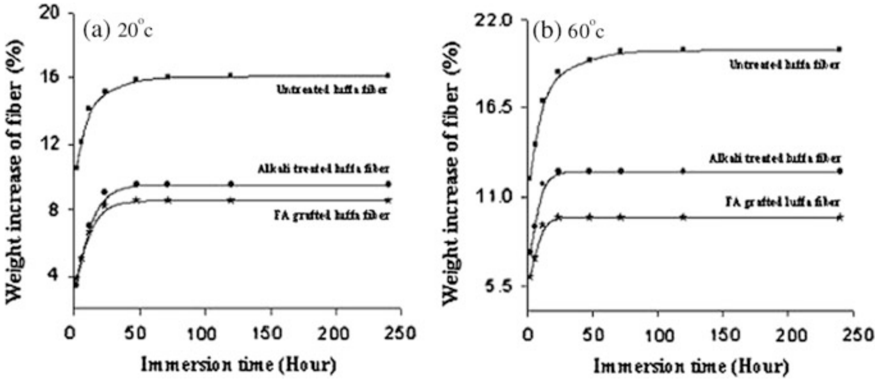


Fig. 6 The percent of water absorption curves as a function of immersion time for untreated and various treated luffa fibers at different temperature i.e. **a** 20 °C and **b** 60 °C

higher diffusion coefficient causes higher water absorption (Megiatto et al. 2008). The alkali treated luffa fibers showed comparable water absorption of 9.52 and 12.56 % at 25 and 60 °C, respectively. Thus, alkalization of luffa fibers reduced the polar groups in fiber by replacing some of the hydroxyl groups on the surfaces of the fibers. The FA-grafted luffa fibers yielded a value of 8.57 and 9.78 % at 25 and 60 °C, respectively. These results indicate lower hydrophilic nature of the FA-grafted fibers. Thus, the introduction of polymeric coating of furfuryl alcohol (aromatic nature) onto fiber surface layer made the fiber more hydrophobic (Alvarez et al. 2004; Bismarck et al. 2002).

5 Conclusions and Future Perspectives

In conclusion, we have described simple methods to reduce the hydrophilicity of natural fibers with increased physical, mechanical and thermal properties. Chemical treatments confirm the reduction of hydrophilic character of the fibers, thus treated fibers have good adhesion with hydrophobic resins. The ultraviolet-visible absorption and contact angle measurements reveal that treated fibers shows the removal of non-cellulosic constituents and improved the crystallinity index of cellulosic constituent. It has been found that furfurylation has a diminutive effect on the crystalline structure of luffa fibers. The increase in char residue at 700 °C from 0 to 25 % for alkali treated and 32 % for FA-grafted luffa fibers place it also in the category of engineering materials. The morphology of treated fibers shows the separation of fibrils along with smooth surface. The luffa fiber surfaces is found rough on alkali treatment and oxidation, whereas grafting of FA resulted in a smooth and shiny surface due to bioprocessing or polymeric coating. Since both treatments result in enhanced thermal stability and crystallinity with different morphological structure and reduced hydrophilicity, so modified fibers can be used as fillers in composites for enhancement in mechanical properties. Effort is being made towards the possibility of harnessing, converting and utilization of agro waste into most effective reinforcement for polymer composites and solving problem in environment. This emerging cash crop will improve the economies of many nations in the nearest future because of its numerous potentials. It further confirms the improvement in the interfacial adhesion after chemical treatments. It was found to be more effective in improving the interfacial adhesion in treated fiber surfaces.

For future application of luffa fiber, the hybrid composites could be studied with other plant fibers that complement them. The thermal insulation performance should be detected further. Also, the optimization design of the luffa fiber hybrid composite must be performed. The dielectric and corrosion studies of composites are need to be investigated for finding their potential applications as dielectric materials.

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Characterization and Properties of Rattan Fibre/Natural Rubber Biocomposites

Komethi Muniandy, Nadras Othman and Hanafi Ismail

Abstract Natural rubber (NR) composites were prepared by the incorporation of Rattan (*Calamus Manan*) fibre (RF) at filler loading range of 0–30 phr into a NR matrix with a laboratory size two roll mill. Degradation of rattan fibre filled natural rubber composites (NR/RF) is studied by conducting natural weathering and soil burial test as a function of 3-aminopropyltrimethoxysilane (AMEO) as coupling agent and partial replacement of RF with commercial fillers such as carbon black, mica and calcium carbonate. 1 phr of AMEO was added into the NR/RF composites, while, the RF/commercial filler ratio was fixed to 30 phr. The natural weathering and soil burial test were carried out in the outdoor exposed rack and garden soil respectively, for six months. Deterioration in the properties of NR/RF composites was observed for both soil buried and weathered composites which indicates that the composites had undergone biodegradation and photo-oxidative degradation process with respect to soil burial and natural weathering tests. The degradation of the composites was further confirmed by SEM and FTIR studies.

Keywords Natural rubber · Rattan · Biodegradation · Natural weathering

1 Introduction

Lately, the ever-growing worldwide litter problems have raised environmental consciousness among consumers, manufacturers, and governments. Thus, the principal of sustainability and environmental impacts are becoming the factors to be considered in the development of the next generation materials and products, alongside with the cost and technical performance. Composite materials are also included in this new concept. Nowadays, most manufactures are planning and working towards making their product 'greener' to the maximum possible extent.

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Consequently, in recent years, natural fibres have attracted the interest of many researchers to be used as reinforcement in polymer composites. Natural fibres are biodegradable, environmentally friendly, cause no health threats, cheap, low density and help to solve the environmental pollution by discovering new usages for waste materials. Besides, natural fibres provide an opportunity for many growing countries to utilize their own natural resources in their composite manufacturing as these natural fibres are readily available in their countries (Hassan et al. 2010; Satyanarayana et al. 2009).

This new generation of natural fibre reinforced polymeric products which are sustainable and environmentally friendly can compete with current products in the market which are dominated by non-renewable materials as well as commercial fillers in applications such as packaging, furniture, automotive and consumer goods (Mohanty et al. 2005). It is not important to produce 100 % greener materials immediately. A possible way is to combine both non-renewable (polymer) and renewable resources (natural fibre) to manufacture a valuable product that has the required cost-performance properties for real world applications. Thus, the challenge to scientists and engineers is to make the natural fibre based polymer composites revolution a reality and compete with synthetic composites.

For this research study, the use of waste rattans as filler in natural rubber composites has been explored. Rattan canes are much valued in furniture industries and contribute for a significant proportion of the export incomes for Malaysia. However, these furniture industries produce larger amount of rattan waste materials and become problematic to the environment through open burning and discarding illegally. The wastage rate could be as high as 10 % and financially as much of USD 0.20 per cane is wasted (Ariffin et al. 2001). The natural properties of rattan cane such as lightweight, strong and durable also has attracted the attention of rattan to be used as filler besides the larger amount of waste rattan. Successful use of waste rattan as filler will help to produce a more environmentally friendly product.

Natural fibres experience serious problem in polymer composites due to their polarity nature which results in poor compatibility with hydrophobic matrix. This poor compatibility causes a decline in the mechanical properties of the composites and the effect is increased at greater filler loading. For that reason, different approaches have been applied to overcome the poor compatibility and improve the properties of natural fibre reinforced polymer composite. Coupling agents and hybrid composites are among the most common approaches. Hybrid composites are made to gain benefit from different properties of the fillers involved to give a synergistic enhancements in the properties of a composite. For instance, a combination of natural fibre and carbon black in a rubber composite provides comparatively inexpensive composites owing to the low cost of the natural fibre. At the same time, the mechanical properties are improved by the excellent stiffness of carbon black (Matthews and Rawlings 1999). Coupling agents are used to overcome the poor compatibility by enhancing the wettability of natural fibre by polymers and promote interfacial adhesion. Coupling agents contain bi-functional groups. This groups help to form linkages between natural fibre and polymer matrix, thus a uniform composite structure is formed (Taj et al. 2007; Yan et al. 2005).

Thus, research on improving the properties of rattan fibre-filled natural rubber (NR/RF) composites is studied by adding silane coupling agent which is 3-aminopropyltrimethoxysilane (AMEO) and also partially replacing commercial fillers into NR/RF composites. These studies have been reported in previous research papers (Muniandy et al. 2012b; Ismail et al. 2011). As extension of previous papers, this book chapter highlights on the degradation of rattan fibre-filled natural rubber composites by soil burial and natural weathering test. The degradation properties are studied on both NR/RF composites added with silane and NR/RF composites partially filled with commercial fillers by performing tensile test, Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM).

Natural rubber (NR) is a versatile raw material with a very high structural regularity that offers the material with some unique and valuable characteristics known as "strain induced crystallization", where the rubber has the ability to crystallize under strain. This means, upon stretching NR, crystallization occurs and this reinforces the rubber so that it resists deformation and enhances strength. Thus, the natural rubber has high tensile strength (Chapman 2007). Natural rubber is biodegradable but it is less degradable compare to other natural polymers. This is due to the activities of microorganisms which are very low in normal ecological conditions (Rose and Steinbuchel 2005; Shubhra et al. 2010). Rattan filler and natural rubber are biodegradable, thus, a composite made from these materials also be expected to be biodegradable.

Natural weathering is a practical approach of collecting information regarding material performances under natural outdoor environments. Polymeric materials are exposed to various types of environmental conditions directly or indirectly throughout their service such as sunlight, heat, oxygen, moisture and ozone (Noriman et al. 2010). Environmental degradation for products made of natural rubber is primarily caused by oxygen and ozone molecules. It is because the natural rubber consists of unsaturated backbone which can be easily attacked by these molecules. These molecules attack the natural rubber through different chemical mechanisms, causing different effects on the end properties of natural rubber. Ozone degradation is a surface phenomenon which results in discoloration and cracking of rubber, whereas, oxygen degradation results in hardening or softening of the rubber (Datta and Huntink 2008).

2 Experimental

2.1 Materials

Natural rubber grade STR 5L was supplied by Rubber Research Institute, Malaysia. Other compounding ingredients such as sulphur, zinc oxide, stearic acid, *N*-cyclohexyl-2-benzolthyazolsulfenamide, carbon black (N330), calcium carbonate,

Table 1 Chemical composition, physical and mechanical properties of rattan, *Calamus Manan* (Ali and Khoo 1995)

Properties		Approximate value
Physical properties	Specific gravity	0.55
	Density	0.54 g/cm^3
Mechanical properties	Tensile strength	690 kg/cm^2
	Bending strength	636 kg/cm^2
	Compressive strength	216 kg/cm^2
	Modulus of elasticity	31,302 kg/cm^2
Chemical composition	Holocellulose	78.43 %
	Lignin	21.97 %
	Ash	1.37 %
	Hot water soluble	6.01 %
	Cold water soluble	3.63 %
	1 % alkali soluble	22.47 %
	Alcohol-benzene soluble	2.9 %

mica, 3-aminopropyltrimethoxysilane (AMEO) and 2,2 methylene-bis-(4-methyl-6-tert-butylphenol) were purchased from Bayer (M) Ltd. Rattan (*Calamus Manan*) wastes were collected, cleaned, grounded and sieved to obtain rattan fibre with an average particle size less than 180 µm. The chemical compositions, physical and mechanical properties of rattan are described in Table 1.

2.2 Sample Preparation

Mixing and compounding of natural rubber composites were carried out in a laboratory model two roll mill, model XK-160. The overall mixing time was maintained to a minimum of about 25 min to prevent damage of the rubber compounds at the initial stage. The rubber compounds were moulded into sheets using hot press machine with cure time, t_{90} at 150 °C which was obtained from Monsanto Rheometer, model MDR 2000. The flow chart of preparation of rattan fibre-filled natural rubber composites is shown in Fig. 1.

2.3 Testing

2.3.1 Weathering Test

The natural weathering test was performed for 6 months in accordance to ISO 877.2 Dumbbell shaped samples were arranged on the exposed rack (exposed to all environmental effects) at inclined angle of 45 °C and placed at an open space to

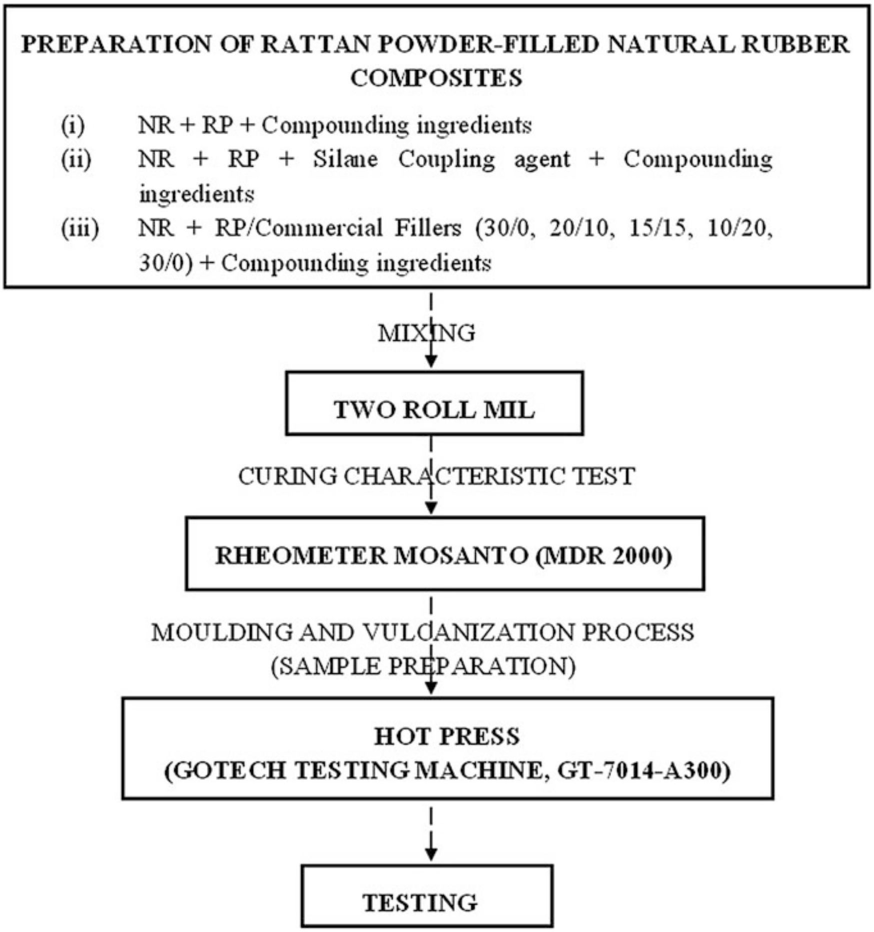

Fig. 1 Flow chart of preparation of NR/RF composites

avoid being overshadowed by other objects. Samples were withdrawn after six months of natural weathering. The degradation was measured by evaluating tensile properties before and after the weathering test. Tensile test were conducted in accordance to ASTM D 412 by Instron Universal testing machine, model 3366 at a constant rate of 500 mm/min. Five samples were tested and average three results were reported.

2.3.2 Soil Burial Test

Soil burial test was performed for 6 months. Dumbbell-shaped samples were arranged in a polybag with decomposed soil and buried in garden soil. Samples were withdrawn after six months of soil burial test. The degradation was measured by evaluating tensile properties before and after the soil burial test. Tensile test were conducted in accordance to ASTM D 412 by Instron Universal testing machine, model 3366 at a constant rate of 500 mm/min. Five samples were tested and average three results were reported.

2.3.3 Scanning Electron Microscopy (SEM)

Analysis on the surfaces of the natural weathered and soil buried sample were performed using a scanning electron microscopy (model, Zeiss Supra 35vp). The surfaces of samples were sputter coated with gold to avoid electrostatic changing and poor image resolution. The degrees of the degradation of samples were assessed from the micrograph.

2.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

The chemical changes in natural weathered and soil buried samples were detected using Fourier-transform infrared spectroscopy (Perkin Elmer System 2000). The FTIR spectra were recorded in the range of 550–4000 cm^{-1} wave numbers with an average of 24 scans.

3 Results and Discussion

3.1 Characterization of Rattan Fibre

The particle size of the rattan fibre (RF) was analysed and the result obtained from the particle size analysis is displayed in Fig. 2. The particle size distribution of RF fell in the range of 0.2–180 µm. The mean particle size, D (v, 0.5) was 24.84 µm. The D (v, 0.1) is 2.39 µm signifying that 10 % of the RF are smaller than this diameter. Whereas, D (v, 0.9) is 73 µm which indicates 90 % RF were noticed smaller than this diameter. The morphology of RFs are illustrated in Figs. 3 and 4. From Fig. 3, it can be observed that the RFs do not have an exact shape, size and length. They vary to each other in size, shape and length. The diameters of few RFs are shown in Fig. 4, proved the particle size of the rattan fibres are less than 180 µm.

The presence of functional groups in RF was identified using Fourier Transform Infrared (FTIR). The FTIR spectrum of RF in the frequency of 400–4000 cm^{-1} was displayed in Fig. 5. The major peaks were found in the region of 3398, 2929, 1736, 1610, 1241 and 1049 cm^{-1}. The strong and broad peak at 3398 cm^{-1} was attributed to the OH stretching from aliphatic (C–OH) and phenolic hydroxyl groups, with

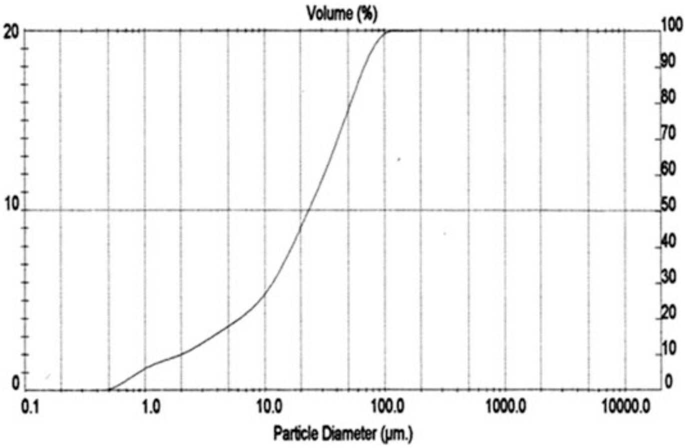

Fig. 2 Graph of particle size distribution of rattan fibre [Reproduced with permission from (Muniandy et al. 2012c), BioResources 7(3):4001]

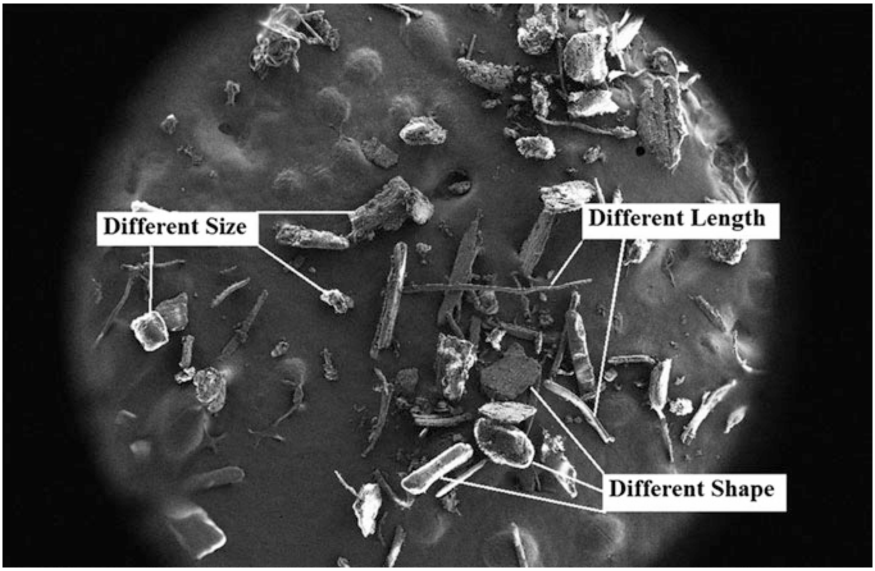

Fig. 3 Scanning electron micrograph of rattan fibre at magnification of 30×

respect to the cellulose or hemicelluloses and lignin. The alkyl (C–H, CH_2, C–CH_3) groups were noticed in the region of 2929 cm^{-1} which were found in the cellulose, hemicelluloses and lignin. The frequency at 1736 cm^{-1} showed a weak intensity which was principally attributed to the carbonyl group stretching from the hemicelluloses (Han and Jung 2008). The existence of alkene C=C bond from lignin was

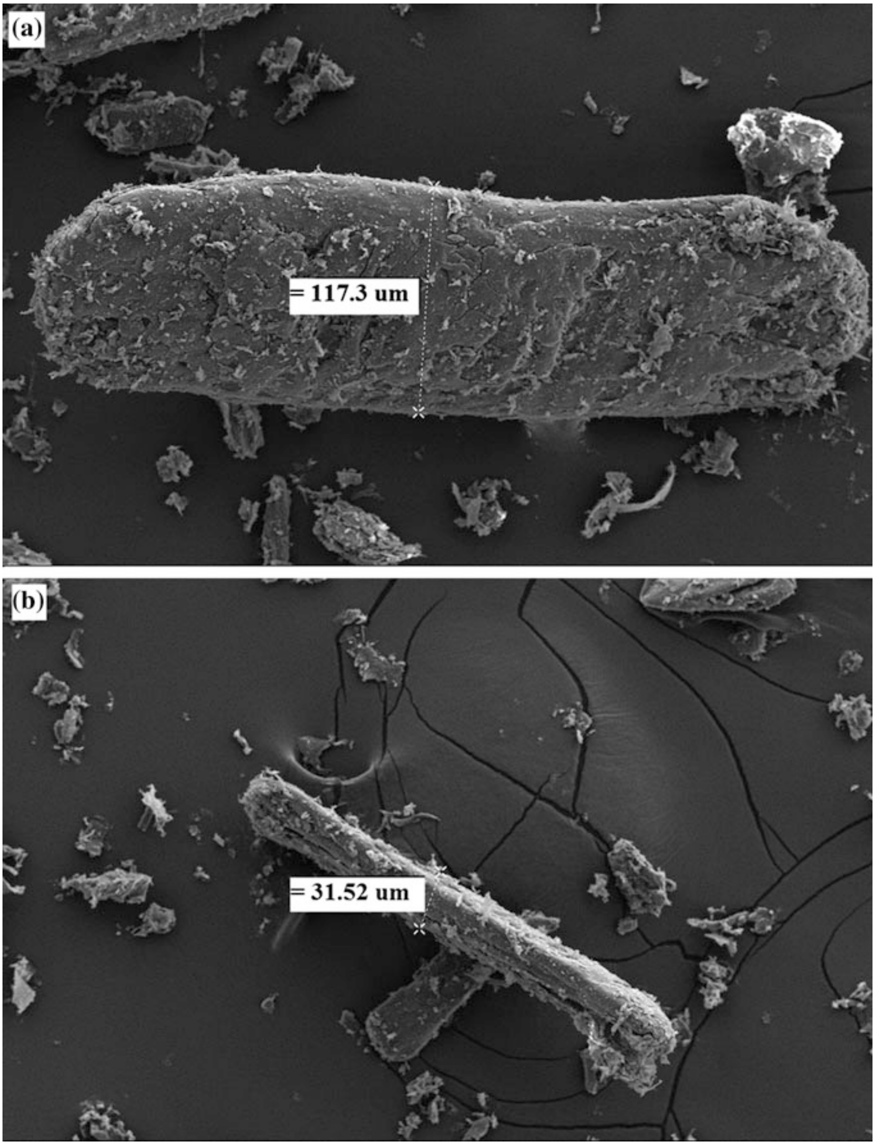

Fig. 4 Scanning electron micrographs of rattan fibre at magnification of 250×

seen in the region of 1610 cm^{-1} which is weak in intensity. A complex lignin-carbohydrate structure with medium intensity was identified in the region of 1241 cm^{-1}. The frequency of 1049 cm^{-1} was detected due to the existence of C–O–C bond whose intensity is sharp and strong (Dai and Fan 2011).

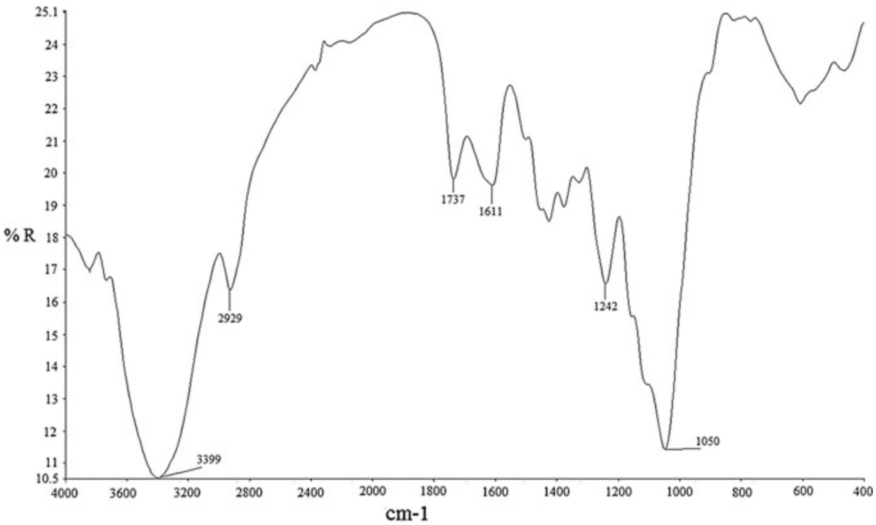

Fig. 5 Fourier transform infrared spectrum of rattan fibre

3.2 *Properties of Natural Weathered NR/RF Composites*

3.2.1 Tensile Properties

The results of tensile properties of unfilled natural rubber (NR) vulcanizate and rattan fibre filled natural rubber (NR/RF) composites with and without silane coupling agent, before and after 6 months of natural weathering are reviewed in Figs. 6, 7 and 8. After 6 months of exposure to natural weathering, deterioration in tensile properties was observed for both NR/RF composites with and without silane in comparison with the un-weathered composites. A severe drop with an average of 90 % for all composites (with and without silane) in comparison with the un-weathered composites was observed for tensile strength, and decrease of about 80 % for the elongation at break. The M100 of composites with silane experienced an average decrement of 22 %, whilst, increment of 4 % was seen for M100 of the composites without silane. These observations were owed to the degradation of natural rubber and the rattan filler upon exposure to the natural environment.

During weathering, degradation of polymer matrix would be initiated by the photo-oxidation process which breaks down the polymer chains with the aid of ultraviolet radiation(Abu Bakar et al. 2005; Beg and Pickering 2008). NR can be easily degraded by the photo-oxidation process as it consist of unsaturated backbone which is susceptible to the attack by the oxygen and ozone molecules (Datta and Huntink 2008). Thus, the decline in the tensile strength of all composites was mainly due to the joined effects of oxidative and ozone degradation. These degradations usually results in cleavage of the rubber chains and intermolecular

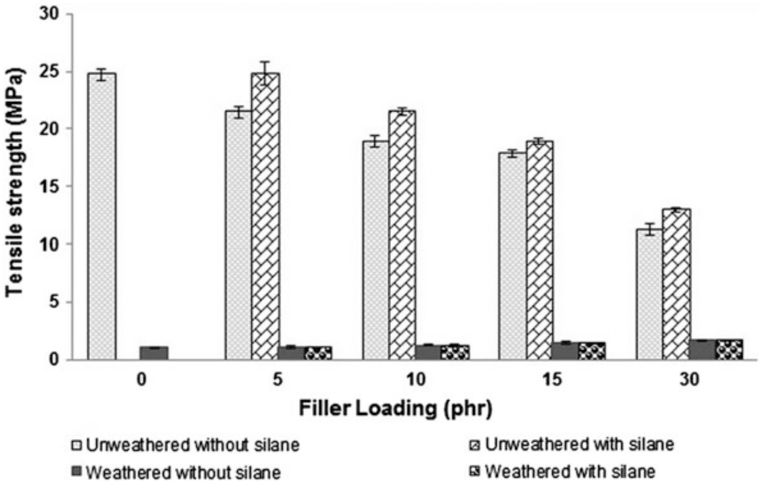

Fig. 6 The effect of filler loading and silane coupling agent on the tensile strength of rattan fibre-filled natural rubber composites after 6 months of natural weathering [Reproduced with permission from (Muniandy et al. 2012c), BioResources 7(3):4004]

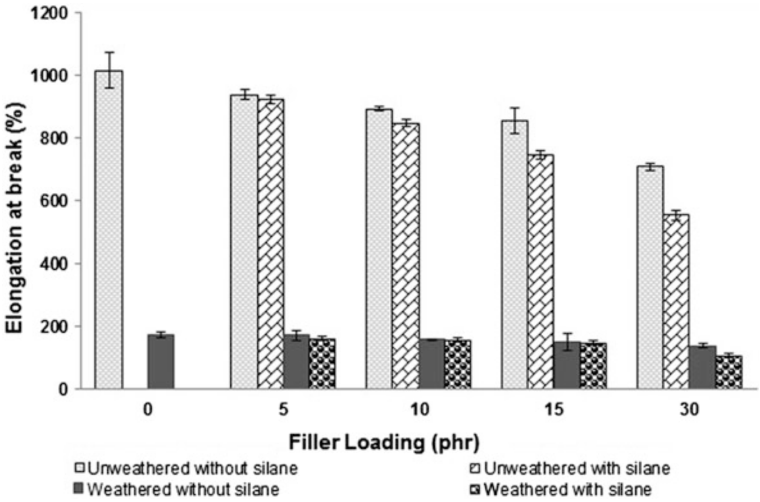

Fig. 7 The effect of filler loading and silane coupling agent on the elongation at break of rattan fibre-filled natural rubber composites after 6 months of natural weathering [Reproduced with permission from (Muniandy et al. 2012c), BioResources 7(3):4005]

crosslinking under UV exposure. Cleavage of the longer molecular chains rises the number of shorter chains which leads to less entanglements, while, intermolecular cross-linking results in material embrittlement (Ismail and Awang 2008; Noriman et al. 2010). As an outcome, natural rubber fails to retain its elastomeric properties

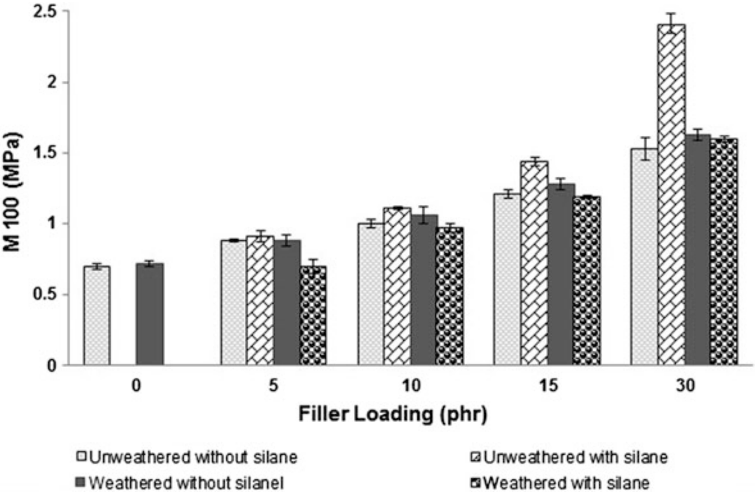

Fig. 8 The effect of filler loading and silane coupling agent on the stress at 100 % elongation (M100) of rattan fibre-filled natural rubber composites after 6 months of natural weathering [Reproduced with permission from (Muniandy et al. 2012c), BioResources 7(3):4006]

and its ability to perform as an effective matrix material to transfer stress. Therefore, the tensile strength reduced after 6 months of weathering as illustrated in Fig. 6.

As stated for tensile strength, the scissioning of rubber chains and embrittlement weakens the slipping nature and rubber chain's ability to stretch. Therefore, the elasticity of composite reduced and composite's resistance to break was reduced as shown in Fig. 7. The M100 (Fig. 8) of the composites is also influenced by the chain scissioning and the crosslinking reactions. An increase was seen for M100 of composites without silane after exposure to weathering. This increment might be credited to some crosslinking reactions due to radical recombination which become dominant throughout the exposure to weathering. Whereas, a decrease in M100 was noted for composites with silane after exposed to weathering. This owed to the cleavage reactions which became dominant and the damage of interaction provided by silane coupling agent, changing the rubber to soft.

Upon extended exposure to outdoor condition, the degradation of composites which initially took place at the outer surface penetrated steadily into the bulk rubber matrix (Ismail et al. 2008). This had led to the formation of surface cracks, causing the RF fillers to be visible and in direct contact with the outdoor condition. Thus, the direct contact of RF fillers was also expected to be degraded by natural weathering. The components of RF which are hemicelluloses and lignin are likely to be responsible for the RF degradation. Hemicellulose was hydrolysed by acidic rain water while lignin degraded by UV radiation. Both of the components were detached by leaching process during the time of weathering. Leaching of lignin was obvious due to the discoloration of the composites. (Pattamasattayasonthi et al.

2011) observed and stated that the reason for discoloration in wood components was due to photo-degradation of the lignin in the wood components.

However, the major effect of weathered rattan fillers on the properties of composites were the visual effects such as surface checking and development of sap staining fungi which can be noticed in SEM micrograph (will be discussed in Sect. 3.2.3) and also the colour change. For example, the results of tensile strength were in a comparable range for all composite, evidencing that the degradation of rattan filler did not add effect to the deterioration of tensile properties. Instead, degradation of the rubber matrix was the major contributor for the drop in tensile properties.

When investigating the effect of filler loading on weathering regardless of with or without silane, it can be concluded that the trend of the results obtained as the filler loading increased is similar to the results obtained before weathering except for the tensile strength. A very slight increase in tensile strength was observed after natural weathering with increasing the filler loading. According to (Crabtree and Kemp 1946), filler has the ability to reduce the rate of oxygen absorption by NR when it is exposed to UV light. This is owed to the tendency of filler which is able make the compound opaque and prevents the diffusion of UV light into the NR matrix. Hence, it is concluded that adding RF into the rubber matrix reduces the inner damage of the matrix and provide additional strength to samples as compared to without or less RF filler.

Referring to Figs. 6, 7 and 8, it is noticeable that the addition of silane has not improved the tensile properties of the composites after weathering compared to before weathering. This proposes that the adhesion formed by the silane between the RF filler and NR matrix had dissolved in rain water and leached off during weathering (George et al. 1998). This phenomenon had further damaged the filler matrix adhesion and resulted in reduction of tensile strength, elongation at break and M100. The damage in the rubber-rattan interaction had been proven by FTIR study (will be discussed later in Sect. 3.2.2).

Apart from the effect of filler loading and silane coupling agent, the addition of the commercial fillers to the NR/RF composites and its influence on the properties of weathered NR/RF composites was studied at a fixed filler loading of 30 phr. The tensile strength and elongation at break of NR/RF/CB, NR/RF/mica and NR/RF/$CaCO_3$ were dropped along with an increase of M100 after the exposure of the composites to the outdoor environment, shown in Figs. 9, 10 and 11. The NR/RF/CB composites exhibited a slight changes in the tensile properties compared to NR/RF/mica and NR/RF/$CaCO_3$, which had a drastic change in the properties. All the composites displayed similar trend in tensile strength, elongation at break and M100 upon the replacement of the commercial fillers as for before the natural weathering.

The drop in tensile strength of NR/RF/CB composites were minimal, thus, the composites able to retain an average of 88 % of its initial tensile strength. Meanwhile, the NR/RF/mica and NR/RF/$CaCO_3$ retained only about an average of 11 and 9 %, correspondingly. On the other hand, NR/RF/CB composites showed the highest retention for E_b, about an average of 99 % followed by NR/RF/mica and

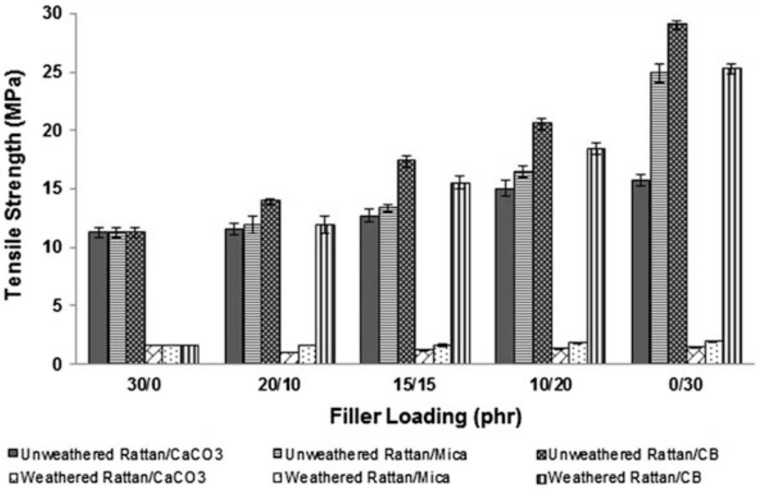

Fig. 9 The effect of partial replacement of rattan fibre with commercial fillers on the tensile strength of natural rubber composites after natural weathering

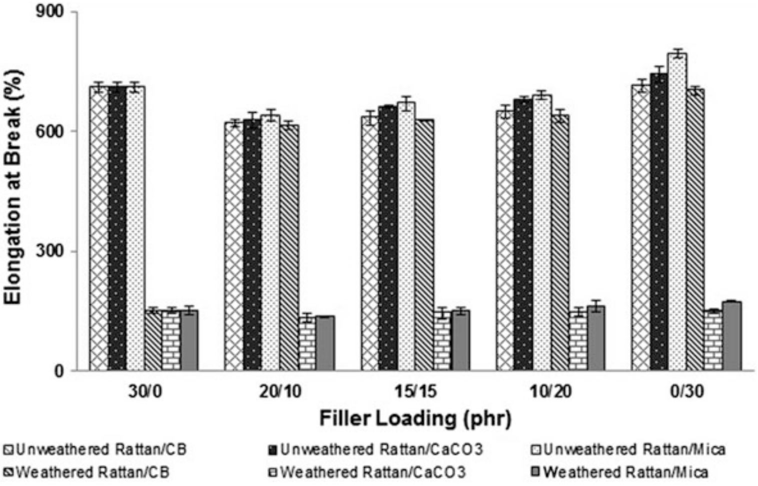

Fig. 10 The effect of partial replacement of rattan fibre with commercial fillers on the elongation at break of natural rubber composites after natural weathering

NR/RF/$CaCO_3$ about 22 and 21 %, respectively. For M100, the NR/RF/CB, NR/RF/mica and NR/RF/$CaCO_3$ composites retained an average of 101, 114 and 115 % respectively. This change in tensile properties indicates that all the composites have undergone the photo-oxidative degradation upon the 6 months exposure to the environment even with the addition of commercial fillers.

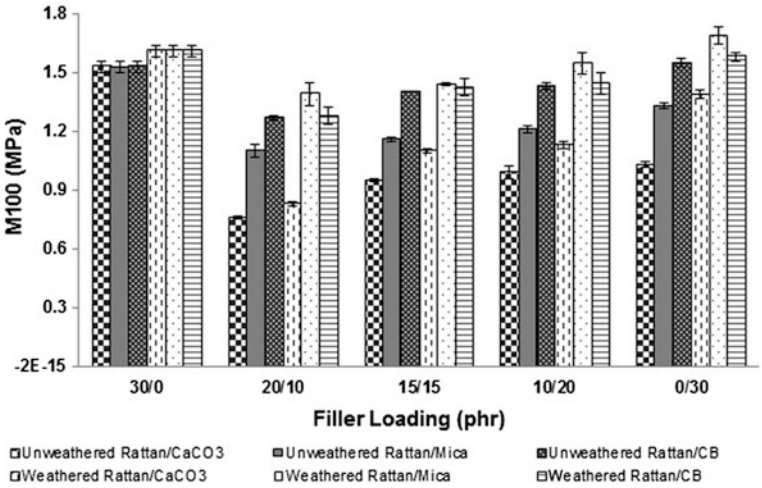

Fig. 11 The effect of partial replacement of rattan fibre with commercial fillers on the stress at 100 % elongation (M100) of natural rubber composites after natural weathering

On the same time, comparison was made in between the single filler filled composites. The NR/RF composite retained an average of 5, 17 and 103 % of tensile strength, E_b and M100, correspondingly. In respect to tensile strength, E_b and M100, the NR/CB composite showed 87, 92 and 102 % retention, the NR/mica composites retained about 8, 22 and 121 % whilst, the NR/RF/$CaCO_3$ composite exhibited 6, 20 and 126 % of retention. From the results obtained, it can be concluded that the NR/RF composites substituted partially or completely with CB showed the best tensile retention properties followed by mica and $CaCO_3$ replaced composites. The NR/RF showed comparable retention of tensile and E_b with the mica and $CaCO_3$, and M100 retention with the CB.

Fundamentally, CB is known to be an outstanding UV absorber which is able to provide an excellent protection against the UV light (Ciesielski 1999) by suppressing the formation of C=O bonds under UV exposure(Rich and Zerda 2006). Apart from that, CB able to impart a superior interaction with the rubber matrix enhancing good stress distribution and obstruct the oxygen access into the rubber matrix (Zhao et al. 2012). Thus, the good rubber-filler interaction along with UV absorbency resulted in poor photo-oxidative degradation, enabling a good retention in tensile properties.

Whereas, both mica and $CaCO_3$ imparted comparable retention in tensile properties after the natural weathering, even though, mica showed slightly better tensile retention compared to $CaCO_3$. Mica and $CaCO_3$ also identified as UV absorber in polymer composites (Leblanc 2010). Nevertheless, from the results collected, both fillers unable to enhance the photostability of the composites as CB did. This might due to the poor rubber-filler interaction which has become a path for the degradation to take place. The poor rubber filler interaction provides more sites in the NR matrix to be contact with the oxygen during the exposure of the composites to the natural outdoor conditions

3.2.2 Fourier Transform Infrared (FTIR) Analysis

Various chemical reactions had occurred in the composites when exposed to the natural weathering which has modified the FTIR spectrum as compared to un-weathered composites. The results of FTIR spectrum of rattan fibre-filled natural rubber (NR/RF) composites before and after exposure to natural weathering for both with and without silane coupling agent is presented in Fig. 12.

Appearance and disappearance of a number of peaks in the FTIR spectrum were observed after weathering. The presence of hydroxyl (OH), carbonyl (C=O) and ether (C–O–C) groups were noticed in the region of 3200–3400, 1717 and 1020–1050 cm^{-1} respectively before (Fig. 12a-i, b-i) and after weathering (Fig. 12a-ii, b-ii). Referring to Fig. 12a-ii, b-ii, after exposed to weathering, a wider peak with a stronger shoulder was noticed in the hydroxyl region, while, an increase in the intensity of carbonyl and ether bonds was seen. In addition, after been weathered, formation of new peak at 1762 cm^{-1} was noticed which indicates the carbonyl (C=O) group from ester bonds. Generally, the peroxides (OOH) which are produced by UV oxidation on unsaturated bonds during natural weathering were detected as hydroxyl groups in FTIR spectrum (Noriman et al. 2010). Unstable ozonides are formed by the attack of ozone molecules which cleave to a range of oxygenated products, such as acids, esters, ketones, and aldehydes, and also exposes new rubber chains to the effects of ozone (Datta and Huntink 2008).

The intensity of peaks at 2845 and 1456 cm^{-1} which are belongs to alkyl groups disappeared, whilst, the intensity of 2916 cm^{-1} which is also assigned to alkyl group was reduced noticeably with exposure, displayed in Fig. 12a-ii, b-ii. The changes in the intensity of peaks show that significant degradation had occurred in the matrix of the composites. For composites with silane coupling agent, the peaks at 1172 and 1584 cm^{-1} (Fig. 12b-i) have disappeared after weathering (Fig. 12b-ii). This evidences that the links formed between RF filler and rubber matrix had been damaged during natural weathering.

Figures 13 until 15 illustrate the FTIR spectrum of NR/RF/CB, NR/RF/mica and NR/RF/CaCO3 composites before and after natural weathering, respectively. The 'i' symbolizes composites partially loaded with 15/15 (RF/commercial filler) phr filler ratio composites and 'ii' represents composites replaced completely with 30 phr commercial filler (CB, mica and $CaCO_3$). Whereas, the a and b indicates FTIR spectrum before and after weathering, respectively.

Some common peaks in the region of alkyl groups (C–H) and nitro compound ($-NO_2$) were found in all the partially or completely filled NR composites before the natural weathering is carried out. The alkyl groups with its many rearrangement are corresponding in the frequency of 2920–2830 and 1460–1360 cm^{-1}, contributed from natural rubber. Meanwhile, a peak is observed in the region of 1530–1540 cm^{-1} which implies a nitro compound is present, possibly from the rubber or

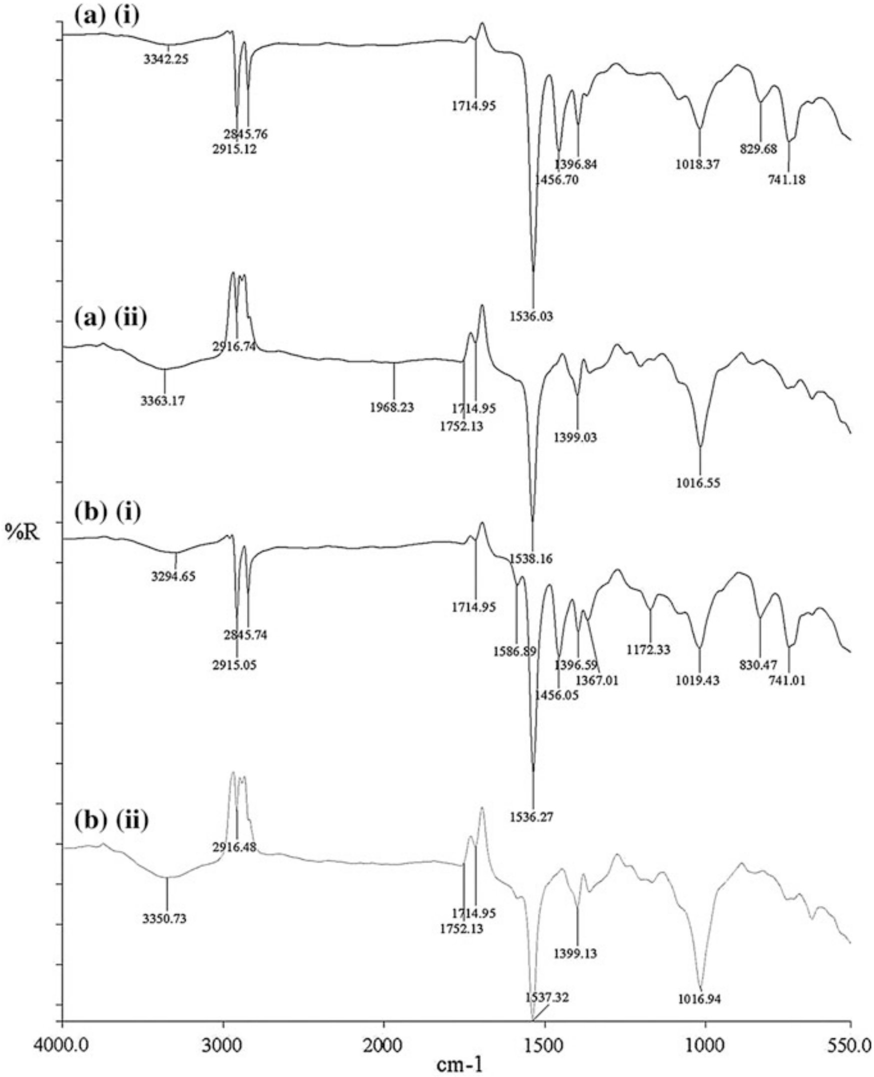

Fig. 12 FTIR spectrum of 30 phr rattan-fibre filled natural rubber composites (**a**) without (**b**) with silane coupling agent; (*i*) before (*ii*) after 6 months of natural weathering [Reproduced with permission from (Muniandy et al. 2012c), BioResources 7(3):4007]

various compounding ingredient of the rubber. Peaks in the fingerprint region, <1000 cm^{-1} region arise from complex deformations of the molecule. They may be characteristic of molecular symmetry, or combination bands arising from multiple bonds deforming simultaneously. Therefore it is extremely difficult to characterize and will be omitted from discussion.

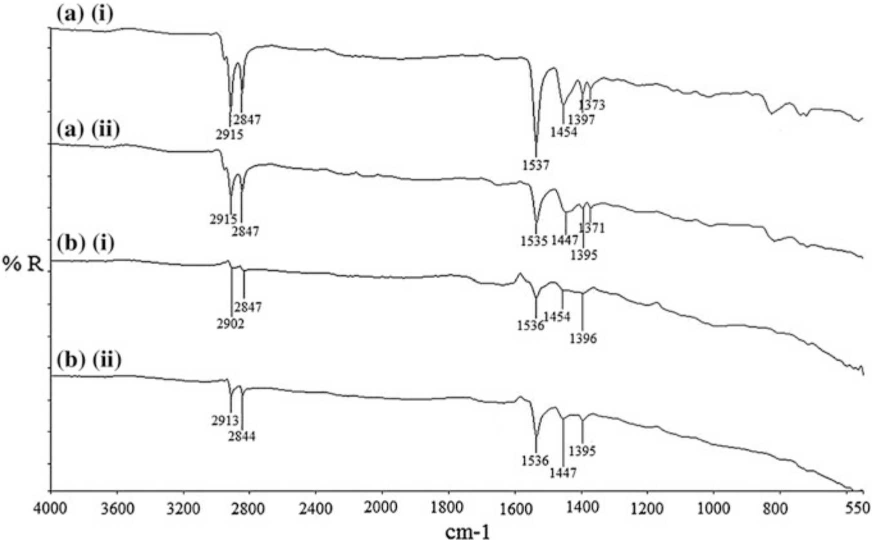

Fig. 13 FTIR spectrum of (**a**) before (**b**) after natural weathering of rattan/carbon black (*i*) partially (15/15) and (*ii*) completely (0/30) filled natural rubber composites

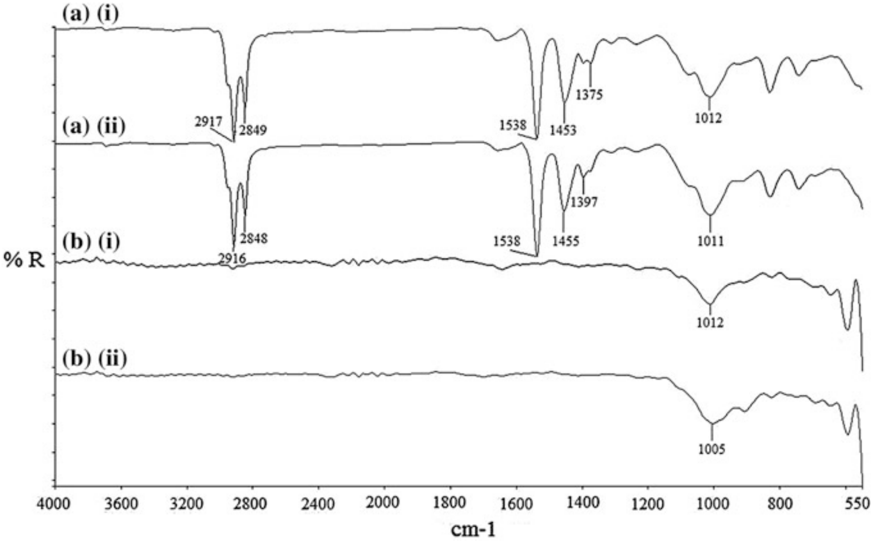

Fig. 14 FTIR spectrum of (**a**) before (**b**) after natural weathering of rattan/mica (*i*) partially (15/15) and (*ii*) completely (0/30) filled natural rubber composites

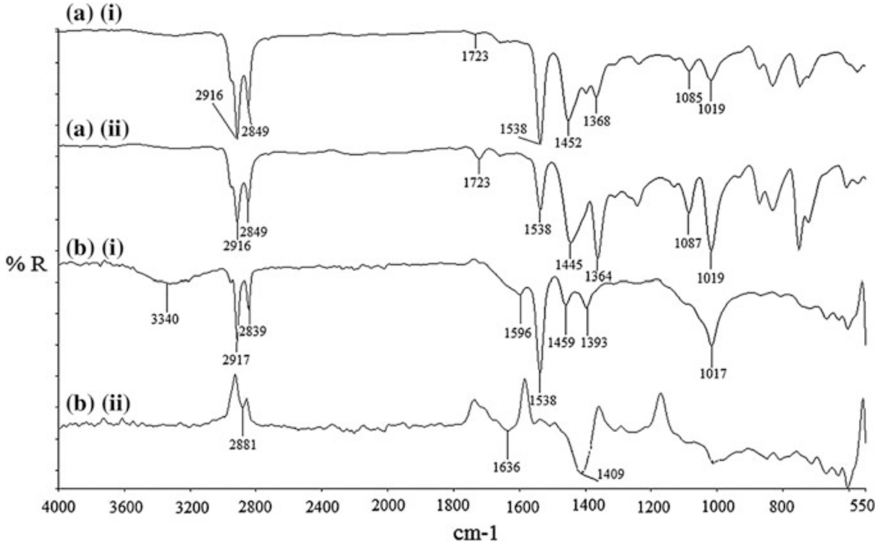

Fig. 15 FTIR spectrum of (**a**) before (**b**) after natural weathering of rattan/calcium carbonate (*i*) partially (15/15) and (*ii*) completely (0/30) filled natural rubber composites

Figure 13 shows the FTIR spectrum of partially and completely CB filled NR composites before (Fig. 13a) and after (Fig. 13b) natural weathering. According to Fig. 13 a-i, a-ii, before weathering, there were no obvious changes in the FTIR spectrum for both composites. No peaks representing CB is observed proving that there is a good interaction between the rubber and the CB. After natural weathering (Fig. 13b), the intensity of peaks in alkyl region has decreased. This change indicates the degradation of matrix has taken place. However, the 30phr filled CB composite (Fig. 13b-ii) showed more intense peaks compared to partially filled CB (Fig. 13b-i). This proves that the CB able to reduce the degradation of the matrix. Moreover, the nitro compounds are still present, although at a smaller peak, indicating less degradation has taken place, presented by Fig. 13b-i, b-ii.

Figure 14 shows the FTIR spectrum of mica filled composites before and after weathering. Before weathering, the peaks observed were almost similar between the partially and completely filled NR/Mica, displayed in Fig. 14a-i, a-ii respectively. Apart from the common peak, a peak in the 1000–1020 cm^{-1} region, corresponding to the Si–O–C was detected. The presence of this bond can be traced from the addition of mica. However, after weathering, all the peaks observed were set to degrade except for Si–O–C, clearly illustrated in Fig. 14b. The addition of mica has induced a drastic degradation, but, the mica itself has not degraded, thus the peak is still observed.

The FTIR spectrums of partially and completely replaced composites with $CaCO_3$ before and after weathering are presented in Fig. 15. Before natural weathering, the peaks in Fig. 15a-i, a-ii are similar to each other. Detected frequencies at 1723, 1368, 1087 and 1019 cm^{-1} are attributed to C=O, C–OH, C–O and C–O–C bonds respectively that can be accredited to the $CaCO_3$ filler. This is proven in Fig. 15a-ii where the intensity of these peaks has been increased correlating with the addition of more $CaCO_3$. According to Fig. 15b-i, after the composite are exposed to the outdoor conditions, hydroxyl (OH) groups and carbonyl (C=O) groups were detected to be present in the region of 3340 and 1596 cm^{-1}. Moreover, the intensity of the alkyl group has diminished. In addition, the frequency at 1017 cm^{-1} indicating the C–O–C bond became broad. All these changes indicate photo-oxidative degradation has occurred. Meanwhile, referring to Fig. 15b-ii, the intensity of alkyl groups reduced drastically with formation of carbonyl (C=O) and carboxylic acid (COOH) in the region of 1630 and 1409 cm^{-1} respectively. These peaks obtained indicate the composite has degraded massively. This is supported by the result of tensile retention where the sample was only able to retain 5 % of its original strength.

3.2.3 Morphological Studies

The surface morphology of the unfilled natural rubber (NR) vulcanizate and the rattan fibre filled NR composites after 6 months of natural weathering for both with and without silane coupling agent are demonstrated through SEM micrographs in Figs. 16, 17 and 18. Figure 19 represents the surface morphology of the weathered NR/CB, NR/mica and NR/$CaCO_3$ composites. The surface morphology of the weathered NR/RF/CB, NR/RF/mica and NR/RF/$CaCO_3$ composites at 15/15 filler ratio are shown in Fig. 20.

These micrographs were being evidence that all the weathered composites are extremely degraded with formation of cracks on their surfaces. However, the pattern of the surface cracks for the 30 phr filled RF and commercial fillers vary for one another. The 30 phr RF filled NR composites showed surface cracks which look alike to a mosaic pattern, shown in Fig. 18a. Referring to Fig. 19a, small cracks were found on the surface of the NR/CB filled composite. Deeper horizontal cracks along the matrix were observed in Fig. 19b for NR/mica composite, whereas, cracks resembling fish scale were noted in the NR/$CaCO_3$ composite, displayed in Fig. 19c.

It is understood that the oxidative degradation and ozone degradation are responsible for cracking to occur. Apart from that, dust was also accountable for the development of cracks. Dust which has settled on the rubber surface can be triggered by the sunlight to produce oxidizing moieties which is ableto crack the rubber (Datta and Huntink 2008). Furthermore, development of cracks also can be caused by thermal stress during outdoor exposures due to the day and night differences in temperature. The cracks found in the RF filled composites (Figs. 17 and 18) are larger compared to the cracks noticed in the commercial fillers, especially CB

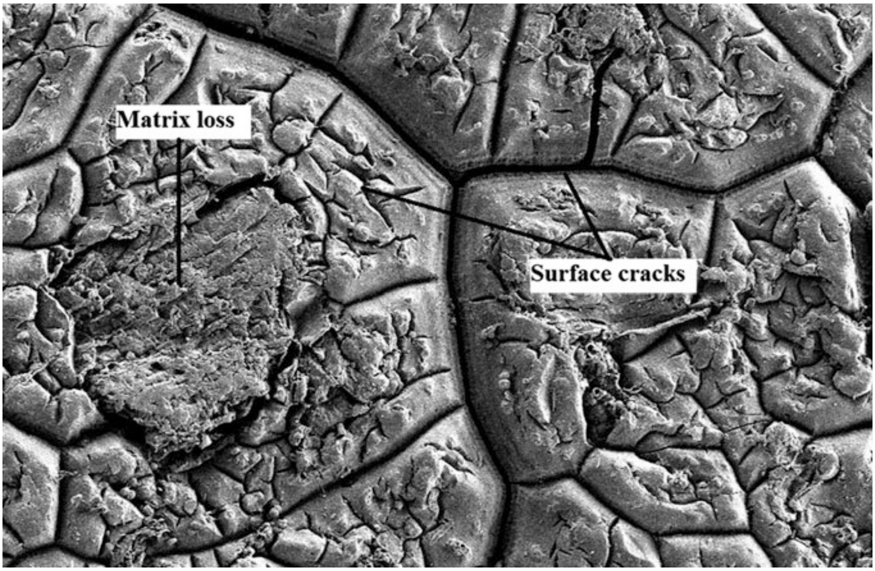

Fig. 16 Surface morphology of unfilled natural rubber vulcanizate after natural weathering at magnification of 200× [Reproduced with permission from (Muniandy et al. 2012c), BioResources 7(3):4009]

(Figs. 19a and 20a), proving smaller filler is able to provide more reinforcing effect and reduce the degradation. Therefore, larger cracks indicate more severe degradation.

From Figs. 16, 17 and 18, it was observed that the coarseness of surface composite increased with the development of more micro cracks as the RF filler loading was increased. These cracks permit more oxygen penetration causing higher degree of photo-oxidative degradation. Moreover, loss of the matrix due to the degradation, which was confirmed from the SEM micrographs of Figs. 16, 17 and 18, gives rise to severe damage of the inner part of the matrix and weakens the rubber-filler interaction (Ismail et al. 2008).

Thus, once the matrix is lost, the RF fillers were visible and easily degrade upon weathering. Development of sap staining fungi, surface checking and separation of rattan filler from rubber matrix verified that the RF filler had experienced degradation upon weathering, displayed in Figs. 17 and 18. Surface checking of rattan are the development of holes on the surface of rattan and splitting in rattan filler. This will lead to further reduction in the interaction between filler and matrix, consequently weaken the mechanical properties. At higher filler loading (30 phr), the matrix loss and rattan filler degradation were more which can be observed in Fig. 18. It is obvious that the degree of degradation of composites with silane (Figs. 17b and 18b) is similar to that of composites without silane (Figs. 17a and 18a). This shows that the bond formed by silane was unable to perform upon weathering as it was probably leached off during weathering.

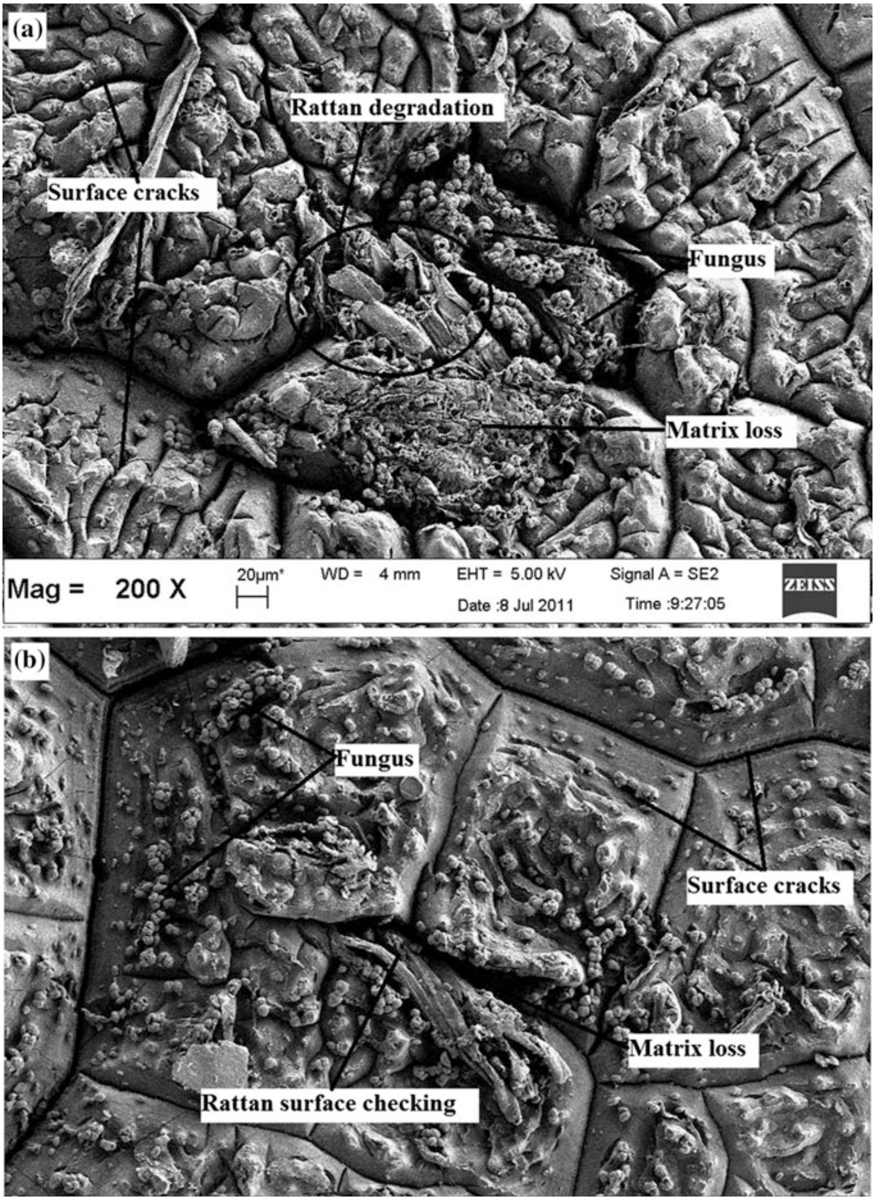

Fig. 17 Surface morphology of 5 phr rattan fibre filled natural rubber composites after natural weathering (**a**) without and (**b**) with silane coupling agent at magnification of 200× [Reproduced with permission from (Muniandy et al. 2012c), BioResources 7(3):4009]

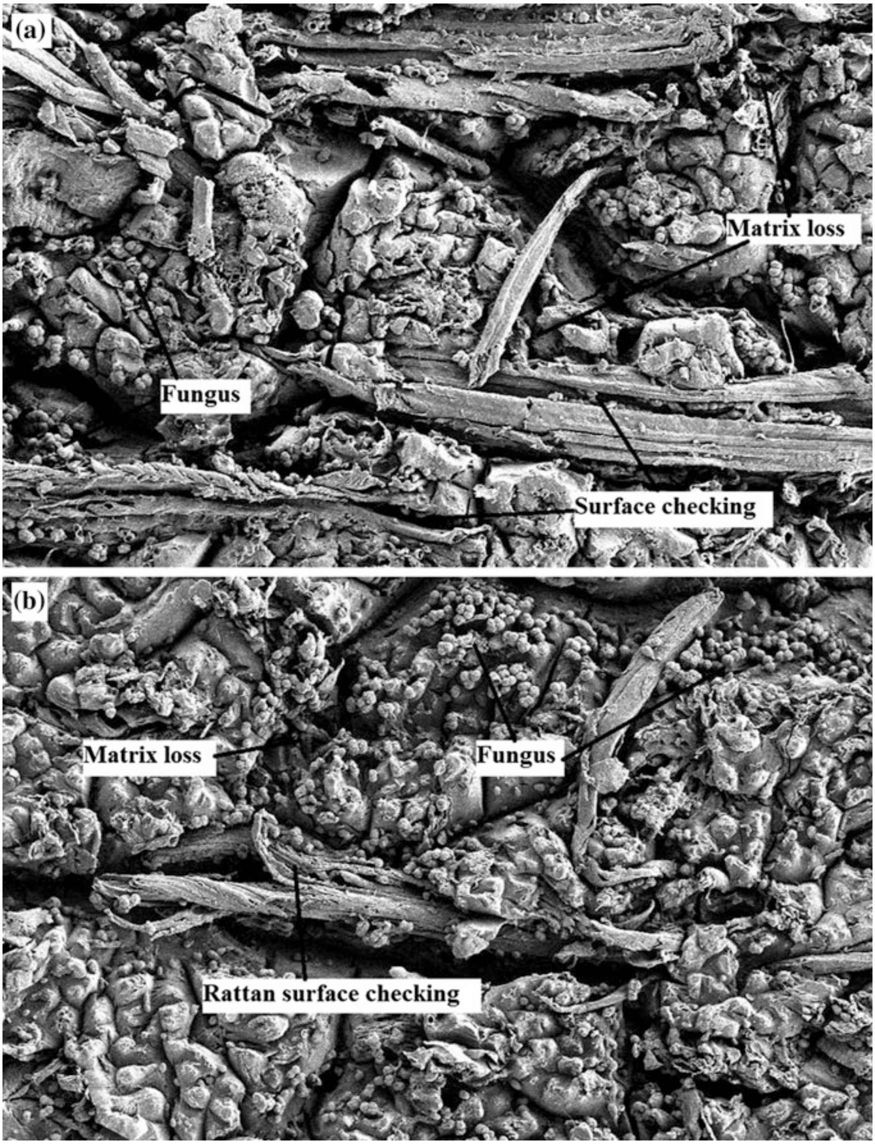

Fig. 18 Surface morphology of 30 phr rattan fibre filled natural rubber composites after natural weathering (**a**) without and (**b**) with silane coupling agent at magnification of 200× [Reproduced with permission from (Muniandy et al. 2012c), BioResources 7(3):4009]

Referring to Figs. 19a and 20a, widely spread small surface cracks were found on the surface of the CB filled composite. However, the depths of these cracks are less deep compared to that of mica and $CaCO_3$ filled composites. This is because the ability of CB to act as UV absorber and carbonyl suppresser has retarded the

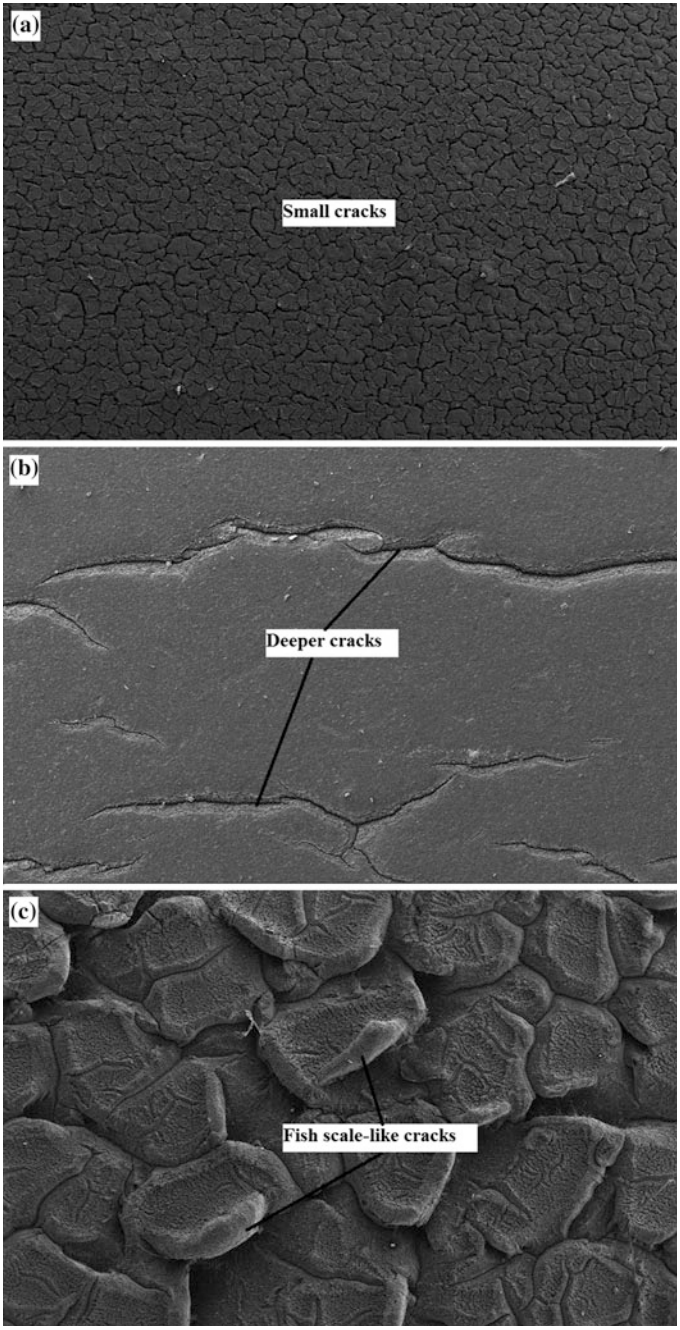

Fig. 19 Surface morphology of 30 phr (**a**) carbon black (**b**) mica and (**c**) calcium carbonate filled natural rubber composites after natural weathering at magnification of 30×

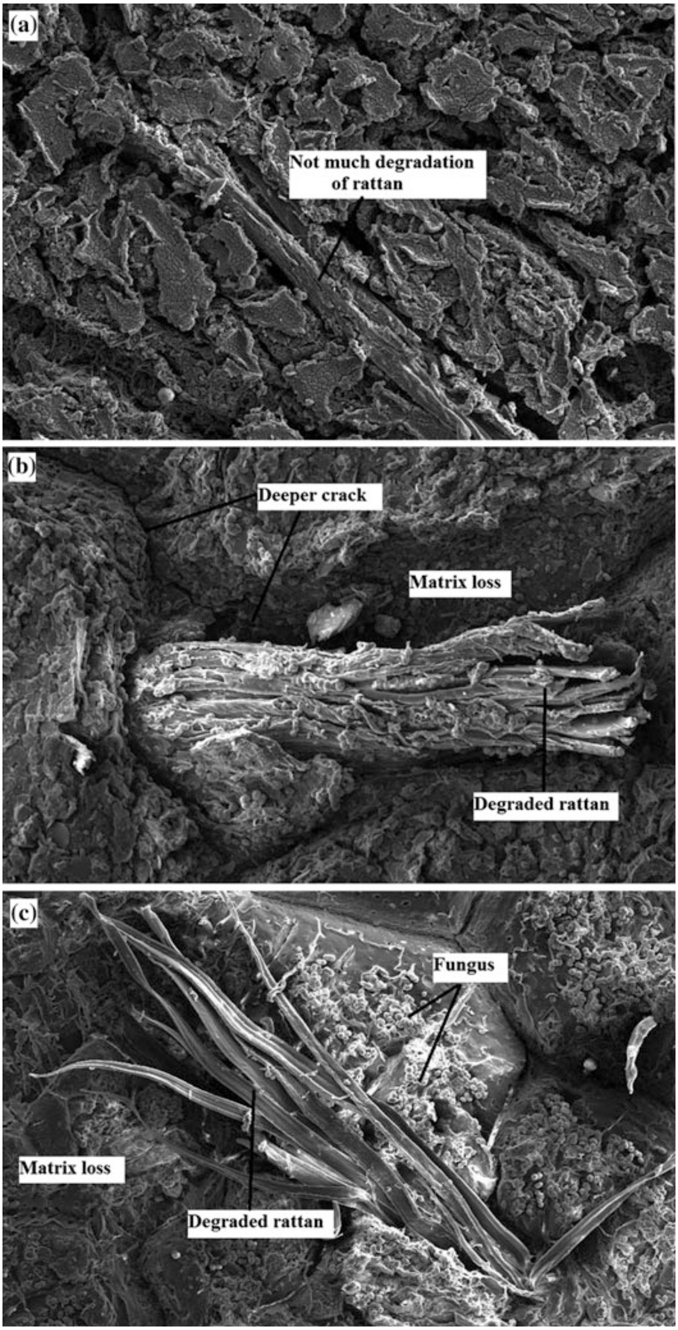

Fig. 20 Surface morphology of partially (15/15) phr (**a**) rattan fibre (RF)/carbon black (**b**) RF/mica and (**c**) RF/calcium carbonate filled natural rubber composites after natural weathering at magnification of 200×

additional damage to the inner part of the matrix. This supports the result of tensile properties where even though, there were many cracks in NR/CB composite, the tensile properties were not seriously affected by weathering.

At the same time, mica filled composites do not show serious deterioration on the surface but exhibited deeper cracks along the matrix, depicted in Fig. 19b. The $CaCO_3$ filled composite on the other hand shows an extensive degradation, where most of the surface are scale-like or are beginning to be peeled off from the matrix (Fig. 19c). Thus, the surface cracks found in mica and $CaCO_3$ might have allowed more oxygen diffusion onto the matrix, giving way to further deterioration of the rubber-filler interaction. As a result, both the mica and $CaCO_3$ composites experienced a drastic reduction in tensile properties.

It is worth noting that there were higher losses of matrix in both mica and $CaCO_3$ filled composites compared to CB. The cracks which were formed in the mica composite are substantially deep. Thus, the loss of matrix and deeper cracks formation contributed to the severity of matrix degradation. This observation is clearly illustrated in the Fig. 20b, c. When comparing the performance of the partially filled rubber composite in Fig. 20, rattan degradation is more widespread in mica (Fig. 20b) and $CaCO_3$ (Fig. 20c) composites compared to the CB (Fig. 20a) variant. Furthermore, no growth of fungus is observed on the CB surface, proving CB is not a water soluble material.

3.3 *Properties of Soil Buried NR/RF Composites*

3.3.1 Tensile Properties

The tensile properties of the rattan fibre-filled natural rubber composites (NR/RF) were compared before and after soil burial test. The effect of the filler loading, the addition of silane coupling agent and the effect of partial replacement of rattan fibre with commercial fillers on the tensile properties of NR/RF composites were evaluated for the soil burial test. The results were compared in the aspect of tensile retention or reduction. Since, the percentage of reduction or retention in tensile properties showed a variable trend as the loading of fillers was increased; thus, an average percentage of reduction or retention in tensile properties was calculated for the comparison.

Figures 21, 22 and 23 display the tensile strength, elongation at break (E_b) and stress at 100 % elongation (M100) of the unfilled natural rubber vulcanizate and the NR/RF composites with and without the silane, before and after soil burial test. A decreasing trend was showed by the tensile strength and elongation at break, whereas, M100 showed an increasing trend with an increase of filler loading for both composites with and without the addition of silane, before and after the soil burial test. According to Figs. 21 through 23, deterioration in tensile properties was witnessed for both composites with and without silane after 6 months of soil exposure as compared to the composites before the soil exposure. This deterioration

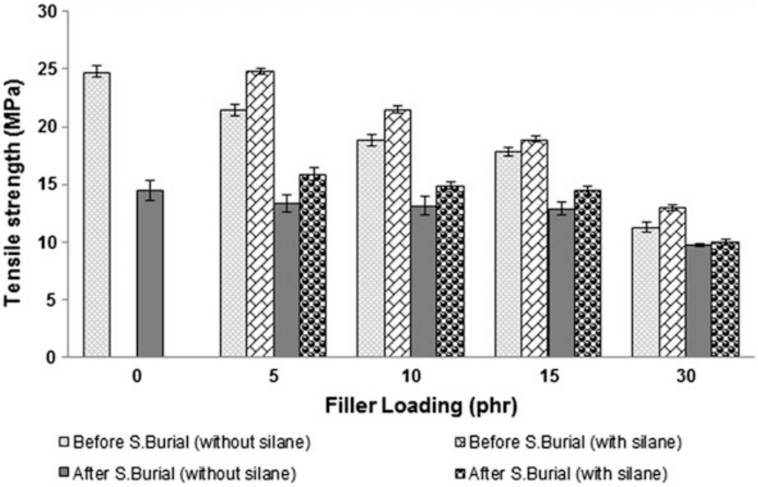

Fig. 21 The effect of filler loading and silane coupling agent on tensile strength of rattan fibre-filled natural rubber composites before and after soil burial [Reproduced with permission from (Muniandy et al. 2012a), BioResources 7(1):961]

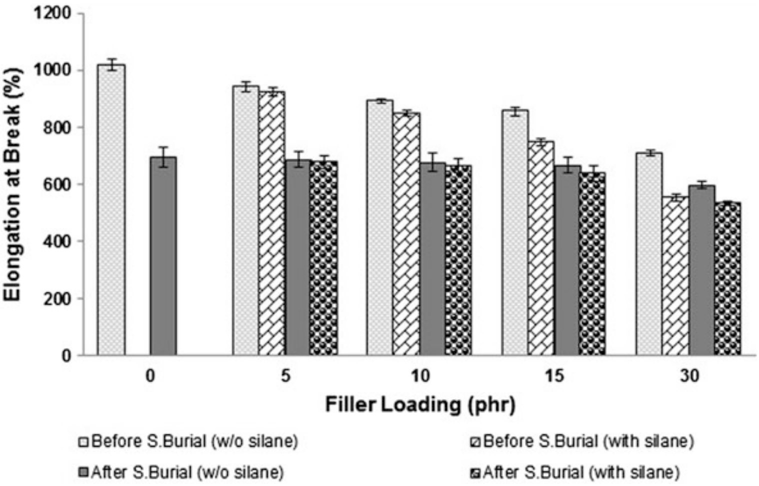

Fig. 22 The effect of filler loading and silane coupling agent on elongation at break of rattan fibre-filled natural rubber composites before and after soil burial [Reproduced with permission from (Muniandy et al. 2012a), BioResources 7(1):962]

was due to the degradation of the natural rubber and the rattan filler after exposed to soil. Overall, a decline with an average of 28, 20 and 8 % was observed in tensile strength, E_b and stress at 100 % elongation (M100) respectively for the composites with and without silane.

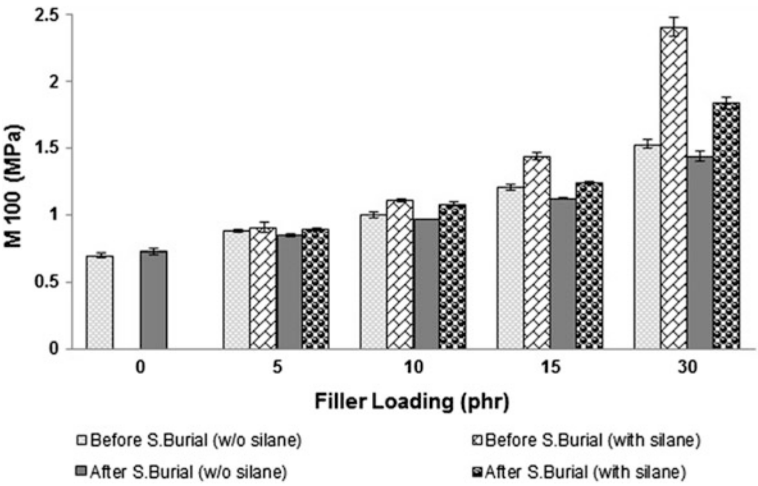

Fig. 23 The effect of filler loading and silane coupling agent on stress at 100 % elongation (M100) of rattan-fibre filled natural rubber composites before and after soil burial [Reproduced with permission from (Muniandy et al. 2012a), BioResources 7(1):963]

Biodegradation of vulcanized rubber is possible, although it is challenging due to the presence of crosslinks in the rubber chains. Biodegradation of natural rubber caused by the action of particular microorganisms such as Pseudomonas which has the capability to consume hydrocarbons (Jacob et al. 2007; Roy et al. 2006). Research works using various microorganisms indicate that during rubber biodegradation, oxidative cleavage of the double bond in the rubber backbone should be initiated. This is due to the high molecular mass of natural rubber compound which is too huge for the bacteria to consume. Natural rubber which is highly unsaturated and prone to oxidative degradation generates short oligomers by the cleavage of longer polymeric chains of natural rubber (Rose and Steinbuchel 2005; Rifaat and Yosery 2004). These short oligomers were then metabolized by the microorganisms as the soil exposure extended. In addition, this shorter oligomers or chains also caused the entanglement of the rubber chain to be reduced. As a consequent, the efficiency of rubber matrix to transmit stress is also reduced. Therefore, the tensile strength reduced after exposed to soil, represented by Fig. 21.

The E_b and M100 of the composites also reduced owing to the reduction in rubber chain entanglements. The E_b decreases as the shorter rubber chains were not able to entangle with each other and could not be stretched much. Thus, the flexibility of the rubber chains reduced and the E_b also reduced, shown in Fig. 22. Whereas, M100 (Fig. 23) of all NR/RF composites are noted to decline slightly upon the soil exposure. This is because the rubber becomes soft and the stiffness dropped due to the reduction of rubber chain entanglement with the loss of some shorter rubber chains upon soil exposure.

Rattan fillers are also exposed to soil and degraded upon soil burial. Rattan can be degraded biologically as they made of cellulose and lignin which are more vulnerable to decomposition by microorganisms (Huq et al. 2010). Microorganisms can identify the carbohydrate polymers in the cell wall and have very particular enzyme systems capable of hydrolysing these polymers into digestible units so that fibre structure is weakened and fibre strength reduced (Rowell 1995; Jacob et al. 2007). However, the degree of degradation of RF is less in comparison to rubber matrix. This is because the biodegradation of natural rubber is a slow process, and the growth of bacteria utilizing rubber as a only carbon source is also slow (Shubhra et al. 2010). The microorganism will attack the surface and lead to surface erosion. The rattan fillers are expected to degrade soon after the matrix degradation. Thus, not much rattan is seen to degrade (illustrated in SEM micrograph in Sect. 3.3.3). Moreover, for the similar period of soil exposure, the RF helps to further slow the process of biodegradation even it will be degraded after some time. Consequently, the RF filled composites showed higher retention in tensile properties compared to the unfilled NR vulacnizate. The unfilled NR vulcanizate retained 59 % of its tensile strength, 68 % of E_b and 104 % of M100 as compared to NR/RF composites that able to retain an average of 72, 80 and 92 % with respect to tensile strength, E_b and M100. The main contribution of RF degradation towards the properties of samples is visual effects such as surface checking and development of hyphae.

However, the addition of the silane has enhanced the tensile strength and the durability of the composites. Based on Figs. 21 and 23, an improvement is seen for tensile strength and M100 with an average of 10 and 12 % respectively for the samples with silane as compared to without silane after exposed to the soil. In the meantime, a drop with an average of 5 % is seen for E_b, shown in Fig. 22. As stated previously, this enhancement resulted from the proper wetting of silane coupling agent in between the rubber matrix and the rattan filler, leading to improved interfacial adhesion. The interfacial adhesion between rubber matrix and rattan filler can act as protective layer to the act of microorganism which exist in soil (Jacob et al. 2007).

When the effect of partial replacement of RF with commercial fillers was studied, again, reduction in tensile strength and E_b was observed, shown in Fig. 24 and 25. The M100 was seen to increase after exposure to soil burial, presented in Fig. 26. The partially replaced composites with CB showed the highest tensile retention, 94 % followed by $CaCO_3$ and mica, 87 and 84 %, respectively. On the other hand, all the composites partially filled with commercial filler exhibited almost comparable retention of E_b and M100. The NR/RF/CB retained an average of 92 % of E_b and 104 % of M100. The E_b retention of NR/RF/mica was 96 % and M100 retention was 104 %. NR/RF/$CaCO_3$ showed E_b retention similar to the NR/RF/mica which was 92 % along with 106 % of M100 retention.

The retention of tensile properties of the single filler filled NR composites at 30 phr filler loading was also examined. The NR/RF composite demonstrated about 83, 84 and 94 % of retention with respect to the tensile strength, E_b and M100. The tensile, E_b and M100 of NR/CB composite were maintained respectively with 95, 87 and 107 % of its original properties. The NR/mica composite retained about

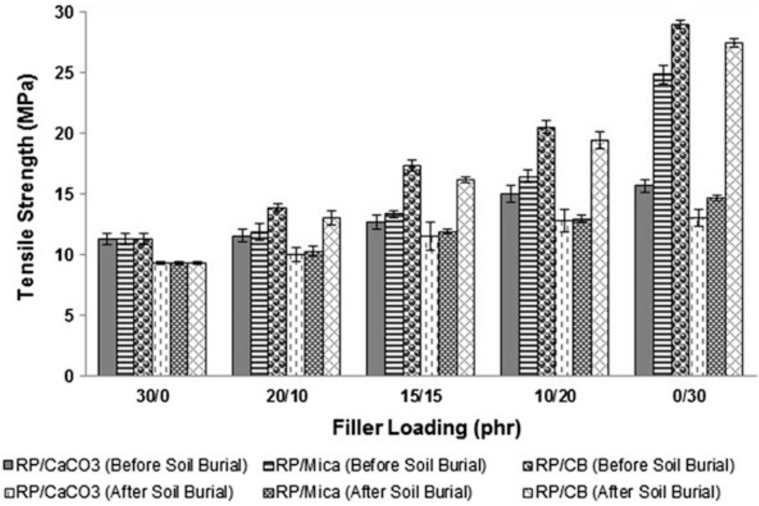

Fig. 24 The effect of partial replacement of rattan fibre with commercial fillers on the tensile strength of natural rubber composites after soil burial

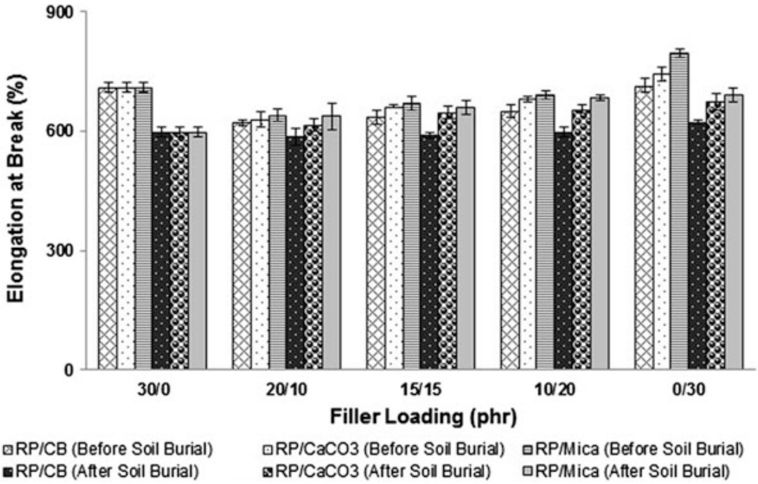

Fig. 25 The effect of partial replacement of rattan fibre with commercial fillers on the elongation at break of natural rubber composites after soil burial

59 % of tensile retention, 87 and 103 % of its E_b and M100. About 83 % of tensile strength was maintained for NR/$CaCO_3$ composite with retention of E_b and M100 about 91 and 103 %, orderly.

As an overall, it can be mentioned that the composites replaced with CB showed better retention in tensile properties upon soil exposure. According to (Services

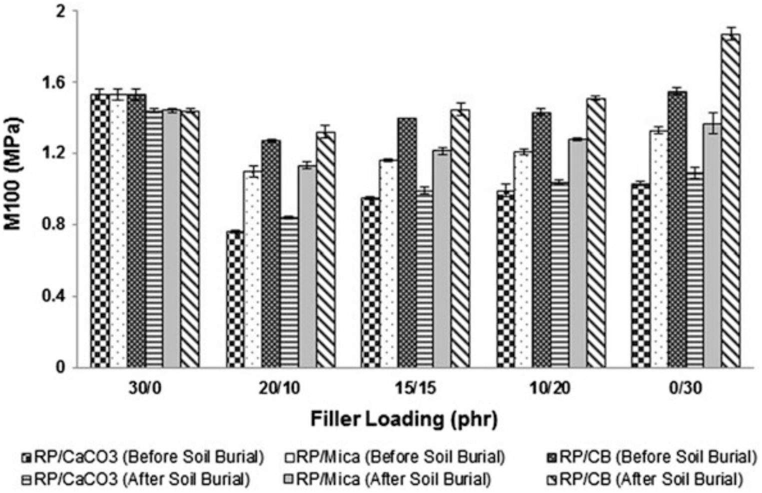

Fig. 26 The effect of partial replacement of rattan fibre with commercial fillers on the stress at 100 % elongation (M100) of natural rubber composites after soil burial

2011), CB is not biodegradable and is insoluble in both water and organic solvents. It is known that water medium is an important condition for the microorganism attack to take place (Wypych 2003). Thus, since CB is insoluble in water, so no reaction is likely to occur between the CB and the soil environment. Apart from that, CB provided greater reinforcement to the composite by providing good rubber-filler interaction (Wypych 2000). This reduced the extent of the biodegradation of the rubber matrix, which led to slight reduction in tensile strength.

After CB, $CaCO_3$ filled NR/RF/$CaCO_3$ or NR/$CaCO_3$ composites showed second highest tensile strength followed by NR/RF/mica composites. The NR/mica composite showed the poorest tensile strength. $CaCO_3$ and mica, both are inert mineral fillers which cannot be degraded by the microorganism present in the soil. However, mica which has silicate structure (hydrophilic) can be readily absorbs water (Kondelchuk and Miskovsky 2009). On the other hand, the $CaCO_3$ is not very water-soluble but can react with acidic raining water (Foundation 1999). Thus, the reaction between the fillers and the raining water can deteriorate the interaction between the rubber matrix and the fillers. Further reduction in rubber-filler interaction occurred compared to the composites before soil burial test leading to reduced tensile strength. (Kia 2009) reported that the mica has higher moisture absorption property (thrice) than the $CaCO_3$. Thus, the tensile strength of mica filled composites seen to exhibit more reduction.

Figure 25 shows the E_b of the composites. It was noticed that the degradation had led to the reduction of E_b due to the decrease in the flexibility of the rubber chains resulted from the reduction in rubber chain entanglements. On the other hand, the M100 of the composites are noted to increase slightly after the soil exposure, Fig. 26. This might due to the crosslinking of shorter chains resulted in slight increase in stiffness. At the same time, the tensile properties of the NR/RF/CB, NR/RF/mica and NR/RF/$CaCO_3$ composites are higher than the composites without RF. This shows the RF has positive effect on the tensile properties of the composites.

3.3.2 Fourier Transform Infrared (FTIR) Analysis

The results of FTIR spectrum of 30 phr rattan fibre filled natural rubber (NR) composites before the soil burial testing for both without and with silane are displayed in Fig. 27a(i), a(ii), correspondingly. Figure 27b(i), b(ii) present the FTIR results of composites after soil burial test are with respect to composites without and with silane. Based on Fig. 27a(ii), b(ii), composite with the silane showed presence of two additional peaks in the FTIR spectrum before and after exposed to soil as compared to composites without silane (Fig. 27a(i), b(i)). These peaks indicates the C–N stretch and silanes (Si–O–C) which are found in the region of 1172 and 1586 cm^{-1} correspondingly, demonstrated in Fig. 27a (ii), b (ii). The appearance of these bonds proved a better adherence between the rubber matrix and the rattan filler which has been brought by the silane. The visibility of these bonds after soil burial is evidence for the improved tensile properties observed after soil burial test.

Some alterations in FTIR spectrum are noticed after the soil exposure with appearance and disappearance of some peaks in FTIR spectrum as depicted in Fig. 27b(i), b(ii). Carbonyl (C=O) and ether (C–O–C) groups are noticed in the region of 1717 and 1020–1050 cm^{-1} correspondingly before and after the soil exposure. An increase in the intensity of carbonyl and ether bonds was noticed after soil burial test. New peaks are also detected at 3200–3400 and 1632 cm^{-1} which attributes hydroxyl (OH) and carbonyl (C=O) group, correspondingly. The intensity of peaks at 2916, 2845 and 1456 cm^{-1} decreased, whilst, intensity of peak in the region of 744 and 723 cm^{-1} disappeared with the exposure to soil. These peaks are belongs to C–H bonds from alkyl groups. These alterations acknowledge the biodegradation of composites.

The FTIR spectrums of NR/RF/CB, NR/RF/mica and NR/RF/CaCO3 composites before and after soil burial are shown in Figs. 28, 29 and 30. As for weathering, the common peaks were noticed for all composites before the soil burial. After soil burial, there were a few indication of onset of the degradation in all composites were noticed. One is through the detection of peaks at region of 3270–3290 cm^{-1}, which indicates the presence of OH group in the composites. Second is by

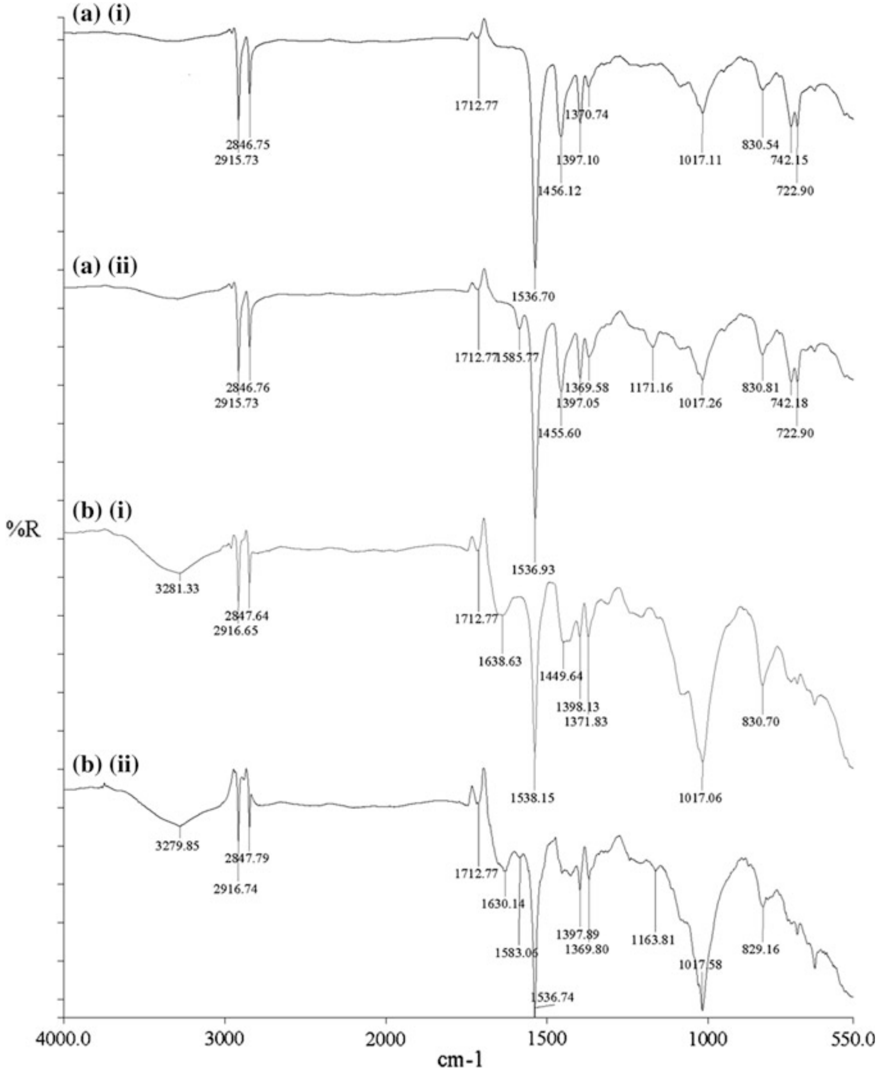

Fig. 27 FTIR spectrum of 30 phr rattan fibre-filled natural rubber composites (**a**) before (**b**) after soil burial test; (*i*) without silane coupling agent (*ii*) with silane coupling agent [Reproduced with permission from (Muniandy et al. 2012a), BioResources 7(1):969]

examining the intensity of the alkyl groups peaks. A lower intensity peak would suggest natural degradation has occurred in the matrix of the rubber. Next is through reduction of the NO_2 bond that was found in the region of 1530–

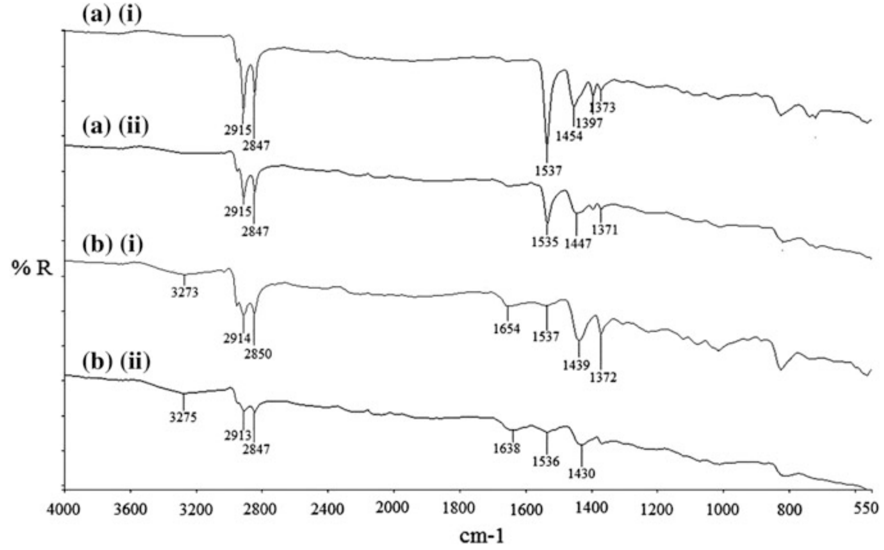

Fig. 28 FTIR spectrum of (**a**) before (**b**) after soil burial of rattan/carbon black (*i*) partially (15/15) and (*ii*) completely (0/30) filled natural rubber composites

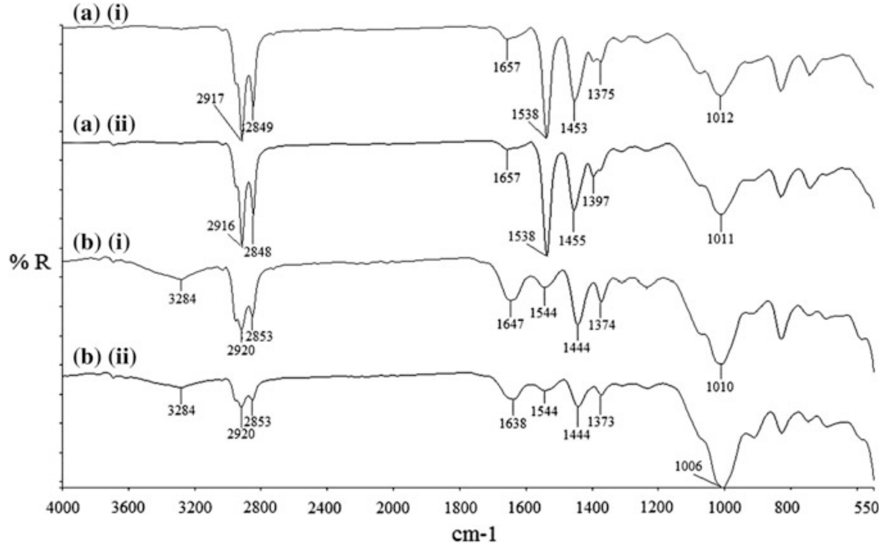

Fig. 29 FTIR spectrum of (**a**) before (**b**) after soil burial of rattan/mica (*i*) partially (15/15) and (*ii*) completely (0/30) filled natural rubber composites

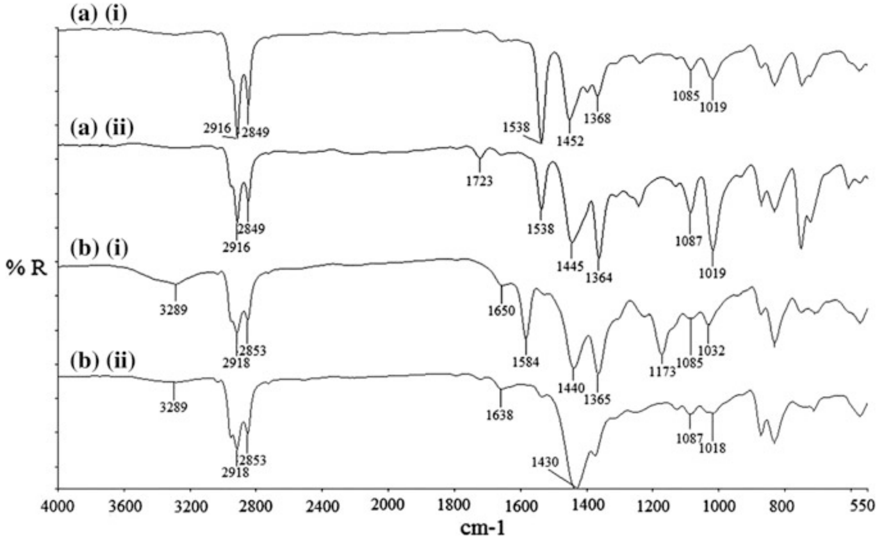

Fig. 30 FTIR spectrum of (**a**) before (**b**) after soil burial of rattan/calcium carbonate (*i*) partially (15/15) and (*ii*) completely (0/30) filled natural rubber composites

1590 cm^{-1} which was originally present in the rubber composite itself into NH_2 which detected in the 1660–1630 cm^{-1} region.

According to Fig. 28, after soil burial, the level of degradation was lower compared to before soil burial. The lower extent of degradation can be attested by the preservation of the alkyl bonds even after soil burial. Also, the formation of hydroxyl (OH) groups detected after degradation was very small. For the mica filled composites (Fig. 29), appearance of phenol group, reduction in the alkyl peaks and high conversions of the NO_2 bonds support that the composite do undergo degradation when subjected to soil burial. The peak at frequency of ~ 1012 cm^{-1} denoted to the Si–O–C bond. This peak becomes stronger and broader after soil burial suggesting that degradation does become higher and resulted in the formation of C–O–C bonds.

Referring to Fig. 30, after soil burial, the peaks affirming the $CaCO_3$ presence has diminished considerably, further proving the loss of the $CaCO_3$ possibly through the reaction with the acid in the soil. The presence of carboxylic acid in the region of 1430 cm^{-1}, proves that the composite is highly degraded along with the detection of hydroxyl groups and the reduction of nitrogen compound to primary amines.

3.3.3 Morphological Studies

Figure 31 shows SEM micrographs of the surfaces of unfilled natural rubber (NR) vulcanizate, whereas Figs. 32 and 33 represent the SEM micrographs of surfaces of the rattan fibre-filled NR (NR/RF) composites with and without silane coupling agent at 5 and 30 phr RF loading, respectively after soil burial.

The microorganism has attacked the surface of sample, which was followed by massive loss of oligomers resulted in eroded surface. This observation was proved through the increase in surface coarseness and erosion, which was noticeable in the rubber matrix as the filler loading was increased. Besides that, cracks and micro voids were also noticed on the samples surfaces. As discussed earlier, oxidative degradation will produce short oligomers which will be metabolized by the microorganisms and result in the formation of micro voids and an eroded surface. This phenomenon was clearly seen in the SEM micrographs at a magnification of 50× as seen in Figs. 31, 32a, b and 33a, b, respectively. (Manzur et al. 2004) described a comparable observations in their research work involving biodegradation of polyethylene and proposed that the absence of a uniform distribution of short branches in the polymer matrix were resulted in formation of cavities on the surface.

A clearer picture of biodegradation of the composites is presented in Fig. 34a, b, at magnification of 300×. The action of bacteria on the filler surface and the rattan filler degradation in the composites are clearly noticed in Fig. 34a. Surface checking such as formation of holes on rattan surface and rattan filler splitting together with formation of hyphae was found in the surface of sample. This verifies that the rattan has undergone degradation. For all composite surfaces, the microorganism attacks are observed to be more on rubber matrix compared to the

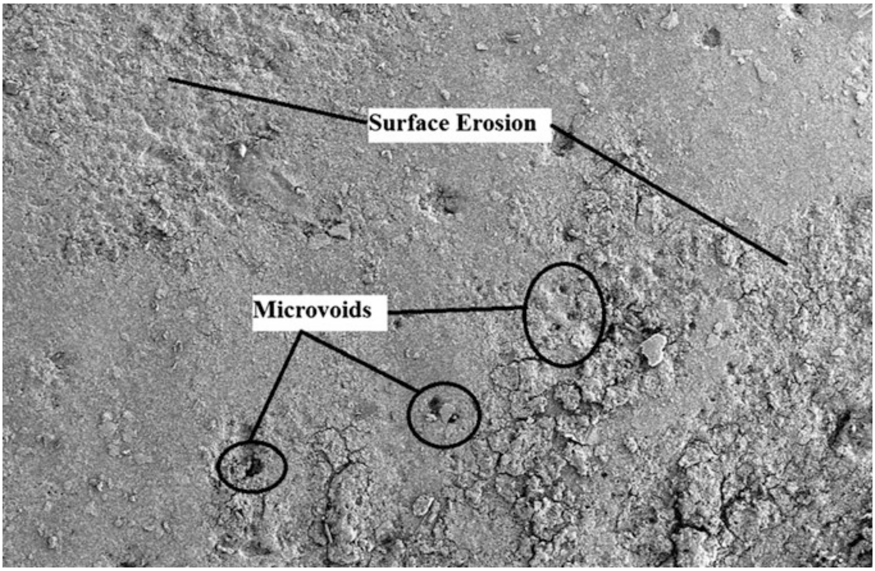

Fig. 31 SEM Micrograph of soil buried surfaces of unfilled natural rubber vulcanizate at magnification of 50× [Reproduced with permission from (Muniandy et al. 2012a), BioResources 7 (1):964]

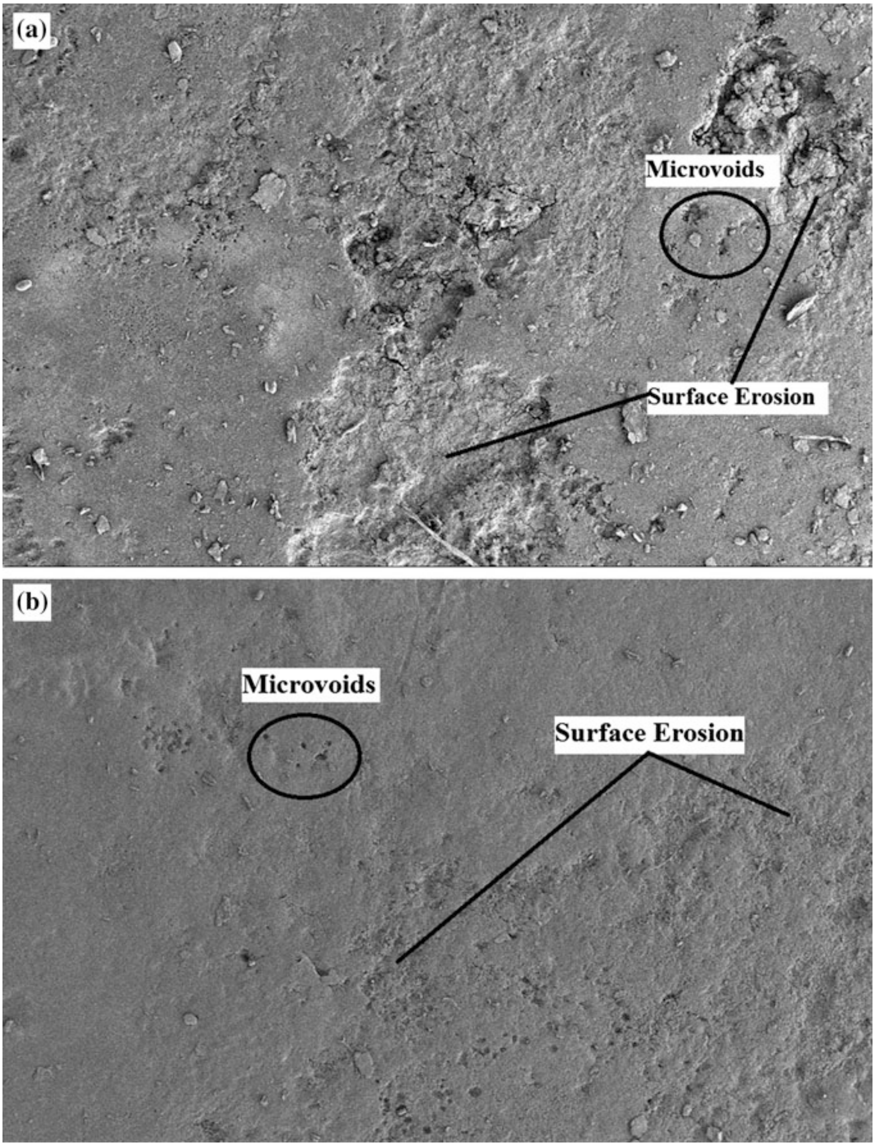

Fig. 32 SEM Micrograph of soil buried surfaces of 5 phr rattan fibre-filled natural rubber composites (**a**) without (**b**) with silane coupling agent at magnification of 50× [Reproduced with permission from (Muniandy et al. 2012a), BioResources 7(1):965]

rattan filler, shown in Figs. 32, 33 and 34. This evidences that the degree of matrix degradation is more compared to rattan degradation.

Figures 32b and 33b shows the SEM micrographs of composites with the presence of the silane coupling agent for both 5 and 30 phr filler loading. The

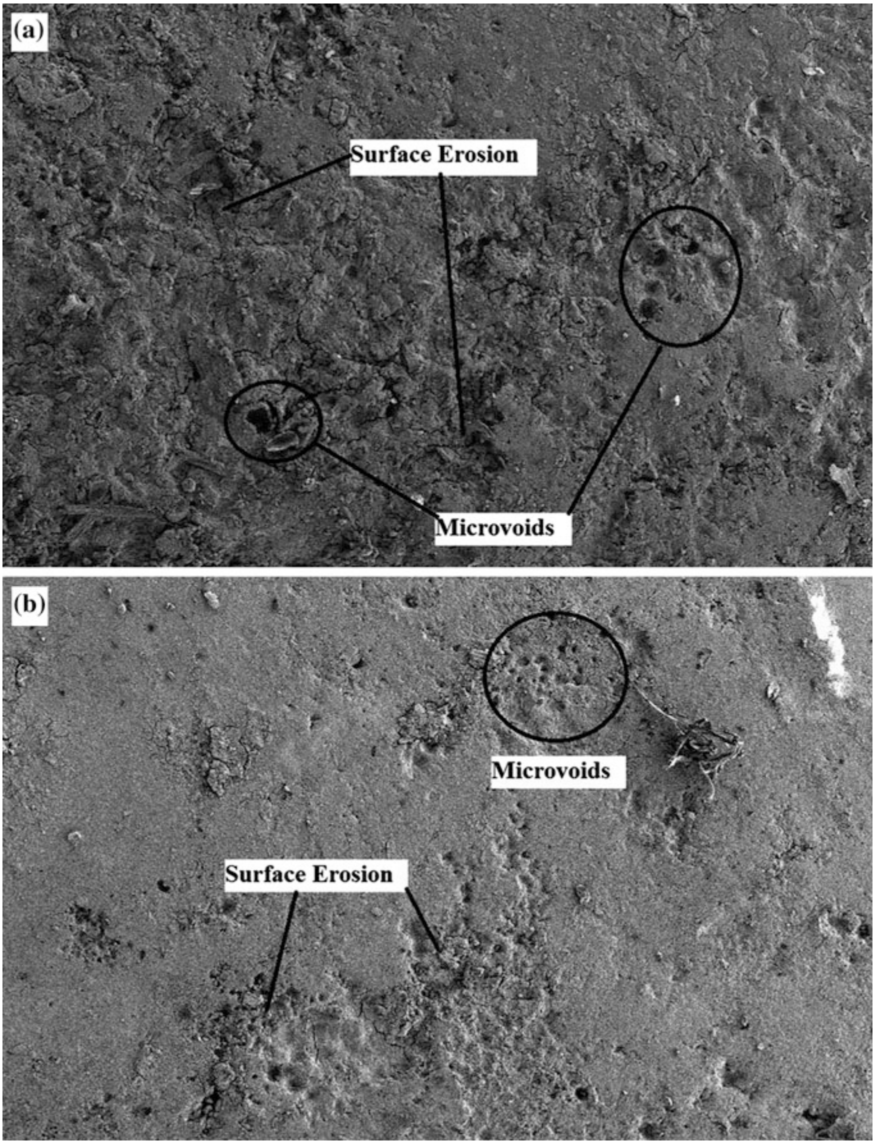

Fig. 33 SEM Micrograph of soil buried surfaces of 30 phr rattan fibre-filled natural rubber composites (**a**) without (**b**) with silane coupling agent at magnification of 50× [Reproduced with permission from (Muniandy et al. 2012a), BioResources 7(1):966]

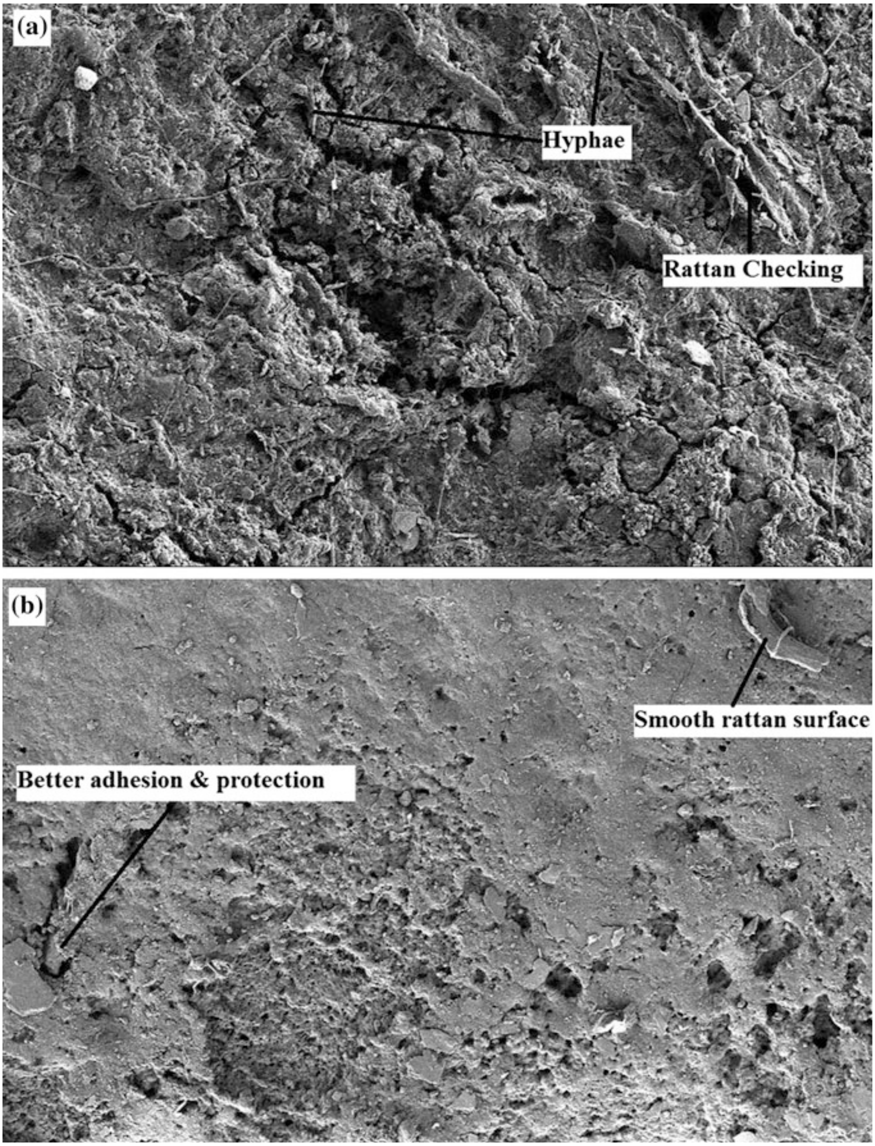

Fig. 34 SEM Micrograph of soil buried surfaces of 30 phr rattan fibre-filled natural rubber composites (**a**) without (**b**) with silane coupling agent at magnification of 300× [Reproduced with permission from (Muniandy et al. 2012a), BioResources 7(1):967]

results of tensile properties are reflected in these SEM micrographs. These SEM micrographs display that less degradation is seen for samples with the presence of the silane than the samples without the silane. At filler loading of 30 phr, higher degradation was experienced by samples without silane compared to samples with the silane, displayed in Fig. 33a, b. Microorganism's action on rattan filler was less, thus it is found to have a smoother appearance. This is due to better interfacial adhesion between the matrix and the rattan. In addition, rattan was protected by the silane coupling agent and prevented from severe degradation process to take place.

The surface morphologies of the degraded NR/RF/CB, NR/RF/mica and NR/RF/$CaCO_3$ composites are illustrated in Fig. 35 and the degraded surfaces of NR/CB, NR/mica and NR/$CaCO_3$ composites are displayed in Fig. 36. The extent of the matrix degradation was seen to be lessened after the partial replacement of commercial fillers when compared with 30 phr RF loaded composite (Fig. 34). The RF was still adhered to the matrix and was not degraded after 6 months of soil exposure, Fig. 35.

From Fig. 35a, it was clearly seen that the partial replacement of RF with CB has reduced the extent of degradation. The complete addition of CB has further reduced the degradation process, evidenced through the Fig. 36a. Less degradation or matrix loss was noticed in the SEM micrograph of CB filled composites, illustrated in Figs. 35a and 36a. The interaction between the rubber and the CB was not destroyed during soil exposure proving the reason for the less severe deterioration in the tensile properties.

The 30 phr $CaCO_3$ (Fig. 36b) filled composite showed comparable degradation to that of partially filled composite, NR/RF/$CaCO_3$ (Fig. 35b). The matrix surface of $CaCO_3$ filled composites were much degraded compared to the other two fillers. This is because after matrix eroded, the filler starts to expose to the soil. $CaCO_3$ that is not resistance to acid reacts with acidic rain water in soil. This further etches away the matrix at the surface of the composite, resulting in more degraded surface. So, deeper holes and erosion were observed (Figs. 35b and 36b). However, the rubber—$CaCO_3$ interaction was preserved. This is shown in the SEM micrograph where the $CaCO_3$ is still intact with rubber matrix. This is due to the fact that the $CaCO_3$ does not absorb as much water as mica.

While, more degradation was observed in NR/mica composite, shown in Fig. 36c compared to NR/RF/mica composite (Fig. 35c). The mica filled composite does not show severe degradation compared to $CaCO_3$. Once a certain portion of the matrix was loss, water penetrated into the matrix making the mica absorb the water/moisture present in the soil. Expansion and retraction process made the rubber-filler interaction to severely destroy and the mica filler debonded away from the matrix. This will disrupt the packing of mica in the rubber matrix creating microvoids, leading to easier failing of the composite, resulting lowered tensile retention. Thus, not much matrix degradation was observed.

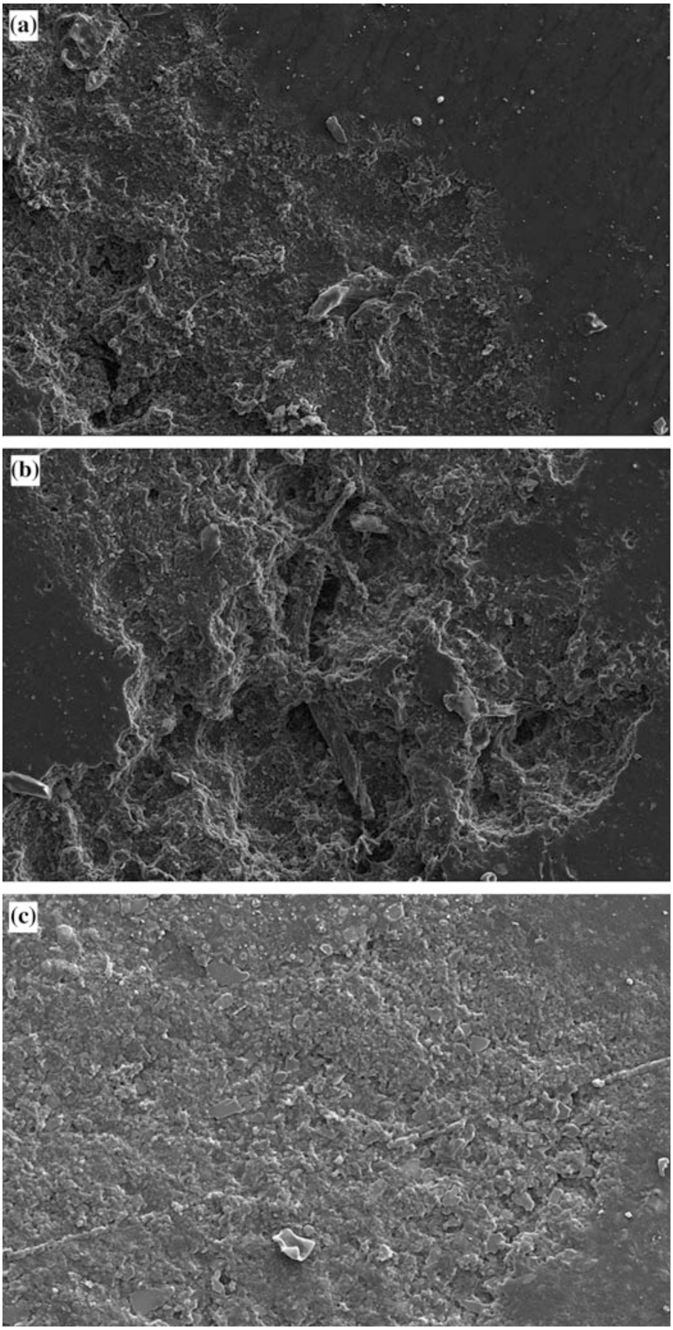

Fig. 35 Surface morphology of partially (15/15) phr (**a**) rattan fibre (RF)/carbon black (**b**) RF/calcium carbonate and (**c**) RF/mica filled natural rubber composites after soil burial at magnification of 200×

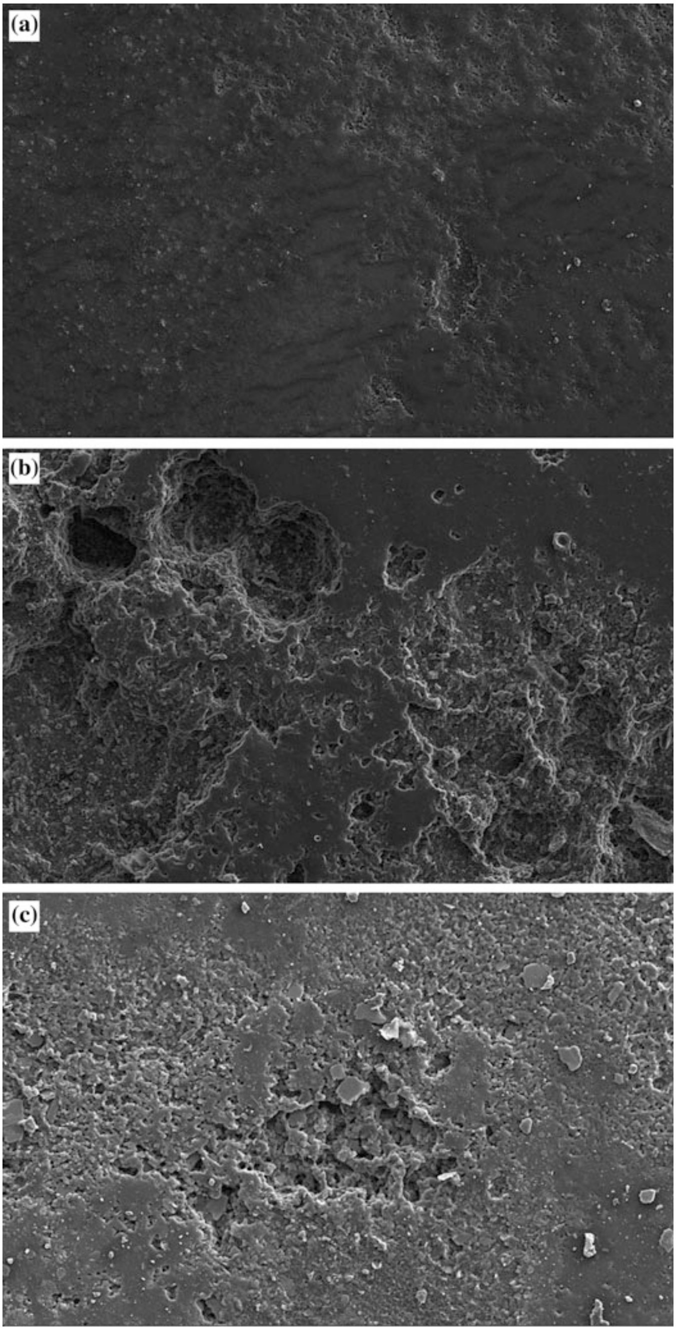

Fig. 36 Surface morphology of 30 phr (**a**) carbon black (**b**) calcium carbonate (**c**) mica and filled natural rubber composites after soil burial at magnification of 200×

4 Conclusion

From the results and discussion, conclusions are drawn as follows;

1. The tensile properties of the weathered NR/RF composite with and without silane coupling agent, and partially replaced with commercial fillers showed decline compared to the un-weathered composites. The reduction in tensile strength for the all composites was mainly due to the combined effects of oxidative and ozone degradation on the rubber matrix. The RF filler also showed degradation but the major contribution was the aesthetic effects such as surface checking and growth of sap staining fungi. It was noticeable that the addition of silane did not improve the tensile properties of the weathered composites due to the destruction of adhesion formed between the RF filler and NR matrix during weathering. The NR/RF composites substituted partially or completely with CB showed the best tensile retention properties followed by mica and $CaCO_3$ replaced composites after the exposure to the outdoor environment. However, the NR/RF showed comparable retention of tensile and E_b with the mica and $CaCO_3$, and M100 retention with the CB. The extents of degradation of all composites were supported by the FTIR and SEM studies.
2. As for weathering, after soil exposure, all composites showed reduction in the tensile properties compared to the composites before soil burial. The deterioration in the tensile properties was due to the degradation of the natural rubber and the rattan filler upon soil exposure. The biodegradation of rubber matrix and RF filler is possible but it is expected to take some time for the complete degradation to occur. The addition of silane coupling agent has improved the resistance towards the biodegradation. The presence of silane with the better adhesion between rubber matrix and rattan filler acted as protective covering to the action of microorganism present in soil. The composites partially filled with commercial fillers also showed reduction in tensile properties. The NR/RF/CB composites exhibited less degradation, followed by NR/RF/$CaCO_3$ and NR/RF/mica. The extents of degradation of all composites were examined and supported by the FTIR and SEM studies.

5 Future Work

1. Alternative techniques should be employed to grind the rattan canes into fibre form. For example, mill is used instead of crusher. Mill is able to produce a finer or smaller particle sized rattan fibres compared to the crusher. The reduction in particle size is believed to result in better properties to the composites.
2. It is suggested to investigate the effectiveness of rattan fibre as filler in synthetic rubbers as well as in thermoplastic and thermoset polymers due to their importance and usage in various applications which continues to grow.

3. Apart from using coupling agents, an appropriate surface modification of rattan (cane or fibre) should be studied to enhance the properties of the composites.
4. The performance of rattan fibre-filled natural composites is encouraged to be explored according to specific applications and their requirements.

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Mechanical Properties of Natural Fiber/Synthetic Fiber Reinforced Polymer Hybrid Composites

Asim Shahzad and Sana Ullah Nasir

Abstract Natural fiber composites are often poorer in properties, mostly mechanical, compared to synthetic fiber composites. A possible solution to this issue is the use of natural fiber/synthetic fiber combination in polymer hybrid composites. Although the biodegradability of the composites is compromised by synthetic fibers, this is compensated by the improvement in their mechanical and physical properties. Hybrid composites use more than one kind of fibers in the same matrix and the idea is to get the synergistic effect of the properties of both fibers on the overall properties of composites. There has been a significant increase in research on natural fiber/synthetic fiber hybrid composites in recent years. Natural fibers are mostly hybridized with glass fibers because of their comparable properties and low cost. Some studies, however, have been done on hybridization of natural fibers with the more expensive carbon and aramid fibers. The natural fibers mostly used in these studies are hemp, jute, coir, flax, sisal, and ramie. Conventional thermosets and thermoplastics and biodegradable polymers have been used as matrix material for these composites. There is a considerable improvement in mechanical properties of these composites following hybridization, especially when synthetic fiber plies are used as skin and natural fiber plies are used as core. Various natural fiber surface treatments have been used to improve their interfacial adhesion with the matrices and, hence, their mechanical properties. This chapter aims to present an overview of the work done on the mechanical properties of these hybrid composites.

Keywords Natural fibers · Glass fibers · Mechanical properties · Surface treatment · Moisture

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1 Introduction

Hybrid composites use more than one kind of reinforcements in the same matrix or same reinforcement in more than one kind of matrices and the purpose is to get the synergistic effect of the properties of constituents on the overall properties of composites. American Society of Materials (ASM) Handbook on Composites, Volume 21, defines hybrid composite as: "A composite laminate consisting of at least two distinct types of matrix or reinforcement. Each matrix or reinforcement type can be distinct because of its (a) physical and/or mechanical properties, (b) material form, and (c) chemical composition." With hybrid composites it may be possible to have greater control of the properties, achieving a more favourable balance between the advantages and disadvantages inherent in any composite material.

The most widely used form of hybrid composites is the one in which more than one kind of reinforcement (typically fibers) are used in the same polymer matrix and this chapter will deal with this form. Hybrid composites offer three main advantages over composites made from one kind of reinforcement. First, composites designers have the flexibility of tailoring composites design to achieve required properties. Second, the overall cost of the composites can be lowered by replacing expensive carbon and boron fibers partially with less expensive fibers such as glass and aramid. Third, the attainment of balance in properties such as strength, stiffness and ductility. Additional advantages of hybrid composites include weight savings, reduced notch sensitivity, improved fracture toughness, longer fatigue life and excellent impact resistance (Chou 1992).

Earlier attempts at hybridisation were made by combining stiffer fibers (carbon, boron) with more compliant fibers (glass, aramid) to increase the strain to failure of composite and hence enhanced toughness and impact properties. The effect was greater when the proportion of stiffer fiber was small and it was finely dispersed in the composite. Besides improving the impact performance, the incorporation of glass fibers also reduced the cost.

Because of these advantages, hybrid composites are now being extensively used in various high-tech and everyday applications. These include civilian and military aircraft parts, bicycle frames, snowboards, ice skates, water skis, canoe paddles, fishing rods, turbine blades, ship hulls, helmets, bridges, etc.

The following variables have been found to influence the behaviour of the hybrid composites (Agarwal et al. 2006): volume and weight fraction of each component fiber, lay-up sequence and orientation, relative properties of resin and fibers and interlaminar shear strength between plies, and extent and nature of voids and any other quality defects.

The two fiber types can be combined in three basic configurations in the design of hybrid composites as shown in Fig. 1: interply, intraply, and intrayarn.

In the interply configuration (Fig. 1a), adjacent laminae (plies) are composed of different materials. This is the simplest and cheapest method of producing a hybrid composite. In this configuration, plies forming the outermost layers are called skin

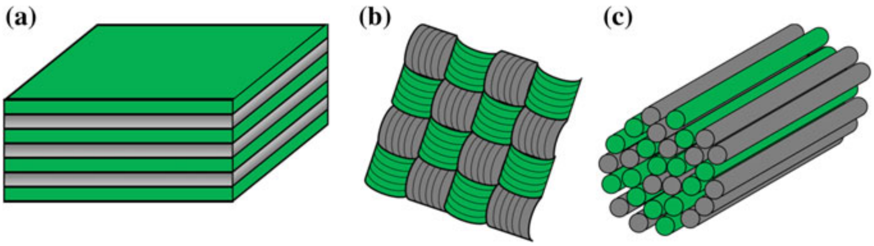


Fig. 1 Fiber configurations used in hybrid composites: **a** interply, **b** intraply, and **c** intrayarn (Swolfs et al. 2014)

plies whereas those forming the inside layers are called core plies. In the intraply configuration (Fig. 1b), different materials are used within a specific layer or band. The two fiber types can also be mixed or co-mingled on the fiber level, resulting in intrayarn hybrid fabric (Fig. 1c). The most common example of this is the graphite/aramid hybrid fabric.

Considerable data have been generated for hybrid composites in the areas of analysis, design, applications, and fabrication methods. The well-known rule of mixtures may not accurately predict the properties of hybrid composites from a direct consideration of the independent properties of individual fibers and matrices. Therefore a term ‘hybrid effect’ has been coined to represent this anomaly. A positive or negative hybrid effect is defined as a positive or negative deviation from a certain mechanical property from the rule of mixture behavior (Marom and Fischer 1978). From their work on carbon/carbon hybrids and carbon/glass hybrids, Marom and Fischer (1978) concluded that a prerequisite for the occurrence of hybrid effect is that the two types of fibers should differ by both their mechanical properties and by the interface which they form with the matrix. The hybrid effect may be positive or negative depending on the following factors: the relative volume fraction of the two types of fibers, the construction of the layers in the hybrid, and the loading configuration (e.g., translaminar or interlaminar).

The two fibers used in hybrid composites normally have considerable difference in their strain to failures elongation, commonly referred to as low elongation (LE) and high elongation (HE) fibers. This difference is reflected in their performance in mechanical loading. The first fiber to fail is normally the LE fiber. The HE fiber does not necessarily have a high failure strain, but it is always higher than that of LE fiber. The hybrid effect is explained by assuming that the weakest LE fibers that break first form cracks that are bridged by the surrounding HE fibers, provided there is sufficient amount of them, transferring the load to the stronger LE fibers and thus allowing them to reach their ultimate strength (Kretsis 1987). The minimum amount of HE fibers that fulfill this condition is given by Aveston and Kelly (1980),

$$V_{HE} \geq \frac{\sigma_{Lu}}{\sigma_{Hu} + \sigma_{Lu} - \sigma'_{HE}} \tag{1}$$

where σ_{Lu} and σ_{Hu} are the ultimate tensile strength of LE and HE fibers respectively, and σ'_{HE} is the stress on HE fibers at the failure of LE fibers.

The ultimate strength of hybrid composites has been reported to exhibit a negative hybrid effect. This is because the strength of a composite is not only a function of strength of the constituents; it is also dependent on the fiber/matrix interface quality. In tensile test, any microscopic imperfection in the specimen may lead to stress build-up and failure cannot be predicted accurately by rule of mixtures (Bannerjee and Sankar 2014). Aveston and Kelly (1980) have proposed the following equation for the ultimate tensile strength of unidirectional interply hybrid composites,

$$\sigma_c = \sigma_{Lu} V_{LE} + \varepsilon_{Lu} E_{HE} V_{HE} \tag{2}$$

where V_{LE} is the volume fraction of low elongation fibers, ε_{Lu} is the strain to failure of low elongation fibers, and E_{HE} and V_{HE} are the tensile modulus and volume fraction of high elongation fibers, respectively. For low volume fraction of HE fibers, the failure of low elongation fibers leads to the fracture of the hybrid, there is no multiple fracture, and Eq. (2) gives the composite strength. As the concentration of HE fibers increases and approaches the value given by Eq. (1), a transition in failure modes occurs because there is sufficient amount of these fibers to carry the load on the fracture of LE fibers. The fracture mode then is the multiple fractures of brittle fibers and the ultimate tensile strength is given by,

$$\sigma_c = \sigma_{Hu} V_{HE} \tag{3}$$

Equations (2) and (3) have been found to agree with the experimental results of carbon/glass-epoxy unidirectional interply hybrid composites.

The elastic moduli of hybrid composites have been reported to follow the rule of mixture equation and thus exhibit positive hybrid effect (Kretsis 1987). This is because elastic constants of a composite are volume averaged over the constituent microphases, hence the overall stiffness for a given fiber volume fraction is not affected much by the variability in fiber location (Bannerjee and Sankar 2014). The elastic modulus of unidirectional hybrid composite in the fiber direction is given by Bannerjee and Sankar (2014),

$$E_{1c} = E_{LE} V_{LE} + E_{HE} V_{HE} + E_m V_m \tag{4}$$

where E_{LE} and E_{HE} are the elastic moduli of LE and HE fibers respectively, and E_m and V_m are the elastic modulus and volume fraction of the matrix respectively.

The transverse modulus may be found using the modified Halpin-Tsai equation (Bannerjee and Sankar 2014),

$$\frac{E_{2c}}{E_m} = \frac{1 + \xi(\eta_{LE} V_{LE} + \eta_{HE} V_{HE})}{1 - (\eta_{LE} V_{LE} + \eta_{HE} V_{HE})} \tag{5}$$

In this equation,

$$\eta_{LE} = \frac{\left(\frac{E_{LE}}{E_m}\right) - 1}{\left(\frac{E_{LE}}{E_m}\right) + \xi} \text{ and } \eta_{HE} = \frac{\left(\frac{E_{HE}}{E_m}\right) - 1}{\left(\frac{E_{HE}}{E_m}\right) + \xi} \quad (6)$$

The parameter ξ in these equations depends on the packing arrangement and the fiber type. Its value evaluated by Bannerjee and Sankar (2014) for carbon/glass fiber hybrids is 1.165.

Similarly strain to failure has also been shown to exhibit positive hybrid effect. A comprehensive literature review of hybrid composites by Swolfs et al. (2014) showed that majority of the studies reported positive hybrid effect for failure strain with the values ranging from 2 to 116 %.

Flexural properties of hybrid composites are more difficult to predict than their tensile properties and just like tensile modulus, the flexural modulus can be predicted more accurately. While simple rule of mixtures is used to predict tensile moduli, the classical laminate theory is commonly used to predict flexural moduli (Swolfs et al. 2014). It has been shown that the flexural strength of a composite can be increased by replacing LE carbon fiber in the skin ply on the compressive side by HE glass fibers. This is because carbon fiber composites have lower compressive strength/tensile strength ratio (0.34) than glass fiber composites (0.73) (Swolfs et al. 2014). When carbon fiber plies form the compressive side, the failure occurs because of crushing of these plies instead of plies forming the tension side, precluding the composite from reaching its full strength. There is some evidence to suggest (Giancaspro et al. 2012; Dong and Davies 2012) that an optimal level of glass fiber loading exists (12.5 % of glass fibers for carbon/glass hybrids) to achieve maximum flexural strength of hybrid composite. Additionally, a symmetric layup may not be the optimal design for a hybrid composite subjected to flexural loads.

The hybridisation of LE fibers with HE fibers results in an increase in energy absorption capacity (toughness) and hence improved impact resistance of the hybrid composite. This property has been widely used in improving the impact resistance of carbon/glass and carbon/aramid fiber hybrids whereby HE glass or aramid fibers are incorporated in LE carbon fibers. A number of studies in 1970s (Chamis et al. 1972; Beaumont et al. 1974; Dorey et al. 1978; Adams et al. 1975) showed the improved impact properties of these hybrid composites. Charpy and Izod impact tests and drop weight method were utilised in these studies. It was also reported (Chamis and Lark 1977) that addition of just 20 vo1.% of aramid fibers almost doubled the Izod impact strength of HMS graphite/epoxy composites. It has also been shown that having carbon fibers on the impacted side improves the impact resistance, since HE glass/aramid fibers on the tensile side can absorb more energy, and penetration impact resistance can also be improved by placing LE fibers in the middle of symmetric interply composites.

Fatigue performance of hybrid composites is a relatively less studied area. Hybrid composites display improved fatigue resistance compared to single fiber composites. This is due to the fact that HE fibers in a hybrid composite can act as crack arrestors for the broken LE fibers, thus increasing the fatigue life of hybrid composites. This has been confirmed for fatigue resistance of carbon/glass and carbon/aramid fiber hybrids (Philips 1976) in tensile fatigue loading. This is also attributed to the increased stiffness of hybrids because of carbon fibers. A symmetric lay up in interply hybrid composites displays improved fatigue resistance compared to asymmetric layup in which glass fiber plies are in the core and carbon fiber plies are in the skin. This is attributed to carbon/glass fiber modulus mismatch at the interface, leading to high interlaminar shear stresses and promoting early failure (Hofer et al. 1978).

Following a comprehensive survey of mechanical properties of hybrid composites, Swolfs et al. (2014) concluded that, in many cases, positive hybrid effects can be achieved, although this is not applicable to all hybrid composites.

2 Natural Fiber/Synthetic Fiber Polymer Hybrid Composites

Most of the natural fiber composites have been found to be lacking in their mechanical properties compared to synthetic fiber composites. This is because mechanical properties of natural fibers are considerably poorer than synthetic fibers. Other drawbacks of natural fiber composites are their high susceptibility to moisture absorption, poor dimensional stability, variability in properties, low thermal resistance and incompatibility of natural fibers with polymeric matrices resulting in poor fiber/matrix interfacial adhesion. A viable method of overcoming these drawbacks is to hybridize natural fibers with another synthetic fiber in the same matrix. Synthetic fibers, owing to their relatively superior mechanical properties, negligible moisture absorption, compatibility with polymer matrices, and uniform properties are very effective at mitigating these drawbacks. The synthetic fiber mostly used for this purpose is glass fiber, although carbon and aramid fibers are also being increasingly used. This is because glass fibers are cheaper and have comparable properties to natural fibers. Although the biodegradability of the composite is compromised following the introduction of synthetic fibers, this can be compensated by the advantages gained by the increase in mechanical properties and other benefits explained earlier.

A comparison of the mechanical properties of selected natural fibers and synthetic fibers is given in Table 1. It is clear from the table that although the tensile strengths of natural fibers are considerably lower than E-glass and Kevlar fibers, their Young’s modulus and elongation at break values are comparable.

Although two different natural fibers have also been successfully used in making hybrid composites, this chapter will only concentrate on the mechanical properties

Table 1 Comparison of mechanical properties of natural and synthetic fibers (Bismarck et al. 2005)

Fiber	Density (g cm^{-3})	Diameter (μm)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
Flax	1.5	40–600	345–1500	27.6	2.7–3.2
Hemp	1.47	25–500	690	70	1.6
Jute	1.3–1.49	25–200	393–800	13–26.5	1.16–1.5
Kenaf			930	53	1.6
Ramie	1.55	–	400–938	61.4–128	1.2–3.8
Nettle			650	38	1.7
Sisal	1.45	50–200	468–700	9.4–22	3–7
Henequen					
PALF		20–80	413–1627	34.5–82.5	1.6
Abaca			430–760		
Oil palm EFB	0.7–1.55	150–500	248	3.2	25
Oil palm mesocarp			80	0.5	17
Cotton	1.5–1.6	12–38	287–800	5.5–12.6	7–8
Coir	1.15–1.46	100–460	131–220	4–6	15–40
E-glass	2.55	<17	3400	73	2.5
Kevlar	1.44		3000	60	2.5–3.7
Carbon	1.78	5–7	3400[a]–4800[b]	240[b]–425[a]	1.4–1.8

[a] Ultra-high modulus carbon fibers
[b] Ultra-high tenacity carbon fibers

of natural fiber/synthetic fiber hybrid polymer composites. The number of research papers on natural fiber composites has increased exponentially in the last decade or so. This is also true of the number of papers on natural fiber/synthetic fiber hybrid composites. It will not be possible to include all of them in this chapter. Therefore this chapter will only survey the most relevant and recent work on this subject.

These hybrid composites are slowly but steadily being put to many every day and industrial applications. The Composite Technology Park, Bangalore, India (www.compositestechnologypark.com) has developed natural fiber/glass fiber hybrid building materials in collaboration with University of Texas at Austin, USA. The natural fibers used are bamboo, coir and jute. The materials produced are roofing panels, decks, bridges, interior and exterior building walls and floors, structurally insulated panels, emergency shelters and off-shore deck platforms. Some entrepreneurs have also tried to hybridize natural fibers with stronger and stiffer but more expensive carbon fibers. For example, a bicycle has been made of flax/carbon reinforced composite. The CARBIO project (www.carbioproject.com) have developed a carbon/flax fiber hybrid automotive roof using Composite Evolution's Biotex flax material for Jaguar Land Rover. With equal bending stiffness to carbon fiber, the hybrid biocomposite has 15 % lower cost, 7 % lower weight and 58 % higher vibration damping. Composites Evolution (www.compositesevolution.com) have also developed three types of carbon/flax hybrids—hybrid woven yarn fabrics, hybrid spread tow fabrics and a layered hybrid approach. These hybrids offer reduced cost, reduced weight, increased shock absorption and improved environmental impact and are ideal for use in automotive and sporting goods industries. A recent study (Birat et al. 2015) reported that sisal/glass fiber hybrid biocomposites can offer a balance of properties like strength, impact, heat deflection, and flow properties required for automotive structural applications. Comparison of hybrid biocomposites with the currently used battery tray specifications showed that they met critical performance criteria such as stiffness, HDT, and impact resistance and had potential to be used in a prototype development. Similarly hybrids of kenaf/glass-epoxy composites were manufactured for use as car bumper beams (Davoodi et al. 2010) and compared with the currently used car bumper beam material (GMT-glass mat thermoplastic). Tensile strength and modulus of hybrid composites exhibited higher values than typical car bumper beam material. All these examples point at huge potential of these materials for use in various industrial applications.

However hybridization of natural fibers with synthetic fibers has some associated issues which need to be considered before the hybridization process (Jawaid and Khalil 2011). These are: reinforcing efficiency of the two fibers (the hybrid effect discussed earlier), moisture content of natural fibers, dispersion of natural fibers in the matrix, fiber/matrix interface, thermal stability of natural fibers, and biodegradability of the composites.

The hybrid effect has been discussed in Sect. 1 and it has been found that, generally, natural fiber/synthetic fibers hybrid composites exhibit positive hybrid effect in their mechanical properties. The hydrophilic nature of natural fibers makes them absorb moisture from the atmosphere; however synthetic fibers inhibit this effect. Natural fibers are not compatible with polymer resins for the same reason and form poor fiber/matrix adhesion. This effect is improved following hybridization because synthetic fibers are more compatible with polymer matrices and are more resistant to moisture absorption. Various physical and chemical surface treatments of natural fibers have also been found to be successful at improving fiber/matrix interfacial adhesion. Natural fibers also have low thermal stability, and this effect will also improve following hybridization because synthetic fibers are more thermally stable. Finally, the biodegradability of the hybrid composites will be reduced because of the presence of synthetic fibers. However this can be compensated with the increase in their mechanical and physical properties.

2.1 Mechanical Properties

A comprehensive overview of the mechanical properties of these hybrid composites is given in Tables 2 and 3. Since these Tables contain overwhelming data, a comparison of range of these properties has been shown in easy-to-interpret Figs. 2 and 3, based on the data of Tables 2 and 3. It should be pointed that a small range of properties for a particular hybrid composite in these figures means that these

Table 2 Mechanical properties of untreated natural fiber/synthetic fiber reinforced polymer hybrid composites

Hybrid reinforcement		Matrix system	Additional description	Layup configuration	Making technique	Overall fiber content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength	References
Fibers and form	Content (%)											
Short (kenaf/carbon)	70/30 wt	TPNR	–	–	CM	20 v	–	–	17	–	11.4 kJ/m^2	Anuar et al. (2008b)
	50/50 wt						–	–	18.5	–	14.9 kJ/m^2	
	30/70 wt						–	–	18	–	20.5 kJ/m^2	
Kenaf mat/CSM glass	7.5/22.5 v	UP	–	[K/G/K/G/K]	CM	30 v	35	1.3	–	8	62 J/m	Atiqah et al. (2014)
	15/15 v						27	1.4	–	11	135 J/m	
	22.5/7.5 v						21.5	1.2	–	13.5	70 J/m	
Short (coir/glass)	5/20 wt	Epoxy	Coir length 5 mm	–	CM	25 wt	15.2	1.2	40	–	–	Bhagat et al. (2014)
			Coir length 10 mm				16.2	1.5	50	–	–	
			Coir length 15 mm				17.1	1.6	56	–	–	
			Coir length 20 mm				14.9	1.8	52	–	–	
	10/20 wt		Coir length 5 mm			30 wt	14.9	1.3	51	–	–	
			Coir length 10 mm				16.6	1.6	54	–	–	
			Coir length 15 mm				18	1.7	63	–	–	
			Coir length 20 mm				13.4	1.6	57	–	–	

(continued)

Table 2 (continued)

Hybrid reinforcement		Matrix system	Additional description	Layup configuration	Making technique	Overall fiber content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength	References
Fibers and form	Content (%)											
Short (sisal/glass)	20/10 wt	PP + compatibilizer (3.5 % wt)	–	–	CM	30 wt	40	–	–	3.4	100 J/m	Birat et al. (2015)
	10/20 wt						44	–	–	3.8		
Woven kenaf/woven PET	15/15 wt	POM	Tested along kenaf orientation	–	CM	30 wt	82	4.2	132.5	0.6	12.5 J/cm	Dan–Mallam et al. (2014)
Interwoven (kenaf/PET)	10/10 wt					20 wt	72	3.5	160.1	1.4	12.1 J/cm	
	15/15 wt					30 wt	85	3.8	104.9	0.7	13.1 J/cm	
Woven kenaf/woven PET	15/15 wt		Tested along PET orientation			30 wt	82	4.2	–	–	–	
Interwoven (kenaf/PET)	10/10 wt					20 wt	80	3.1	–	–	–	
	15/15 wt					30 wt	89	3.3	–	–	–	
Short (PALF/glass)	90/10 wt	Polyester with additives	–	–	CM	30 v	83.41	3.78	–	–	900 J/m	Devi et al. (2012)
	80/20 wt						67.73	2.6	–	–	870 J/m	
	70/30 wt						69.54	2.56	–	–	1200 J/m	
	50/50 wt						70.52	2.4	–	–	1130 J/m	
	30/70 wt						94.4	2.85	–	–	1190 J/m	
	10/90 wt						102.1	2.73	–	–	1170 J/m	
Woven kenaf/woven aramid	19/20 v	Epoxy	–	–	HL	39 v	145.2	25.59	133	3.9	–	Yahaya et al. (2015a)
$0/90^0$ kenaf/woven aramid	19/23 v					42 v	164.6	43.9	105	3.2	–	
	21/23 v					44 v	67.6	20.39	7	0.1	–	

(continued)

Table 2 (continued)

Hybrid reinforcement		Matrix system	Additional description	Layup configuration	Making technique	Overall fiber content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength	References
Fibers and form	Content (%)											
Kenaf mat/woven aramid												
Short (Jute/glass)	10/10 wt	PP	Twisted short fibers	–	P	20 wt	43.92	5.8	72.75	3.55	7.81 kJ/m^2	Uawongsuwan et al. (2015)
	20/10 wt					30 wt	46.2	6.55	87.17	5.06	6.97 kJ/m^2	
	30/10 wt					40 wt	43.85	7.17	80.23	5.39	4.97 kJ/m^2	
	10/10 wt		Untwisted short fibers			20 wt	50.67	5.65	96.89	4.02	11.42 kJ/m^2	
	20/10 wt					30 wt	47.47	5.53	84.04	5.01	6.81 kJ/m^2	
	30/10 wt					40 wt	42.04	6.46	75.72	5.53	5.17 kJ/m^2	
	10/10 wt		Re-Pelletized (RP)		E	20 wt	52.26	4.66	95.55	4.22	16.25 kJ/m^2	
	20/10 wt					30 wt	60.02	6.36	106.24	5.23	11.62 kJ/m^2	
	30/10 wt					40 wt	63.02	7.65	102.48	5.96	6.9 kJ/m^2	
Woven jute/woven glass	50/50 wt	Epoxy	Fly ash filler (5 %)	[G/J/G/J]	HL/CM	17 wt	80	–	172	6.6	–	Raghavendra et al. (2014)
			Fly ash filler (10 %)	[J/G/G/J]			85	–	135	6	–	
			Fly ash filler (10 %)	[G/J/J/G]			108	–	146	5.7	–	
Short (hemp/glass)	35/5 wt	PP + MAPP (5 % wt)	–	–	IM	40 wt	53.7	4.07	97.5	5	48 J/m	Panthapulakkal and Sain (2007)
	30/10 wt						57.9	4.25	99.5	5.2	53 J/m	
	25/15 wt						59.5	4.4	101.5	5.4	55 J/m	
Short (sisal/glass)	70/30 wt	LDPE	–	–	CM	–	27.86	0.8	–	–	–	Kalaprasad et al. (2004)
	50/50 wt						29.75	1	–	–	–	
	30/70 wt						31.23	1.136	–	–	–	

(continued)

Table 2 (continued)

Hybrid reinforcement		Matrix system	Additional description	Layup configuration	Making technique	Overall fiber content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength	References
Fibers and form	Content (%)											
Short (curaua/glass)	30/70 v	Polyester	–	–	CM	20 v	95	9.8	99	3.7	–	Júnior et al. (2013)
	70/30 v					30 v	59	8.2	125	7.9	–	
	50/50 v					30 v	90	10.1	175	9.8	–	
	30/70 v					30 v	110	10	185	11.8	–	
	30/70 v					40 v	125	8.2	150	12	–	
Banana mat/CSM glass	–	PF resole	–	[G/Bn/G]	HL/CM	30 v	31	1.4	48.5	2.65	67 kJ/m^2	Joseph et al. (2007)
				[G/Bn]			26	1	33	2.3	54.5 kJ/m^2	
				[Bn/G/Bn]			27.6	0.55	45	3.55	56.5 kJ/m^2	
				[G/Bn/G/Bn/G]			37	1.3	64.5	2.6	70 kJ/m^2	
				Intimate G/Bn mixture			45	1.35	55.5	3.4	36.5 kJ/m^2	
EFB mat/CSM glass	50/50 wt	Vinyl ester	–	[EFB/G/G/G/EFB]	RTM	–	58	0.58	148	4.2	1150 J/m	Khalil et al. (2009)
				[FEB/G/EFB/G/EFB]			56	0.5	185	4.5	1205 J/m	
				[EFB/EFB/G/EFB/EFB]			100	0.67	102	3.7	1200 J/m	
				[G/EFB/EFB/EFB/G]			83	0.83	235	8.1	1005 J/m	
				[G/EFB/G/EFB/G]			63	0.79	230	7.7	990 J/m	
				[G/G/EFB/G/G]			58	0.77	220	8.1	800 J/m	
Woven jute/CSM glass	35/8 wt	Polyester	Warp direction testing	–	HL	43 wt	87.85	10.95	139.98	9.11	92.76 kJ/m^2	Ahmed et al. (2006)
	25/16 wt					41.5 wt	109.9	11.29	159.8	11.6	169.9 kJ/m^2	
	17/25 wt					42.3 wt	123.94	12.47	159.85	12.38	214.38 kJ/m^2	
	35/8 wt		Weft direction testing			43 wt	62.5	7.3	139.8	9.11	92.76 kJ/m^2	
	25/16 wt					41.5 wt	77.52	7.93	159.8	11.6	169.9 kJ/m^2	

(continued)

Table 2 (continued)

Hybrid reinforcement		Matrix system	Additional description	Layup configuration	Making technique	Overall fiber content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength	References
Fibers and form	Content (%)											
	17/25 wt					42.3 wt	100.58	9.83	159.85	12.38	214.38 kJ/m^2	
Long jute/long kenaf (K)/ CSM glass/ polyester surface veil (S)	40/40/25 wt	UP	–	[S/G/J/J/G/S]	P	65 wt	–	–	200	18	–	Akil et al. (2010)
				[G/J/J/G]			–	–	360	24.5	–	
				[S/G/K/G/S]			–	–	112	11	–	
Curaua mat/CSM glass	–	Polyester	–	[Cu2/G2]s	CM	35 v	127	6.3	46	0.92	–	Angrizani et al. (2014)
				[Cu/G]2s		35 v	109	5.5	58	0.83	–	
				[G/Cu]$_2$s		40 v	119	7	86	1.2	–	
				[G2/Cu2]s		34 v	119	6.4	72	1.65	–	
Short (kenaf/glass)	50/50 v	TPNR	Effect of temperature	–	CM	10 v	27	–	–	–	–	Anuar et al. (2008a)
			Effect of speed				32	–	–	–	–	
			Effect of period				31	–	–	–	–	
Short (kenaf/glass)	30/70 v		–				24	0.6	–	–	–	
	50/50 v						23	0.55	–	–	–	
	70/30 v						21	0.54	–	–	–	
Short (flax/glass)	10/30 v	PP + MAPP (4.9 % v)	–	–	CM	40 v	25.5	0.63	–	–	–	Barvarz et al. (2015)
	20/20 v						21.9	0.57	–	–	–	
	10/10 v						23.8	0.55	–	–	–	
	30/10 v						24.2	0.58	–	–		
	30/70 wt	UP	–	[G/K/G]	HL	37 v	155	0.08	275	0.16	–	Sharba et al. (2015)
	45/55 wt					37 v	111	0.07	213	0.15	–	

(continued)

Table 2 (continued)

Hybrid reinforcement		Matrix system	Additional description	Layup configuration	Making technique	Overall fiber content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength	References
Fibers and form	Content (%)											
Woven kenaf/woven glass	70/30 wt					32 v	55	0.05	147	0.1	–	
Jute fabric/glass fabric	25/7 wt	Epoxy	–	[J/G/J]	HL	32 wt	49.8		28.74		3.53 J	Braga and Magalhaes (2015)
	18/19 wt			[G/J/G]		37 wt	56.68		28.81	1.83	5.49 J	
Cross ply flax/UD carbon	–	Epoxy	Prepreg sheets of flax and carbon	[C/C/C/C/F/F]	CM	–	285	4.4	145	10	–	Dhakal et al. (2013)
UD flax/UD carbon				[C/C/C/C/F/F]			–		314	29	–	
Woven jute/CSM glass	50/50 wt	Epoxy	–	[G/J/G/J]	HL	17.5 v	78	3.1	165	6.5	–	Gujjala et al. (2014)
				[J/G/G/J]			73	2.6	93	4.6	–	
				[G/J/J/G]			87	4.8	133	6.4	–	
Short (banana/glass)	30/70 wt	Polystyrene	–	–	IM/CM	20 v	38.8	1.55	–	–	–	Haneefa et al. (2008)
	50/50 wt						33.2	1.52	–	–	–	
	70/30 wt						28.9	1.46	8.7	0.57	–	
Woven coir/woven glass	50/50 wt	Polyester	–	–	HL	–	47.7	–	65	–	92.5 kJ/m^2	Jayabal et al. (2011)
Woven (jute/carbon) hybrid fabric	–	Epoxy	Warp direction testing	–	VARIT	45	97.82	9.58	–	–	12 kJ/m^2	Karahan and Karahan (2015)
			Weft direction testing				95.74	9.76	–	–		

(continued)

Table 2 (continued)

Hybrid reinforcement		Matrix system	Additional description	Layup configuration	Making technique	Overall fiber content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength	References
Fibers and form	Content (%)											
EFB mat/CSM glass	70/30 wt	UP	–	–	RTM	45 wt	50	3.8	70	4.5	13.2 kJ/m^2	Khalil et al. (2007)
	10/90 wt					45 wt	77	5.5	90	6	16.7 kJ/m^2	
						35 wt	70	5.3	136	8.1	17 kJ/m^2	
Short (coir/CSM glass)	2/1 v	Phenolic	–	–	CM/HL	9 v	34.63	8.46	109.58	8.3	–	Kumar et al. (2009)
	1/2 v						71.58	8.54	179.21	8.6	–	
Woven bamboo/woven glass	–	Epoxy	–	[G/Bm/G/Bm]	HL	22 v	95	4.5	156	7.1	–	Latha et al. (2015)
				[Bm/G/G/Bm]			92	3.6	145	5.6	–	
				[G/Bm/Bm/G]			100	5.4	165	6.6	–	
Short (kenaf/glass)	50/50 wt	Epoxy	–	–	CM	9 wt	–	–	59	2.9	7 kJ/m^2	Muhammad et al. (2015)
		Epoxy + LENR					–	–	65	3.9	10.6 kJ/m^2	
Short (sisal/glass)	15/15 wt	PP	–	–	IM	30 wt	45	1.09	54	2.26	63.27 J/m	Nayak and Mohanty (2010)
		PP+ MAPP (2 % wt)					55	1.68	67	2.8	81.57 J/m	
Woven jute/woven glass	37/40 v	Epoxy	–	[G/J/G]	RI	77 v	73	4.8	365	–	–	Pandita et al. (2014)
Woven silk/woven glass	90/10 wt	Epoxy	–	–	HL	25 wt	61	0.9	94	1.8	–	Priya and Rai (2006)
	50/50 wt						84	1	114	5.4	–	
Short (bamboo/glass)	10/30 wt	Epoxy	–	–	CM	–	206	9.2	–	–	–	Rao et al. (2010)
	30/10 wt						113	9.2	–	–	–	
Kapok mat/CSM glass	75/25 v	UP	–	–	HL	9 v	78	1.1	–	–	12 J/m	Reddy et al. (2008a, b)
	25/75 v						102.55	1.2	–	–	13.6 J/m	

(continued)

Table 2 (continued)

Hybrid reinforcement		Matrix system	Additional description	Layup configuration	Making technique	Overall fiber content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength	References
Fibers and form	Content (%)											
Short (bamboo/glass)	30/10 wt	UP	–	–	CM	40 wt	166	7.9	–	–	–	Reddy et al. (2010)
	20/20 wt						94	4.9	–	–	–	
Short (palmyra/glass)	–	Rooflite	Fiber length 30 mm	–	CM	55 wt	39.83	1.4	56.2	2.62	3.83 J/cm^2	Velmurugan and Manikandan (2007)
			Fiber length 40 mm				39.3	1.43	56.24	2.6	5.3 J/cm^2	
			Fiber length 50 mm				42.65	1.51	59.19	3.54	6.05 J/cm^2	
Palmyra mat/CSM glass	28/27 wt		–	[G/P/G]			86	–	190	7	11.9 J/cm^2	
Short (Roystonea regia/glass)	15/5 wt	Epoxy	–	–	CM	20 wt	31.98	2.4	40.12	3.98	151 J/m	Goud and Rao (2012)
	5/15 wt						34.42	2.64	48.66	4	168.46 J/m	
Long curaua/CSM glass	–	Polyester	–	[G/Cu/G/Cu/G/Cu/G]	HL	–	92	2.34	144.5	7.58		Silva et al. (2009)
Sisal paper/CSM glass	3.4/18.8 v	Epoxy	–	[G/S/S/S]	HL	23 wt	43	1.04	–	–	20 kJ/m^2	Hashmi et al. (2011)
	14/8.45 v			[G/G/G/S]			71	1.04	–	–	35 kJ/m^2	
Jute fabric/glass fabric	50/50 wt	Epoxy	–	[G/J/G/J]	HL	25 wt	40	2.9	170	4	–	Dalbehera and Acharya (2014)
				[J/G/G/J]			36	2.4	210	9	–	
				[G/J/J/G]			42	2.9	241	13.5	–	
Ridge gourd fabric/glass fabric	–	Phenolic	–	[G/R/G]	HL	–	28.4	2.4	–	–	–	Rajulu and Devi (2007)
		Phenolic + CA1, CA2					31.3	2.66	–	–	–	

(continued)

Table 2 (continued)

Hybrid reinforcement		Matrix system	Additional description	Layup configuration	Making technique	Overall fiber content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength	References
Fibers and form	Content (%)											
Random vetiver/woven glass	19/15 wt	Vinyl ester	–	–	HL	44 wt	53.21	1	97.29	2	8.7 J	Vinayagamourthy and Rajeswari (2014)
Kenaf mat/aramid fabric	–	Epoxy	–	[K/A/K]	HL	51 wt	–	–	–	–	90 J	Yahaya et al. (2014)
				[A/K/A]			–	–	–	–	131 J	
				[A/K/A/K]			–	–	–	–	88 J	
Woven kenaf/woven aramid	42/60 wt	Epoxy	–	[A/K/A]	HL	–	105	3	66	4.5	32 kJ/m^2	Yahaya et al. (2015b)
	42/61 wt			[K/A/K]			100	4	44	2	42 kJ/m^2	
	42/62 wt			[A/K/A/K]			125	3.4	80	6.6	53 kJ/m^2	
Flax fabric/UD glass	–	Phenolic	–	[G/F]$_{16T}$	CM	67 v	450	40	–	–	–	Zhang et al. (2013)
				[G/G/F/F]$_{16T}$			412	41	–	–	–	
				[G/G/G/G/F/F/F/F]$_{16T}$			392	40	–	–	–	
Hemp mat/CSM glass	36/11v	UP	–	[H/G/G/H]	CM	47 v	70	8.3	–	–	–	Shahzad (2011)
	36/11v			[G/H/H/G]		47 v	82	7.7	–	–	–	

TNPR thermoplastic natural rubber; *CM* compression molding; *CSM* chopped strand mat; *UP* unsaturated polyester; *K* kenaf; *G* glass; *PET* polyethylene terephthalate; *PP* polypropylene; *POM* polyoxymethylene; *PALF* pineapple leaf fiber; *HL* hand lay-up; *P* pultrusion; *E* extrusion; *J* jute; *MAPP* maleic anhydride polypropylene; *IM* injection molding; *LDPE* low density polyethylene; *Bn* banana; *PF* phenol formaldehyde; *EFB* oil palm fiber; *RTM* resin transfer molding; *Cu* curaua; *C* carbon; *F* flax; *UD* unidirectional; *VARIT* vacuum assisted resin infusion technique; *Bm* bamboo; *LENR* liquid epioxidized natural rubber; *RI* resin infusion; *P* palmyra; *R* ridge gourd; *A* aramid; *H* hemp

Table 3 Mechanical properties of treated natural fiber/synthetic fiber reinforced polymer hybrid composites

Hybrid reinforcement		Matrix system	Treatment	Layup	Making technique	Overall fiber content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength	References
Fibers and form	Content (%)											
Woven flax/CSM glass		M	Flax with NaOH	[F/F/F/G/F/F/F]	CM	60 wt	139	14	101	14.8		Adkunle et al (2012)
		MM					147	16.4	180	17.5		
		MST					168	19	198	16.5	–	
		MMST					126.6	17.9	201	19.7	–	
Short (kenaf/carbon)	70/30 wt	TPNR	Carbon with sulfuric acid	–	CM	–	–	–	18	–	9.1 kJ/m^2	Anuar et al. (2008b)
	50/50 wt						–	–	25.5	–	11.8 kJ/m^2	
	30/70 wt						–	–	22	–	13 kJ/m^2	
Kenaf mat/CSM glass	7.5/22.5 v	UP	Kenaf with NaOH	[K/G/K/G/K]	CM	30 v	36	1.6		8.5	135 J/m	Atiqah et al. (2014)
	15/15 v						38.5	2.35	453	30	146 J/m	
	22.5/7.5 v						25	1.9		37	118 J/m	
Jute mat/CSM glass	–	Polyester	Jute with NaOH	[G/J/G/J/G]	HL	–	23.48	–	37.87	–	–	Trehan et al. (2015)
				[J/G/J/G/J]			15.65		23.18			
				[G/G/J/G/G]			22.94		61.48			
Short (banana/glass)	25/5 wt	PP	Banana with detergent	–	CM	–	44.5	1	51.5	1.9	51 J/m	Nayak and Monaty (2010)
	15/15 wt	PP					57	1.35	58.85	2.19	58 J/m	
		PP + MAPP (2 % wt)					64	1.69	71	2.64	69 J/m	
Flax mat/glass fabric	20/80 wt	Soyabean oil	Flax with acrylonitrile	[G/F/G]	IM	31 wt	123	3.5	130	6.9	17.7 J	Morye and Wool (2005)
	40/60 wt			[G/F/G]		39 wt	109	3.2	115	6	18 J	
	60/40 wt			[G/F/G]		40 wt	83	2.9	83	5.8	18.5 J	
	20/80 wt			[F/G]		31 wt	111.7	3.4	88	6.8	13.3 J	

(continued)

Table 3 (continued)

Hybrid reinforcement		Matrix system	Treatment	Layup	Making technique	Overall fiber content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength	References
Fibers and form	Content (%)											
	40/60 wt			[F/G]		39 wt	91	3.1	80	4	14.7 J	
	60/40 wt			[F/G]		40 wt	68.9	2.7	73.2	3.8	15.1 J	
	20/80 wt			[G/F]		31 wt	–	–	189	5	25.8 J	
	40/60 wt			[G/F]		39 wt	–	–	147	4.7	27.6 J	
	60/40 wt			[G/F]		40 wt	–	–	111	3.3	28.7 J	
Short (Sisal/glass)	30/70 wt	LDPE	Sisal with alkali	–	CM	–	31.45	1.139	–	–	–	Kalaprasad et al. (2004)
	50/50 wt		Sisal with acetylated				32.86	1.11	–	–	–	
	50/50 wt		Sisal with stearic acid				33.93	1.12	–	–	–	
	50/50 wt		Sisal with permanganate				34.63	1.182	–	–	–	
	50/50 wt		Sisal with MAPE				36.23	1.228	–	–	–	
	30/70 wt		Sisal with silane				38.98	1.606	–	–	–	
	30/70 wt		Sisal with peroxide DCP				40.73	1.726	–	–	–	
	30/70 wt		Sisal with peroxide BPO				41.92	1.776	–	–	-	

(continued)

Table 3 (continued)

Hybrid reinforcement		Matrix system	Treatment	Layup	Making technique	Overall fiber content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength	References
Fibers and form	Content (%)											
Short (kenaf/glass)	30/70 v	TPNR	Kenaf and glass with MAPP + silane	–	CM	20 v	30	1.05	–	–	–	Anuar et al. (2008a)
	50/50 v						26	0.9	–	–	–	
	70/30 v						26.2	0.8	–	–	–	
Short (flax/glass)	10/30 v	PP	MAPP (4.9 % v)	–	CM	40 v	21	0.6	–	–	–	Barvarz et al. (2015)
	20/20 v		MAPP (3.9 % v)				27	0.66	–	–	–	
	10/30 v		MAPP (4.9 % v)				29	0.62	–	–	–	
	10/30 v		MAPP (4.9 % v)				31	0.8	–	–	–	
	30/10 v		MAPP (2.9 % v)				26	0.59	–	–	–	
	20/20 v		MAPP (3.9 % v)				20	0.65	–	–	–	
Short (banana/glass)	70/30 wt	Polystyrene	Banana with NaOH	–	IM/CM	20 v	44.5	1.98	11.3	0.69	–	Haneefa et al. (2008)
			Banana with Benzoylated				35	1.78	7.9	0.49	–	
			Banana with PSMA				40	1.95	9.1	0.79	–	
Short (sisal/glass)	75/25 v	UP	Sisal with NaOH	–	HL	8 v	23.9	–	58.64	3.26	4 J/m	John and Naidu (2004a, b, c)
	50/50 v						27	–	66.19	3.57	5.46 J/m	
	25/75 v						30.26	–	76.78	3.78	5.76 J/m	

(continued)

Table 3 (continued)

Hybrid reinforcement		Matrix system	Treatment	Layup	Making technique	Overall fiber content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength	References
Fibers and form	Content (%)											
Long jute/long glass	30/10 v	Polyester	Jute with NaOH	–	HL	40 v	59	––	84	–	167 J/m^2	Kumar and Singh (2015)
	10/30 v						96	–	103	–	235 J/m^2	
Short (coir/CSM glass)	2/1 v	Phenolic	Coir with NaOH	–	CM/HL	9 v	35.3	8.49	121.6	8.91	–	Kumar et al. (2009)
	1/2 v						74.58	9.91	192.8	9.74	–	
Bamboo mat and CSM glass	–	Epoxy	Bamboo with NaOH	[G/Bm/Bm/Bm/Bm/Bm/G]	HL		124	–	134	–	–	Kushwaha and Kumar (2010)
		Polyester		[G/Bm/Bm/Bm/Bm/Bm/G]			130	–	120	–	–	
		Epoxy		[G/Bm/Bm/G/Bm/Bm/G]			120	–	121	–	–	
		Polyester		[G/Bm/Bm/G/Bm/Bm/G]			104	–	114	–	–	
Bamboo mat and woven glass	–	Epoxy		[G/Bm/Bm/Bm/Bm/Bm/G]			128	5	170	–	–	
		Polyester		[G/Bm/Bm/Bm/Bm/Bm/G]			–	–	132	–	–	
		Epoxy		[G/Bm/Bm/G/Bm/Bm/G]			160	5.2	172			
		Polyester		[G/Bm/Bm/G/Bm/Bm/G]					144			
Short (kenaf/glass)	50/50 wt	Epoxy	Kenaf with NaOH; glass with silane	–	CM	9 wt	–	–	68	3.7	9.7 kJ/m^2	Muhammad et al. (2015)
		Epoxy + LENR					–	–	73	4.5	13 kJ/m^2	
Short (coir/glass)	30/9.2 v	UP	Coir with alkali	[G/Cr/G]	HL/CM		58	2.8	132.6	8.2	–	Pavithran et al. (1991)
	30/9			[G/GCr/G			55	3	145	7	–	
Short (bamboo/glass)	10/30 wt	Epoxy	Bamboo with alkali	–	CM	40 wt	213	11.5	–	–	–	Rao et al. (2010)
	20/20 wt						168	9.2	–	–	–	
Kapok mat/CSM glass	75/25 V	UP	Kapok with NaOH	–	HL	9 v	94	1.6	–	–	13 J/m	Reddy et al. (2008a, b)
	25/75 v			–			108	2.36	–	–	14.7 J/m	
Short (bamboo/glass)	30/10 wt	UP	Bamboo with NaOH	–	CM	40 wt	220	11.4	–	–		Reddy et al. (2010)
	20/20 wt						243	10.7	–	–		

(continued)

Table 3 (continued)

Hybrid reinforcement		Matrix system	Treatment	Layup	Making technique	Overall fiber content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength	References
Fibers and form	Content (%)											
Long palmyra/CSM glass	75/25 wt	Polyester	Palmyra with alkali	–	HL/CM	30 wt	70.58	3.32	146	6.53	52 kJ/m^2	Shanmugam et al. (2014)
	25/75 wt			–			88.78	4.03	173	5.49	62.27 kJ/m^2	
Ridge gourd fabric/glass fabric	–	Phenolic	Ridge gourd with alkali	[G/R/G]	HL	–	34	2.9	–	–	–	Rajulu and Devi (2007)
		Phenolic + CA1, CA2					41.9	3.7	–	–	–	
Random vetiver/woven jute/woven glass	13/13/8 wt	Vinylester	Vetiver with alkali	–	HL	44 wt	74	2.1	131.9	3.3	15.33 J	Vinayagamourthy and Rajeswari (2014)
	10/10/14 wt						70.96	2.3	137.6	2.9	18.33 J	
Random vetiver/woven glass	10/24 wt						64.2	2.45	120	3.2	16.67 J	
	19/15 wt						69.7	2.1	131.9	3.1	14.33 J	

M methacrylated soyabean oil; *MM* methacrylic anhydride modified soyabean oil; *MST* methacrylated soyabean oil with styrene; *MMST* methacrylic anhydride modified soyabean oil with styrene; *NaOH* sodium hydroxide; *CA1* triethoxymethylsilane; *CA2* 3–aminopropyltriethoxysilane

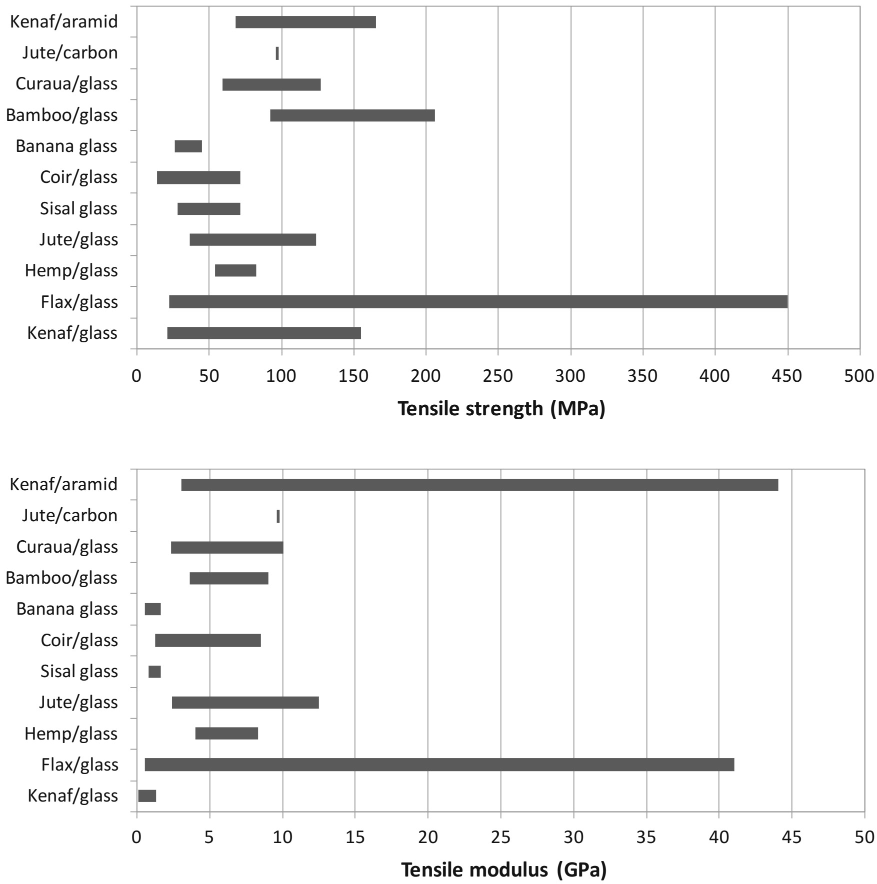


Fig. 2 Comparison of tensile properties of various natural fiber/synthetic fiber hybrid composites

composites have been less studied than other composites and, hence, have fewer data points.

2.1.1 Stress–Strain Response

The mechanical performance of any material is best understood in terms of its stress–strain response to mechanical loading. Hybrid composites are no exception. Figure 4 shows the comparison of stress–strain curves of polypropylene (PP), hemp/PP, and hemp/glass fiber-PP composites in tensile loading (Panthapulakkal and Sain 2007). Both hemp and glass fibers used were in short randomly oriented form and the composite made from them was intraply. Being a thermoplastic, PP shows a non-linear ductile fracture whereas the incorporation of the brittle hemp and glass fibers changes the fracture mode to brittle. The tensile response of neat PP

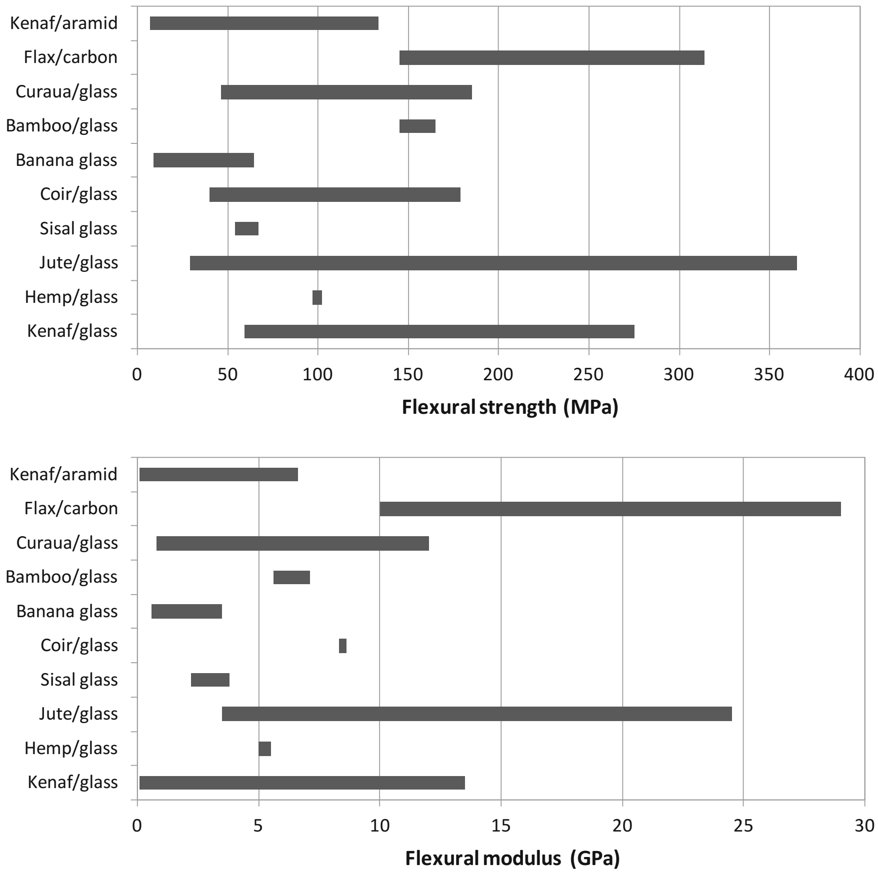
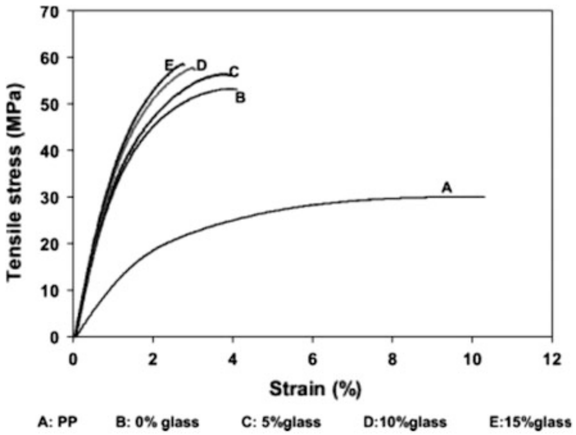


Fig. 3 Comparison of flexural properties of various natural fiber/synthetic fiber hybrid composites

Fig. 4 Tensile stress–strain curves of PP, hemp/PP composite, and hemp/glass-PP hybrid composite (Panthapulakkal and Sain 2007)



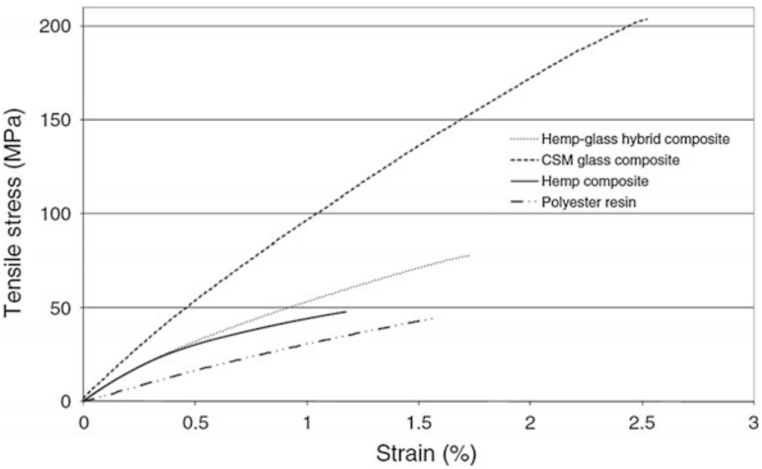


Fig. 5 Tensile stress–strain curves of polyester, hemp-polyester, CSM glass-polyester and hemp/glass-polyester composite (Shahzad 2011)

as well as natural fiber composites starts to deviate from linearity at small strains, typically less than 1 %. The limit of linearity depends on properties of the constituents and the microstructure of composite. The composites exhibit linear deformation at lower strain, where the matrix and fibers behave linearly, and nonlinear deformation at higher strain, which continues until the fracture of the composite. A prominent 'knee' can be observed which is a characteristic of short fiber composites. The nonlinear deformation in the composites is attributed to the following factors:

(i) fracture of weak LE fibers situated at right angles to the loading direction, weakening the laminate and transferring the load to stronger HE fibers,
(ii) microcracks initiation at the fiber end-matrix interphase that propagates along the fiber length,
(iii) plastic deformation of the matrix, and
(iv) microcrack opening in the matrix and the slow crack propagation through the deformed matrix. Near the fracture, catastrophic crack propagation takes place through the matrix, fracturing the fibers and the laminate. As expected, both the modulus and strength of the composites increase with the incorporation of hemp and hemp/glass hybrid fibers.

Figure 5 shows the example of stress–strain response of hybrid composites made of a thermoset matrix unsaturated polyester (Shahzad 2011). Both hemp and glass fibers were in short randomly oriented mat form and the composite was interply. Being a thermoset, the fracture of polyester is brittle and remains so after incorporation of hemp and hemp/glass hybrid fibers. The stress–strain curve of hemp/glass hybrid composite lies between those of hemp fiber and CSM glass fiber composites, signifying improvement in strength and modulus of hybrid composites compared to hemp fiber composites. The curves of composites again show linear and non-linear portions, represented by 'knees' in their curves, although not as prominent as for thermoplastic hybrid composites shown above. The reasons of existence of 'knee' are the same as described above. The 'knee' of the curve for thermoset hybrid composites is less prominent than that for thermoplastic hybrid composites, probably because, unlike the thermoplastic matrix, the thermoset matrix does not show plastic deformation and, hence, does not contribute to curvature of the curve. The mechanisms for fracture are expected to be the same as those for thermoplastic hybrid composites. Hybrid composites made of woven and aligned natural fibers/glass fibers have also been shown to exhibit similar non-linear behaviour.

2.1.2 Effects of Fiber Content, Stacking Sequence, Fiber and Fabric Structure, Interply and Intraply Configurations, and Fiber Length

The foremost parameter that determines the mechanical properties of natural fiber/synthetic fiber hybrid composites is the total fiber content and the natural fiber/synthetic fiber ratio in the composite. The mechanical properties of hybrid composites increase linearly with the increase in total fiber content, just like single fiber composites. The ratio of natural fiber/synthetic fiber content in the composite also affects the mechanical properties of the hybrid composites. As can be seen from Table 1, synthetic fibers have considerably higher tensile properties than natural fibers. Incorporation of synthetic fibers in natural fiber composites results in almost linear increase in tensile properties of the hybrid composites. However there is a limit to how much increase in these properties can be obtained. Beyond this limit, fibers start to agglomerate which hinders effective stress transfer from matrix to fibers, obviating further improvement in tensile properties.

Mishra et al. (2003) reported a maximum content of 8 wt% of glass fibers in pine apple leaf fiber-polyester hybrid composites for ultimate tensile strength, impact strength and flexural strength. Al-Kafi et al. (2006) reported a maximum content of 25 wt% of jute fibers in jute/glass-polyester composites for tensile and flexural properties. Ahmed et al. (2006) reported a maximum content of 16 wt% of glass fiber fibers in jute/glass fabric-polyester composites for flexural and interlaminar shear strength.

In intraply hybrid composites also, there is an upper limit to glass fiber loading above which the properties start to deteriorate. Devi et al. (2012) studied the properties of pineapple leaf fiber (PALF)/glass-polyester composites. The composite was fabricated at constant 30 % volume fraction of fiber, while PALF/glass fiber ratio was varied from 0 to 100 %. Incorporation of 10 % volume fraction of glass fiber increased the tensile strength of the hybrid composite by about 28 %.

However at loading level of 20 % of glass fibers, a decrease in strength was noticed and a leveling off was observed at 50 % loading. The improvement in tensile strength at low glass fiber loading was explained by the fact that at these loadings glass fibers effectively transferred load from weak PALF fibers which broke first. As the loading of glass fiber gradually increased, fiber dispersion became less uniform and the tensile strength decreased. Similar reduction in tensile modulus was reported with increase in glass fiber loading.

The second crucial parameter in the mechanical properties of natural fiber/synthetic fiber hybrid composites is the lay-up configuration, i.e., how successive plies are stacked up. It has been shown earlier that having plies of different fibers as skin and core can have significant effect on the mechanical properties of carbon/glass and aramid/glass hybrid composites. The same principle applies to natural fiber/synthetic fiber hybrid composites. Various studies have been undertaken in this regard and it has been shown that having high strength and stiffness synthetic fiber plies as skin can be more beneficial in terms of improved properties, although the use of natural fiber plies as skin has also been reported to have its advantages, for example, in fatigue loading, and this issue needs further investigation. This is especially true of the flexural and impact properties where the strength and stiffness of skin layers play a major role in these properties. The effect of difference in elongation to failure between the two fiber types on the mechanical properties of composites has also been discussed earlier. In natural fiber/synthetic fiber hybrid composites, natural fibers are generally the LE fibers and glass and aramid fibers are HE fibers. The elongation to failure of natural fibers and carbon fibers are comparable.

The effects of hybrid fiber ratio and fiber plies stacking sequence on the tensile properties of flax/glass-phenolic interply composites were investigated by Zhang et al. (2013). The tensile strength and modulus of unidirectional hybrid composites increased with the increase in the relative volume fraction of glass fibers. However the tensile behavior of the hybrid composites was similar to that of carbon/glass hybrid composites. When the volume fraction of LE flax fibers in the hybrid composites was higher than glass fibers, the hybrid composites failed when the tensile strain reached the failure strain of flax fibers. However when the volume fraction of glass fibers in the hybrid composites was higher, flax fibers failed first, but the hybrid composite still kept its integrity until the failure of HE glass fibers. The following equation was found to agree with the experimental values of tensile strength of hybrid composite,

$$\sigma_c = (1 - V_m)\varepsilon_c\left(E_g V_g + E_f V_f\right) \tag{7}$$

where subscripts c, m, f, and g refer to composite, matrix, flax and glass respectively. The stacking sequence of flax fiber plies and glass fiber plies showed bigger influence on the tensile strength and tensile failure strains than tensile modulus of the hybrid composites. The interlaminar shear strength and the interlaminar fracture toughness of hybrid composites were also higher than those of glass fiber composites.

There have been very few attempts at predicting the theoretical mechanical properties of natural fiber/synthetic fiber hybrid composites by using classical models. Junior et al. (2013) used a modified form of Cox-Krenchel model for predicting the tensile modulus of intraply curaua/glass-polyester composites as follows:

$$E_c = \eta_o V_f \left(\eta_{Lg} C_g E_g + \eta_{Lc} C_{cu} E_{cu}\right) + (1 - V_f) E_m \tag{8}$$

where E_c, E_g, E_{cu} and E_m are the moduli of composite, glass fiber, curaua fiber and matrix respectively, η_{Lg} and η_{Lc} are the length efficiency factors of the glass and curaua fibers respectively, η_o is the Krenchel factor, and V_f is the total fiber volume fraction. The modified Halpin-Tsai equation for short fiber composites was also used:

$$E_c = 3/8\,E_1 + 5/8\,E_2 \tag{9}$$

where E_1 and E_2 are the predicted moduli for short fiber unidirectional composites in the longitudinal and transverse directions. The results are shown in Fig. 6. The horizontal axis represents the composition of the composites, where, for example, 30/70/30 means 30 % total fiber volume fraction, of which 70 % is curaua fiber and 30 % is glass fiber. The elastic moduli of the hybrid composites were also evaluated using nondestructive testing (NDT). It was observed that the theoretical results were generally close to the experimental results, but the Cox-Krenchel model gave a more accurate prediction of elastic modulus. Modulus values increased up to a total fiber volume fraction of 30 %, and the hybrid 30/30/70 represented the highest modulus among the hybrids.

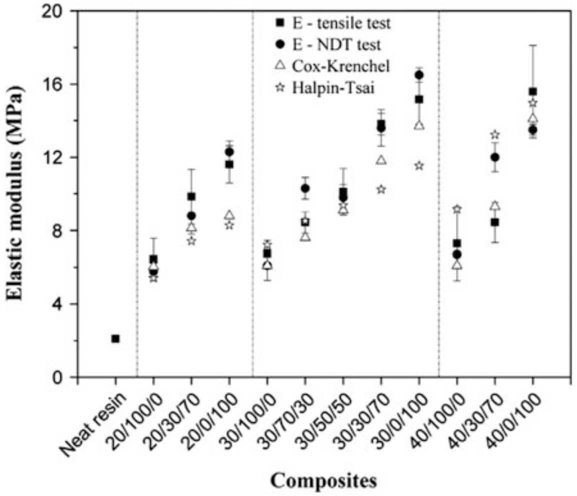


Fig. 6 Hybridization effect on the mechanical properties of curaua/glass fiber composites (Junior et al. 2013)

Yahaya et al. (2014) studied the effect of three different lay-up configurations on quasi-static penetration and ballistic properties of nonwoven kenaf/kevlar-epoxy composites: kenaf as skin layers, core layers and as the alternating layers. The energy absorption and maximum penetration force of hybrid composites in quasi-static penetration was higher than the kevlar-epoxy composite, with kenaf as the core layers (kevlar as the skin layers) giving maximum penetration force and energy absorption. In ballistic testing, hybrid composites recorded lower ballistic limit and energy absorption than the kevlar/epoxy composite. The ballistic limit of hybrid composites with kenaf as the skin layers was superior to other hybrid composites. Thus hybridization of kevlar with kenaf was not found to be useful in their ballistic performance.

In another study, Yahaya et al. (2015b) studied the effect of stacking sequence and chemical treatment on the mechanical properties of woven kenaf/kevlar-epoxy composites. Hybrid composites with kevlar as skin layers showed better tensile and flexural properties but lower impact properties compared to those having kenaf as skin layers. Tensile and flexural properties of alkali treated hybrid composites were better than non-treated fiber hybrid composites. In another study (2014), they examined the effect of three different kenaf fiber structures (woven, non-woven and cross-ply unidirectional) on their hybrid composites with kevlar-epoxy for their potential use as vehicle spall liners. Hybrid composites with unidirectional cross plied at 0°/90° of kenaf yarn exhibited highest tensile strength (164 MPa) compared to woven (145 MPa) and mat fiber (67 MPa) orientation. A similar trend was observed in tensile modulus. In terms of flexural strength and modulus, woven orientation composites exhibited better properties than unidirectional cross ply and nonwoven orientation. Increasing the volume fraction of kenaf fiber resulted in negative effect on the tensile and flexural properties of hybrid composites because of weak kenaf-matrix interfacial bonding.

In a similar study, Yahaya et al. (2015a) used three different kenaf fiber structures (woven, unidirectional and mat) in kevlar-epoxy composites for their potential use as vehicle spall liners. The tensile and Charpy impact strength properties of woven kenaf-kevlar composite were higher than other hybrid composites. On the contrary, the flexural strength of the hybrid composites with unidirectional kenaf fiber was slightly higher compared with a hybrid with woven kenaf. The results of this study indicated that using kenaf in the form of woven structure could produce a hybrid composite material with higher mechanical properties.

Velmurugan and Manikandan (2007) prepared both intraply and interply palmyra/glass fiber—rooflite composites and compared their properties. The interply composites had glass fiber layers as skin and palmyra fiber layers as core. The mechanical properties (tensile, bending, shear and impact) of interply composites were found to be better than intraply composites.

Trehan et al. (2015) studied the effects of stacking sequence on the tensile and flexural strength of jute/glass-thermoplastic polyester composites. Three different kinds of interply stacking sequences were studied: C1 = G–J–G–J–G; C2 = J–G–J–G–J; C3 = G–G–J–G–G, where G stands for glass fiber and J stands for jute fiber plies. The results showed that both the strengths were largely affected by stacking sequences. The sequence C1 was ideal for tensile strength which showed that when glass fiber content was a little more than jute fiber and was used as skin plies, the combination provided higher strength. However the sequence C2 having greater jute fiber content showed lower tensile strength due to increased brittleness. For flexural strength, the increased glass content provided greater stiffness and sequence C3 with glass fiber plies as skin showed optimum results.

Similarly, Dalbehera and Acharya (2015) compared woven glass and jute fabric reinforced epoxy composites with different stacking sequences. It was found that the optimum tensile, flexural and interlaminar shear strength properties were obtained with two jute fabric core plies sandwiched between glass fabric skin plies.

For woven coir/glass-polyester composites having glass layers as skin, Jayabal et al. (2011) showed that their flexural strength (65 MPa) and impact strength (92.6 kJ/m^2) were almost double that than that of coir-polyester composites.

Latha et al. (2015) also showed that, as shown in Fig. 7, the hybrid laminate with skin glass fiber plies on either side of the bamboo fiber plies has optimum strength and modulus. However they reported that stacking sequence with glass and bamboo plies in alternate positions gives good balance between the properties and cost.

Pandita et al. (2014) showed that having glass fabric plies as skin and jute fabric plies as core can almost double the flexural strength of hybrid composites, compared to jute fabric composites. Similarly, in impact testing, the mode of impact damage in jute composites subjected to a falling steel object is perforation. However, at same impact energy, perforation damage did not occur in jute/glass hybrids, having glass fabric plies as skin.

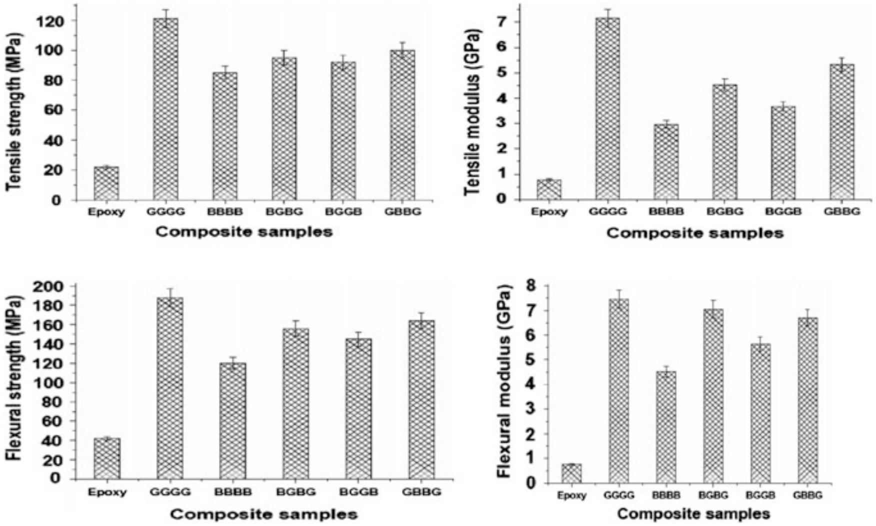


Fig. 7 Effects of stacking sequence on mechanical properties of bamboo/glass fiber-epoxy hybrid composites (Latha et al. 2015)

Angrizani et al. (2014) studied the effects of different stacking sequences on the properties of interply curaua/glass fiber reinforced polyester composites. Hybrid composites with glass layers at skin showed the best results regarding flexural properties, short beam strength and Iosipescu shear strength. On the other hand, tensile properties were less sensitive to the laminate lay-up.

Ahmed and Vijayarangan (2008) investigated the influence of the stacking sequence on the mechanical properties for woven jute/glass fabric-polyester composites. The best flexural properties were reported when the glass plies were used as skin layers. Amico et al. (2010) and Khalil et al. (2009) reached the same conclusion for interply hybrids composed of random mats of sisal/glass and oil palm empty fruit bunch/glass fibers, respectively.

Ahmed et al. (2007) studied the low velocity impact damage characterization of woven jute/glass fabric- polyester composites by varying the jute/glass weight fraction. It was found that the hybrid laminate with jute/glass weight fraction of 25/16 % is the optimum combination of jute and glass fiber with minimum deflection, maximum peak load and better damage tolerance.

Hariharan and Khalil (2005) reported that the hybridization of the glass fibers with the oil palm fibers increased the impact strength of the hybrid composites significantly. At 10 % volume fraction of glass fibers, the impact strength of the hybrid composite increased by about 24 % when impacted at the oil palm fiber skin layer while an increase of 110 % was noted when the hybrid was impacted at the glass fiber skin layer.

From their studies on short uniaxially-oriented kapok/glass fabric-polyester composites, Reddy et al. (2008b) concluded that kapok to glass ratio of 1:3 gave optimum results in terms of tensile properties.

Kushwaha and Kumar (2010) studied the effects of using glass fibers as strand mat and as woven mat with bamboo fiber mat in epoxy and polyester resins. The hybridization with glass mat increased the mechanical and water resistance properties of the hybrid composites. The increase in properties was higher in the woven glass mat reinforced hybrid composites compared to the strand mat. For both the epoxy and polyester matrix composites, when two layers of strand glass mat were used the mechanical properties increased, but with three layers it showed a decrease in value. On the other hand, the mechanical properties of woven glass mat composites increased with the increase in the number of glass mat layers. Addition of glass fiber also resulted in reduction of water absorption by the epoxy- and polyester-bamboo composites. Again the decrease in water absorption by the woven glass mat reinforced hybrid composite was much higher compared to the glass strand mat. It was explained that glass fibers in woven mat are arranged in a close packed manner which provides more effective barrier and prevents the contact between water and the hydrophilic bamboo fibers.

Dan-Mallam et al. (2014) used a novel design technique whereby a hybrid fabric was manufactured with kenaf yarn in the warp and PET yarn in the weft direction (intraply), and reinforced with polyoxymethylene (POM) matrix. The results were compared with the results of woven kenaf/POM and woven PET/POM composites. When tested in kenaf direction, the intraply kenaf/PET hybrid composite showed a significant increase in tensile strength and modulus than woven POM/kenaf composite and woven POM/kenaf/PET hybrid composite. When tested in PET direction, the tensile strength showed slight improvement while tensile modulus showed slight decline than kenaf fiber direction. These results suggest that the PET fiber contributed more in raising the composite tensile strength while the kenaf fiber contributed more in improving the composite elastic modulus. The intraply hybrid composite also showed significant improvement in impact strength compared to the woven POM/kenaf composite. The water absorption of the woven POM/kenaf composite decreased by approximately 30 % due to hybridization with PET fiber.

In a similar study, Karahan and Karahan (2015) studied the properties of intraply plain weave jute/carbon fabric-epoxy composites. The fabric was prepared such that the warp yarns were composed of carbon whereas the weft yarns were composed of jute. Cross-ply laminates were prepared by using vacuum infusion. The tensile modulus of hybrid composites increased by 24 % over jute fabric composites. However the tensile strength increased by only 2.6 %. This lower-than-expected increase in values were explained by the mismatch in properties of jute and carbon fabrics. However there was 65 % increase in impact strength and 51 % increase in fracture toughness of hybrid composites over jute fabric composites, implying good toughening effect of carbon fibers over natural fibers which have poor impact properties. Similarly hybrid composites showed lower water absorption than jute fabric composites.

Fiore et al. (2011) studied the effects of hybridization of two types of flax fabric with carbon fabric in epoxy matrix composites. One flax fabric was unbalanced plain weave normally used to make curtains; the other heavier and more expensive fabric was balanced twill weave usually used as reinforcement in composite structures. The carbon fabric was unidirectional ultra-high modulus nonwoven. Whereas the tensile and flexural properties of composites made from both types of fabrics were quite low, hybridization of just one layer of carbon fabric with five layers of both types of flax fabric resulted in significant improvements (two to three times) in these properties. These properties were considered to be comparable to those of other conventional composites normally used in engineering applications.

Cerbu (2015) studied the mechanical properties of woven flax/glass-epoxy composites having flax fibers of different properties in warp and weft directions. The interply composites had glass fabric plies as skin layers. The maximum values of the tensile strength and the flexural strength measured in the weft direction were 41 and 35 % greater, respectively, than the values corresponding to the warp direction. But the increase in the flexural properties was truly spectacular. The flexural modulus was more than double and almost triple in the weft/warp direction, in comparison with the corresponding values recorded in the same directions of the flax/epoxy composites. The maximum value of the flexural strength in the weft direction was almost double in the case of the hybrid composite than flax/epoxy composites. It was thus convincingly shown that having glass fabric layers as skin results in distinct advantages.

Kalaprasad et al. (2004) studied the effects of fiber lengths on properties of sisal/glass-low density polyethylene (LDPE) composites. Hybrid composites with

50/50 ratio of sisal and glass fibers having an average fiber length of 1, 2, 3, 4, 6, 8 and 10 mm were prepared. Samples of sisal fiber reinforced polymer (SRP) and glass fiber reinforced polymer (GRP) containing various fiber lengths were also prepared. The results showed that in the case of SRP, tensile strength increased with increase in fiber length and reached a maximum at 6–8 mm fiber length. The curly nature of sisal fibers longer than 8 mm prevented the proper alignment of fibers in the composites and was considered to be the reason for decline in tensile strength. The enhancement in tensile strength for GRP was found to be maximum at up to 3 mm fiber length. As glass fibers are more brittle than sisal fibers, they are more susceptible to failure or breakage during normal processing operations such as mixing, extrusion and molding at higher lengths. However in the case of hybrid composites the decrease of tensile strength after 8 mm length was due to the combined effects of curling of sisal fiber and severe breakage of glass fibers. The studies showed that the optimum length of sisal and glass fibers for obtaining maximum tensile properties in hybrid composites is 6 mm.

Bhagat et al. (2014) studied the effects of fiber length and fiber loading on mechanical and water absorption properties of glass/coir-epoxy composites. Composites of eight different compositions reinforced with two different coir fiber loadings (5 and 10 wt%) with four different fiber lengths (5, 10, 15, and 20 mm) were made keeping glass fiber loading constant (20 wt%) with fiber length of 10 mm. A gradual increase in tensile and flexural strength was observed with the increase in the coir fiber length of up to 15 mm of hybrid composites. However further increase in fiber length of 20 mm showed a decrease in tensile and flexural strength which was attributed to the curling effect of the long coir fiber which prevents the proper alignment of fibers in the longitudinal direction of the composites. The maximum tensile and flexural strength values were obtained for the composite with 10 wt% coir fiber loading at 15 mm length. However the tensile modulus gradually went on increasing irrespective of the fiber length. The rate of moisture absorption increased with increase in both fiber loading and fiber length.

Silva et al. (2009) showed that having glass fiber plies as skin layers can be an effective barrier for the hydrophilic nature of curaua/glass-polyester composites, for both distilled water and sea water. Although the saturation water absorption of the laminated hybrid was slightly higher for distilled water (2.10 %) than for sea water (1.95 %), the saturation time was approximately the same for both conditions. Significantly there was no flexural strength decrease for either of the aging conditions, which showed the advantage of having glass fiber plies as skin layers. Pandita et al. (2014) also reported similar improvements in water absorption of jute/glass fabric-epoxy composites, having glass fabric plies as skin. Whereas the saturation water absorption of jute composite was 6.5 %, that of hybrid was 5 %.

Barvaz (2015) studied the effects of water absorption on mechanical properties of flax/glass-PP composites. They found that addition of only 10 vol.% of glass fibers can effectively reduce deterioration of mechanical properties of the hybrid in water and any further addition in glass fiber concentration did not have any appreciable effect.

The fatigue properties of natural fiber/synthetic fiber hybrid composites are a relatively less studied area. Shahzad (2011) studied the effects of stacking sequence on tensile and fatigue properties of random mat hemp/glass-polyester interply composites. Both hemp and glass fibers were used as skin and core plies. For hemp skin–glass core composites, the tensile strength increased by almost 50 % and tensile modulus increased by about 15 %, compared to hemp fiber composites. For glass skin, hemp core composites, the tensile strength increased by about 75 % and tensile modulus increased by about 7 %. The fatigue properties of hybrid composites also showed marked improvements. The endurance limit of hemp skin–glass core composites at one million cycles showed an almost 50 % increase compared to hemp fiber composites. On the other hand, the slope of the S–N curve of glass skin-hemp core composites was steeper than hemp skin–glass core composites, signifying lower fatigue strength at higher fatigue cycles. This was also reflected in their lower value of endurance limit of about 25 MPa, compared to 30 MPa for hemp skin–glass core composites. This suggests that having hemp fibers as skin and glass fibers as core plies may be more beneficial in improving the fatigue strength of hybrid composites. The fatigue sensitivity of materials can be best understood by comparison of their normalised S–N curves. The comparisons of normalised S–N curves of hemp fiber, CSM glass fiber and hemp-glass fiber hybrid composites are shown in Fig. 8. It is clear that, although glass fiber composites have higher fatigue strength, they are more fatigue sensitive than hemp fiber and

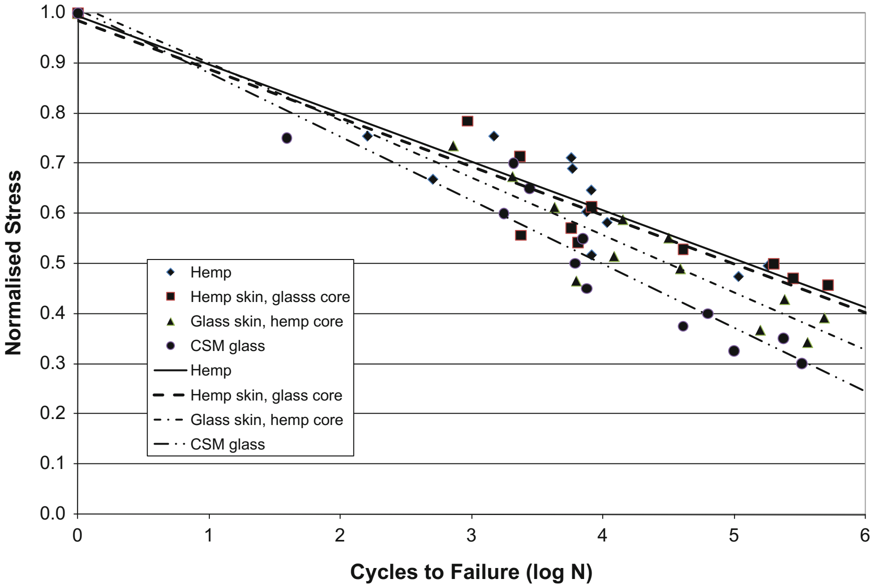


Fig. 8 Normalised S–N curves of hemp, glass, hemp skin/glass core hybrid and glass skin/hemp core hybrid composites (Shahzad 2011)

hemp/glass fiber hybrid composites as shown by the steeper slope of their normalised S–N curve.

Sharba et al. (2015) studied the effects of fiber ratios on fatigue properties of kenaf/glass fabric-polyester composites and validated the low fatigue sensitivity of natural fiber hybrid composites. Three glass/kenaf weight ratios of 70/30 % (H1), 55/45 % (H2), and 30/70 % (H3) were used to manufacture hybrid composites. The results showed that the hybrid composite (H1) offered a good balance and the best static properties, but in tensile fatigue loading (H3), with higher kenaf content, displayed low fatigue sensitivity and lower stiffness degradation than glass and other hybrid composites, confirming good fatigue properties of natural fibers.

The use of biodegradable polymer matrices is an emerging area of natural fiber composites and they are being increasingly employed to augment the biodegradability of the composites. They are also used in natural fiber/synthetic fiber hybrid composites. Morye and Wool (2005) used a modified soybean oil matrix material with flax/glass fibers. This resin is biodegradable which increases the green credentials of the composite. The results showed good mechanical properties of the composites. The soyabean oil was considered to be a good substitute for synthetic polymer matrices.

Adekunle et al. (2012) also used soyabean oil as resin in flax/glass fiber hybrid composites. The flax fibers used were in non-woven and woven forms and glass fibers were in woven form. Different stacking sequences were used. These composites had similar mechanical properties to the ones reported in literature based on synthetic unsaturated polyester and epoxy resins. Thus bio-based thermoset resins have the potential to substitute the conventional synthetic thermosetting polymers.

2.1.3 Effects of Fiber-Matrix Adhesion/Fiber Surface Treatment

As stated earlier, natural fibers are inherently incompatible with polymer matrices, resulting in poor fiber/matrix adhesion which adversely affects the mechanical properties of the composites. A number of methods are available for physical and chemical treatments of natural fibers for improving their adhesion with polymer matrices. These methods have varying degrees of success. A good review of these methods can be found in Kabir et al. (2012). These methods are also useful for improving fiber matrix adhesion in natural fiber/synthetic fiber hybrid composites. The improvements in fiber/matrix adhesion invariably result in improvement in mechanical properties of the composites. A brief survey of the studies on the effects of various fiber surface treatments on the mechanical properties of hybrid composites follows.

Kalaprasad et al. (2004) studied the effects of various surface treatments of sisal fibers on properties of sisal/glass-polyethylene composites. Chemical surface modifications such as alkali, acetic anhydride, stearic acid, permanganate, maleic anhydride, silane and peroxides given to the fibers and matrix were found to be successful in improving the interfacial adhesion and compatibility between the fiber and matrix. It was found that the extent of improvement in tensile properties of hybrid composites varied with respect to the nature of chemical modifications between fiber and matrix. Improved mechanical anchoring and physical and chemical bonding between fiber and polyethylene matrix were considered to be the reasons for superior tensile strength and modulus in treated composites. Several secondary reasons such as high degree of fiber dispersion and reduced hydrophilicity in chemically modified fibers were also believed to play a role. Among the various chemical modifications, the best tensile properties were exhibited by the benzoyl peroxide treated fibers. This was attributed to the peroxide-initiated grafting of polyethylene on to the fibers.

Zhong et al. (2011) studied the effects of sisal fiber microfibrillation on the fiber/matrix adhesion of sisal/aramid-phenolic composites. Development of microfibrils and aggregates on the fiber surface is expected to improve the interfacial adhesion between the sisal fiber and resin by providing a large contact area and by inhibiting the formation of spontaneous cracks in the composites. It was found that, indeed, the compression, tensile and internal bonding strengths, and wear resistance of the hybrid composites were remarkably improved following this method.

Rajulu and Devi (2008) used 2 % alkali treatment with and without coupling agents triethoxymethylsilane (CA1) and 3-aminopropyltriethoxysilane (CA2) for improving fiber matrix adhesion in glass/ridge gourd fabric-phenolic composites. Both kinds of surface treatments increased the tensile properties of the composites. However the combination of alkali treatment with CA2 was found to be most favorable. In this combination the tensile strength increased by 48 %, tensile modulus by 54 % and elongation by 35 % compared to untreated composites.

Nayak and Mohanty (2010) reported positive improvements in mechanical properties of sisal/glass-PP composites following the use of 2 % coupling agent maleic anhydride PP (MAPP). Tensile strength, flexural strength, and impact strength increased by an optimum value at 15 % sisal and 15 % glass fiber loading in the presence of MAPP, whereas the rate of water absorption in the composite decreased due to the presence of glass fiber and coupling agent. They also reported improvements in tensile, flexural and impact properties and reduction in water uptake of banana/glass-PP composites following the same surface treatment and at the same fiber content.

Muhammad et al. (2015) prepared kenaf/glass-epoxy composites with epioxidized natural rubber as toughening agent. Kenaf fibers were treated with 6 % alkali whilst the glass fibers were treated with a silane coupling agent. It was reported that the treatment and the addition of epioxidized natural rubber contributed to the increase in the impact strength by 40 % whilst the flexural properties recorded a 13 and 15 % increase for both flexural strength and flexural modulus, respectively. Both glass fiber and kenaf fibers showed considerable improvement in interfacial adhesion following surface treatments as shown in Fig. 9.

Atiqah et al. (2014) studied the properties of kenaf/glass-polyester composites following 6 % alkalization of kenaf fibers. The composites showed improvements in tensile, flexural and impact properties compared to untreated fiber composites and the maximum values were reported for composites containing 15/15 vol.% of

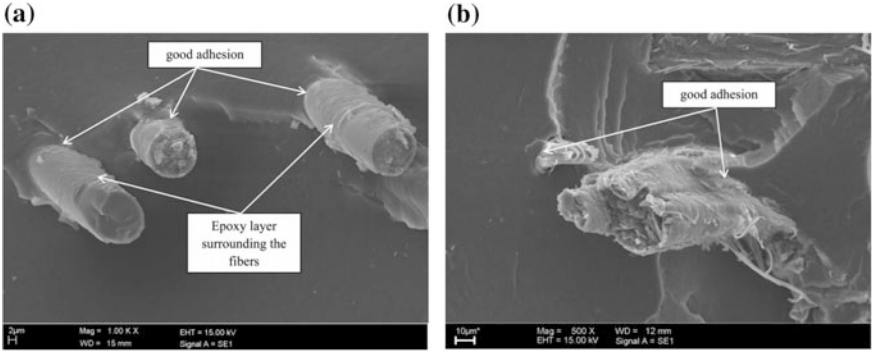


Fig. 9 Good surface adhesion of glass fibers (**a**) and kenaf fibers (**b**) with the matrix following surface treatment (Muhammad et al. 2015)

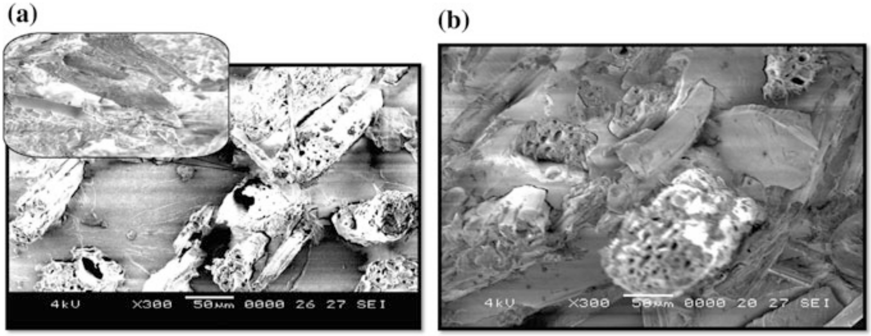


Fig. 10 Fractured surfaces of kenaf/glass-polyester composites showing good interfacial adhesion of alkalized fiber composites (**a**), and fiber pull-out (**b**) because of poor interfacial adhesion of untreated fiber composites (Atiqah et al. 2014)

kenaf/glass fibers. The surface morphology of fracture composites also showed good fiber/matrix interfacial adhesion while untreated fibers composites showed considerable fiber pull out due to poor interfacial adhesion as shown in Fig. 10.

Similarly Haneefa et al. (2008) reported positive effects of alkalization, benzoylation and polystyrene styrene maleic anhydride (PSMA) treatments of banana fibers on tensile properties of banana/glass-polystyrene composites. These chemical modifications resulted in enhanced fiber dispersion in the composites, reduced hydrophilicity of banana fiber, and improved fiber/matrix compatibility through mechanical anchoring, physical and chemical bonding. Improvement in properties followed the order of alkalization > PSMA > benzoylation > untreated.

3 Conclusions

Natural fiber composites have some inherent drawbacks which can be overcome by hybridizing them with synthetic fibers. Mechanical properties of these composites is one area in which significant improvements have been reported following hybridization. Over the years a plethora of research studies have been done on natural fiber/synthetic fiber hybrid composites and, based on their results, a few generalizations can be made of the mechanical properties of these composites.

The mechanical properties of the hybrid composites are found to increase linearly with increase in the volume fraction of synthetic fibers up to certain optimum value beyond which a negative hybrid effect has been observed because of formation of agglomerates. However positive hybrid effect occurs above a minimum threshold value of synthetic fibers, at which these fibers can carry the load following the failure of low strength and low elongation natural fibers.

The behavior of the hybrid composites, especially those with interply configuration, is mainly influenced by the properties of their skin fiber layers. Optimum mechanical properties, especially impact and flexural, are obtained by placing high strength and stiffness synthetic fibers as the skin layers. Having synthetic fiber layers as skin is also an effective method of reducing the moisture absorption of hydrophilic natural fibers. However fatigue sensitivity of hybrid composites is improved at higher natural fiber content and by having natural fiber skin layers. For short fiber composites, there is an upper limit to the natural fiber length beyond which the mechanical properties start to deteriorate. Surface treatment of natural fibers plays a major role in improving the interfacial adhesion between fibers and matrix, thus increasing their mechanical properties and also reducing their moisture absorption.

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Characterization Sugarcane Bagasse Particulate Reinforced Polylactic Acid Composites Prepared by Compounding and Manual Compression Molding Technique

Nadendla Srinivasababu

Abstract Manufacturing plays a vital role in the development of a country. At present the trend of industrialists is turned to green sustainable manufacturing which focuses on reduce, reuse and recycle concept for preparation of materials, products. On the other side petroleum based products are finite, create environmental problems and deplete in specific time period. So, the mankind on this earth has to definitely rely on renewable energy sources and sustainable inexhaustible materials. In the present investigation a novel "Manual Compression Molding" (MCM) technique is introduced to prepare the composites using Polylactic Acid (PLA) and sugarcane bagasse particulate (SBP). Prior to the manufacturing of composites sugarcane bagasse particulate is synthesized using mechanical mixer and is analyzed for its size, morphology. Initially PLA lamina is prepared at different contents and is mechanically characterized to understand the ability of MCM method. Further the composites prepared by compounding and MCM are tested under mechanical loading and the results are compared with the composites made by MCM alone. As a whole MCM technique is successfully employed for making composites. In case of plain PLA, composition P1, P5 have given highest tensile strength, modulus of 11.41 MPa, 0.54 GPa respectively. However, at R1 reinforcement in PLA tensile strength is enhanced by 11 % when compared with PLA. Similar kind of nature is possessed by PLA-SBP composites at R1 whose flexural strength, modulus is 38.43 MPa, 2.71 GPa respectively under bending load. But compounding (C) results in good mixing of reinforcement with the matrix and further MCM method had given flexural strength, modulus of 37.04 MPa, 3.5 GPa respectively. In analyzing PLA-SBP composites C composition has shown 1.84 kJ/m^2 Charpy impact strength. Finally the composites are examined under Scanning Electron Microscope to know the bond between reinforcement and matrix.

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1 Introduction

One of the perennial grasses that grow in humid tropics is sugarcane. This plant require minimum of 1000 mm of rain annually and may be grown in dry conditions also with sufficient supply of water. For satisfactory growth, yield the temperature should be more than 21 °C. Roots, stems that support the leaves and inflorescence are the basic parts of the plant, where the mature stem grows up to 5000 mm. Stem may be thick/thin depends on the variety of seeds. Stems color can range from green through purple. Stems have nodes which are at a distance of 150–200 mm apart (Kiple and Ornelas 2000).

Since prehistoric times sugarcane is cultivated in Asia. Columbus introduced this crop in 1493 and rapidly became most important in various places with respect to economy. Varieties of crops, type of soils influence growth, physical appearance of sugarcane. Hawaiian varieties are described as follows. In a year sugarcane grows up to a length of 305 mm, makes two to four joints per month have a length of 100–125 mm. Joint of sugarcane has an eye, when it is cut and planted in soil, primary shoot is developed. The diameter of stalks range between 25 and 50 mm (Burr et al. 1957).

Banana, sugarcane bagasse, and sponge gourd fibres obtained in Brazil were analyzed for chemical composition and morphology. Cellulose pattern I was identified from the X-ray diffraction studies of the fibres have the crystallinity indices of 39, 48, 50 % respectively against banana, sugarcane bagasse and sponge gourd fibres (Guimarãesa et al. 2009). In an overview of green composites, (Zini and Scandola 2011) the potential ability of natural fibres and their composite made from biodegradable matrices were discussed.

Cassava bagasse and starch were used to prepare thermoplastic starch composites. Bagasse reinforced composites had shown more tensile strength (0.60 MPa) and modulus (41.6 MPa), when compared to cassava starch composites 0.40 and 2.04 MPa, respectively (de Teixeira et al. 2012).

Poorer processability and reduction of the ductility are the bottle necks of natural fibre reinforced polymer composites. With the aid of adhesion promoters, additives or chemical modifications of the reinforcement can reduce the bottlenecks. Further these composites are eco-friendly when the biodegradable polymer matrix is used. Here the main methods and results of academic and industrial research of green materials were reviewed (La Mantia and Morreale 2011). Cellulosic fibres in micro and nano scale composites have replaced man-made fibre composites due to green nature. Here the study processing, extraction, properties, and applications of cellulosic-based nanocomposite materials are reviewed with example applications (Khalil et al. 2012).

Sugarcane bagasse, bagasse cellulose and benzylated bagasse reinforced polypropylene composites were injection molded (Luz et al. 2007). Specimens were cut from the sheet and are analysed for flexural, tensile properties. Fractured surfaces of the samples were analyzed using SEM. Cellulose and cellulignin fibres received from sugarcane bagasse reinforced polypropylene composites were subjected to tensile, flexural tests (Luz et al. 2008). The agricultural residue of sugarcane bagasse is less utilized as a potential material. This waste was used as a fuel in the power plant and house hold cooking purpose. Composites made from bagasse reinforcement were subjected to flexural and weathering tests and the fractured surfaces were seen under SEM (Acharya et al. 2008).

The effects of different jute fibre loadings and the modification of bagasse fibre in hybrid composites was studied (Saw and Datta 2009). Flexural performance of chopped bagasse polyester composites was studied in terms of various parameters like chopped material size, pretreatment of bagasse, mold pressure (de Sousa et al. 2004).

Xu et al. (2010) bagasse fibre reinforced polyvinyl chloride (PVC) and recycled PVC and High Density Polyethylene composites were tested for its creep behavior. At higher temperatures instantaneous deformation, creep rate were increased at the same loading level. The potentiality of sugarcane bagasse (Vallejos et al. 2011) obtained from ethanol water fractionation of bagasse was examined after composites were made for improving mechanical performance.

Sugarcane bagasse residue was pretreated and modified (Mulinari et al. 2009). Cell/ZrO_2_nH_2O (10 %)/HDPE composites had shown better tensile strength than that of cellulose 10 %-HDPE composites (Paiva and Frollini 2002). Using organosolv process lignin was extracted from sugarcane bagasse and utilized as partial substitute of phenol in resole phenolic matrices. Phenolic and lingo-phenolic matrices were used as matrices for making composites and were analyzed for impact strength.

Monteiro et al. (1998) a study was conducted to find the possible uses of bagasse waste as reinforcement in polyester matrix for making composites. Homogeneous structures in composites were observed with good mechanical properties. Vilay et al. (2008) sodium hydroxide, acrylic acid was used to modify fibre surface, and the composites were made using polyester matrix to know the capability of treatment.

Sugarcane bagasse was mechanically modified by stirring ball mill, aluminate coupling agent. Alfa, coir, bagasse fibre reinforced polymer composites was investigated mechanically (Arrakhiz et al. 2013). It was identified that the composites have good performance when compared with the neat polymer (Cao et al. 2006). Biodegradable aliphatic polyester (Randy CP-300) was combined with untreated and alkali treated bagasse fibre to their mechanical performance. In the analysis it was observed that the composites with 1 % NaOH treated fibres were reinforcement shown maximum improvement in properties.

From the works various researcher's on bagasse fibre reinforced composites the following points are identified.

- Bagasse was used in chopped form through modification by chemical and/or mechanical means.
- Different matrices like thermoplastic, thermoset were used along with biodegradable.
- Compression molding, extrusion, hot pressing etc. method of preparation was employed.

In this work an effort is taken to synthesize bagasse particulate (SBP) fibre mechanically. SBP is examined using particle size analyzer. Then bare specimens, biodegradable composites are fabricated by compounding (C) cum manual compression molding (MCM) and MCM. Neat specimens at different weight content are prepared and tested to understand their mechanical behavior. Thereafter the mechanical performance of the composites is investigated at different loading conditions of the SBP.

2 Methods, Manufacturing and Testing

2.1 Synthesizing Sugarcane Bagasse Particulate

In the present work neat sugarcane bagasse is collected from juice shop which is free from hard, thick outer layer. It is in white color, with a length of 50–200 mm. Juice extracted bagasse is in soft form due to compression created by the electric juicer. The collected bagasse is allowed to dry for 22 days under sunlight. Once the bagasse become dry and is sensed through hand, it is peeled into small pieces. Using a mechanical mixer rotating at 1200 rpm bagasse is powdered uniformly. The process of mechanical mixing continued till complete bagasse is converted to powder. The obtained powder is segregated into two varieties viz. rough, fine powder. The present investigation concentrates on rough sugarcane particulate fibre. In order to completely ensure the removal of moisture from SBP fibre is allowed to dry in NSW Oven Universal at 85 °C up to 1 h.

2.2 Lamina Preparation by Manual Compression Molding (MCM)

Green material also called as biodegradable i.e. Poly Lactic acid is used in this work as matrix material, and is procured from Nature Works, Chennai. An induction cooker, Model: Chef Xpress 200, Rating: 2000 W, 230 V, Efficiency: 86 %, 1 unit of water boil 2.6 min is used to melt the matrix at room temperature.

Initially the cooker is placed at a set temperature i.e. 180–200 °C. The predetermined quantity of matrix, matrix-SBP is thoroughly mixed with hand and is poured into a steel vessel. Using an MS rod the pellets of PLA/and SBP is mixed properly and the fumes generated is slowly vanished. Semi liquid stated neat PLA, PLA-SPB, PLA-C-SPB is poured over the tile of 300 mm × 300 mm.

Before the matrix mixture is poured, tile is cleaned using NC thinner and ensured its cleanliness. Then locally available castor oil is applied over the tile as thin layer, which help in easy removal of lamina. After pouring semiliquid mixtures one more tile is placed over it and a weight of 900 N is applied up to 10 min manually. Cured lamina is then taken out and is placed over the bottom tile by reversing it. This process is continued till the lamina reaches to room temperature. This method of manufacturing thermoplastic composite lamina is newly introduced in this work and is named as “Manual Compression Molding” (MCM). The steps involved in the process of manufacturing lamina are depicted in Fig. 1. The lamina compositions prepared in this work and its thickness is given in Table 1.

2.3 Testing

Mechanically synthesized SBP is examined using Microtrac particle size analyzer. The size of the particulate and morphology is examined using Scanning Electron Microscope (SEM). PLA-SPB specimens are tested under tensile, flexural loading using PC 2000 Electronic Tensometer at a cross head speed of 2, 8 mm/min respectively. Charpy impact strength of the composites is determined by using Computerized Izod/Charpy Impact Tester. The fractured samples are analyzed under SEM to know the interfacial bonding between matrix and reinforcement.

3 Results and Discussion

From the average particle size analysis of three samples, it is identified that 95, 50 percentile of particles has 1107, 632 μm respectively and the graph is shown in Fig. 2. Only 10 percentile of the particles are of 86.24 μm in size. Particle size ranges 327.1–1107 μm. Further dried SBP is examined under SEM and is

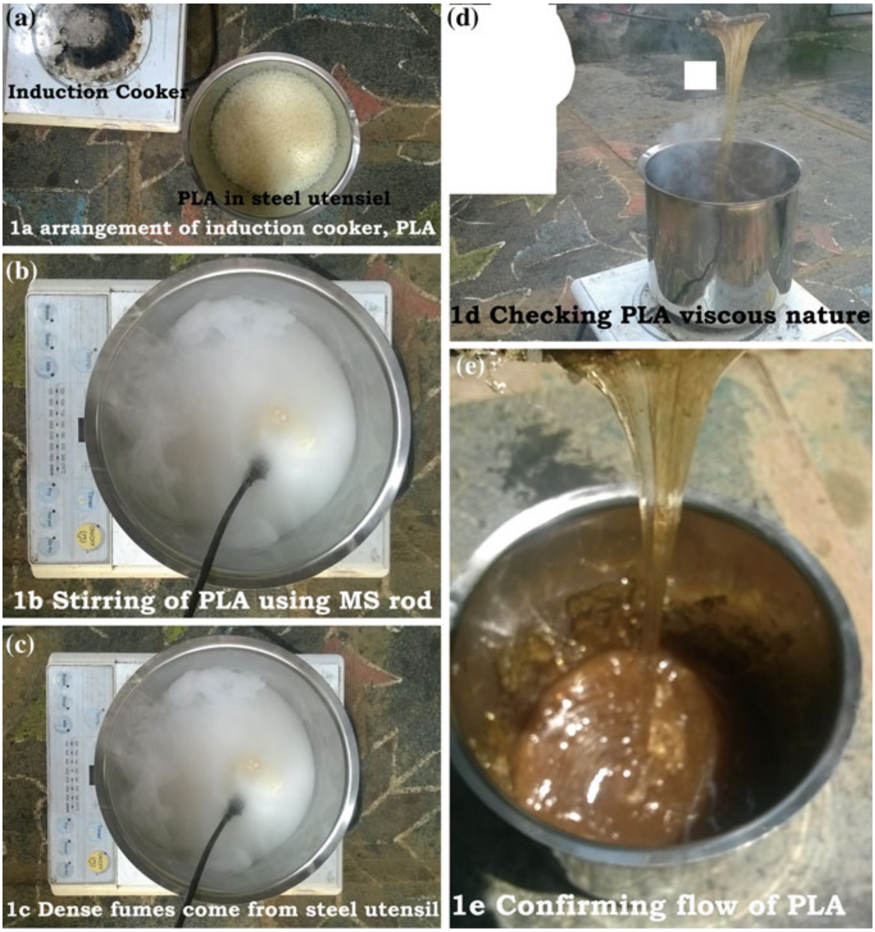


Fig. 1 Steps involved in lamina PLA, PLA-SBP composite lamina preparation and cutting of specimens

represented in Fig. 3. Here from the SEM image, particulate size varied from 179 to 455 μm.

From Table 1, it is understood that the thickness of the lamina (300 mm 300 mm) prepared is of uniform thickness with little variation. But much variation in thickness is observed in P7, P8, and C compositions. The average value of five tensile, flexural and impact tested specimens is calculated and the findings are explained.

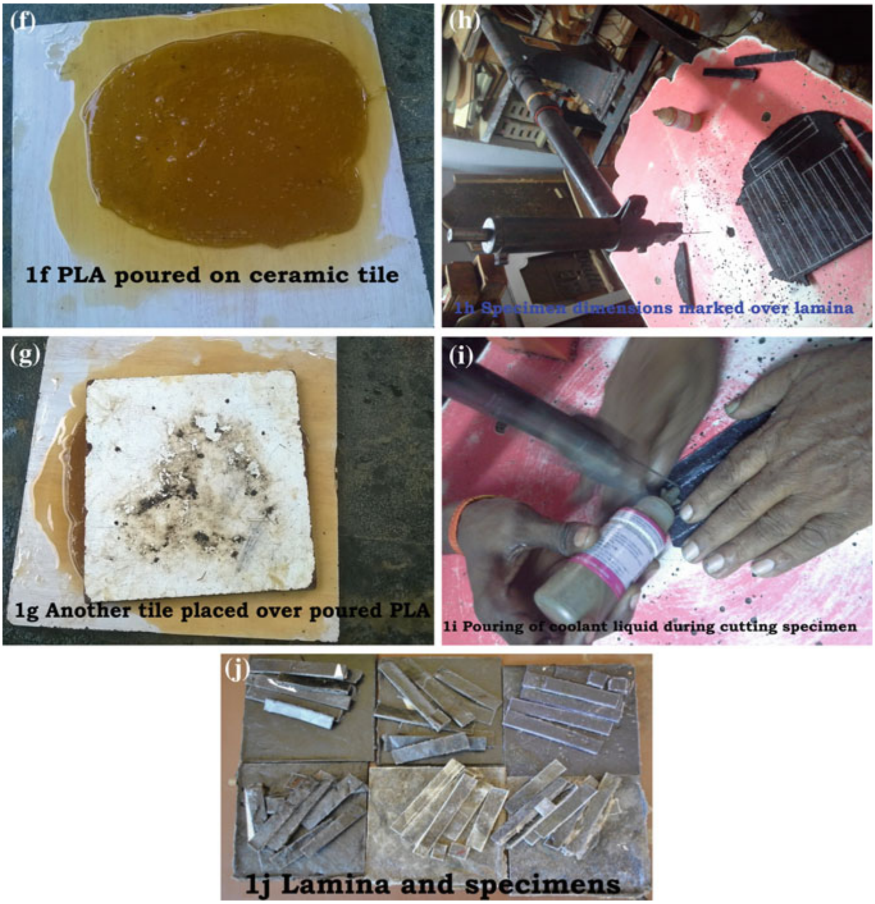


Fig. 1 (continued)

Figures 4 and 5 shows tensile strength, modulus of plain and composite specimens against various compositions. Tensile strength, modulus of PLA varied from 4.7 to 11.41 MPa, 0.261 to 0.522 GPa respectively. When SBP reinforced into PLA results in 12.65 MPa maximum tensile strength in case of R1, modulus of 0.224 GPa for C compositions. Increase in SBP content from 12.5 to 40 % gives rise to decrease in tensile strength due to lack of matrix material. However compounded specimens i.e. C had shown a tensile strength of 8.19 MPa. Similar trend is recognized in modulus case also, where C specimens exhibited tensile modulus of 0.224 GPa. From the fractured specimens after the tensile test, had given

Table 1 Compositions, thickness of PLA, PLA-SBP composite lamina

Composition label	Description	Lamina thickness range (mm)
P1	Plain PLA—800 gm	5.225–5.325
P2	Plain PLA—700 gm	6.320–6.554
P3	Plain PLA—600 gm	4.068–4.297
P4	Plain PLA—500 gm	5.736–6.013
P5	Plain PLA—450 gm	4.554–4.609
P6	Plain PLA—430 gm	6.229–6.747
P7	Plain PLA—410 gm	5.237–6.182
P8	Plain PLA—390 gm	7.327–8.411
R1	12.5 wt% SBP in PLA	6.484–6.631
R2	25 wt% SBP in PLA	7.307–8.287
R3	40 wt% SBP in PLA	5.100–5.436
C	Compounded and MCM 7.14 wt% SBP in PLA	3.777–5.020

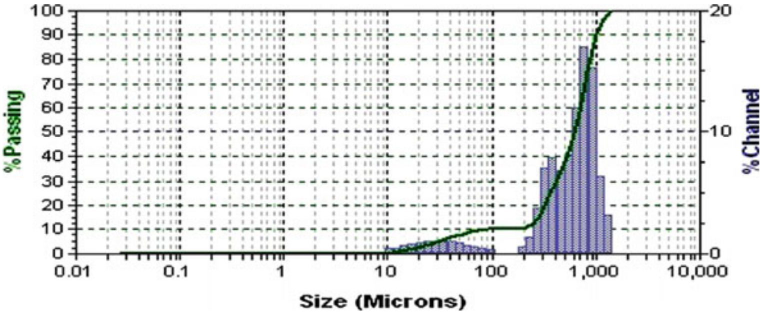


Fig. 2 Particle size of sugarcane bagasse particulate fibre

confidence that the SBP is neatly mixed in the PLA and good bond between particulate fibre and matrix is visible.

Three-point bend test on PLA, PLA-SBP composite specimens had shown good flexural strength, modulus. Flexural strength, modulus of plain PLA ranges 27.48–61.77 MPa, 2.54–4.09 GPa respectively and is identified from Fig. 6 and 7 respectively. Out of compositions R1, R2, and R3 studied in this work R1 specimens showed maximum flexural strength, modulus of 38.43 MPa, 2.71 GPa respectively. Compounded specimens C, given flexural strength, modulus of 37.04 MPa, 3.5 GPa respectively. All the specimens are failed due to bend load only and no separation of SPB is observed from the matrix.

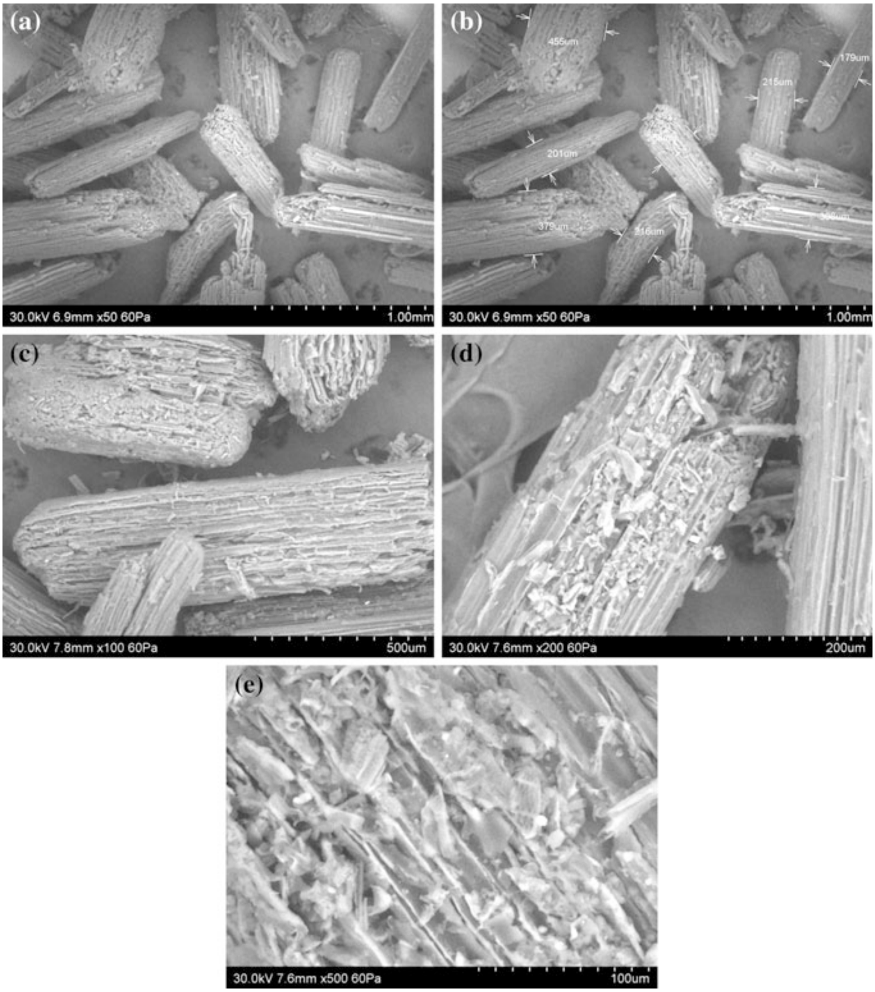


Fig. 3 SEM image of sugarcane bagasse particulate fibre

Charpy impact strength of the plain specimens runs from 1.58 to 2.99 kJ/m^2 and is shown in Fig. 8. SBP reinforced PLA composites maximum impact strength is shown by R1 composition i.e. 1.98 kJ/m^2. Composite specimens which are compounded and MCM also exhibited good impact strength of 1.84 kJ/m^2. All plain, composite specimens are failed in "C" type as per ASTM D6118-08.

The tensile tested compounded SBP fibre reinforced composites are visualized under SEM and is shown in Fig. 9. Particulate is thoroughly mixed in the matrix and good interfacial bonding is observed.

Fig. 4 Tensile strength of PLA, PLA-SBP composites

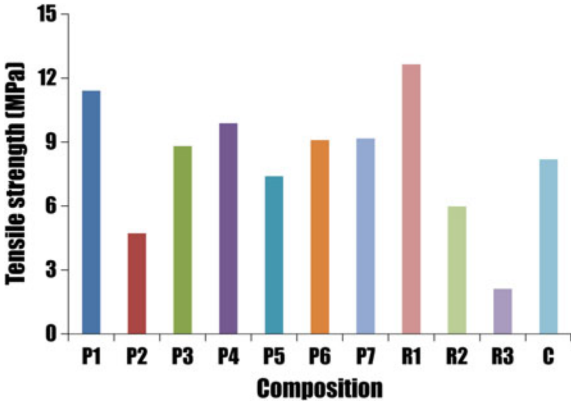


Fig. 5 Tensile modulus of PLA, PLA-SBP composites

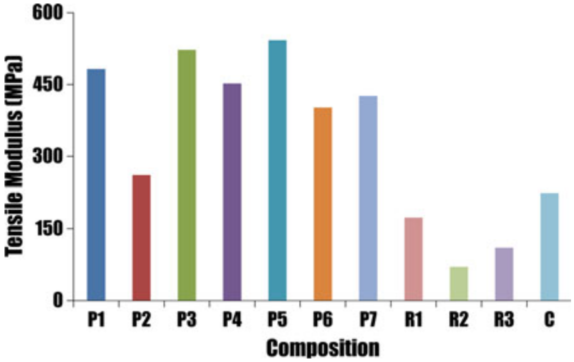


Fig. 6 Flexural strength of PLA, PLA-SBP composites

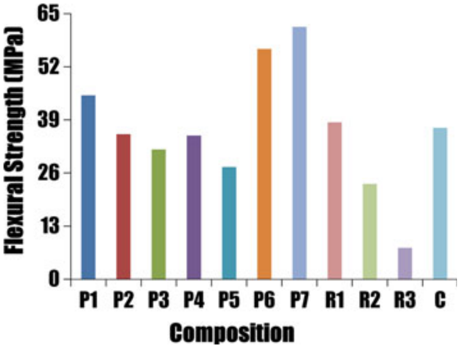


Fig. 7 Flexural modulus of PLA, PLA-SBP composites

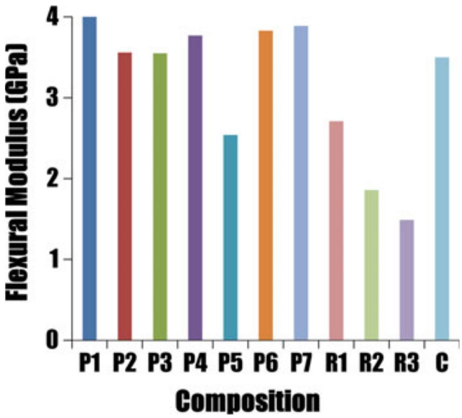
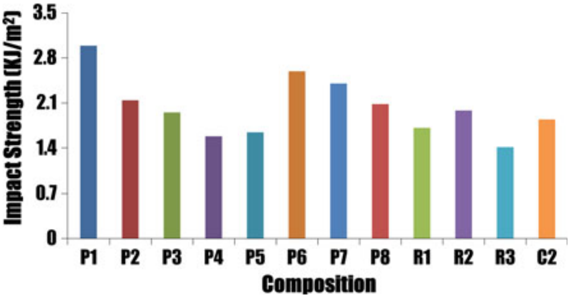


Fig. 8 Impact strength of PLA, PLA-SBP composite



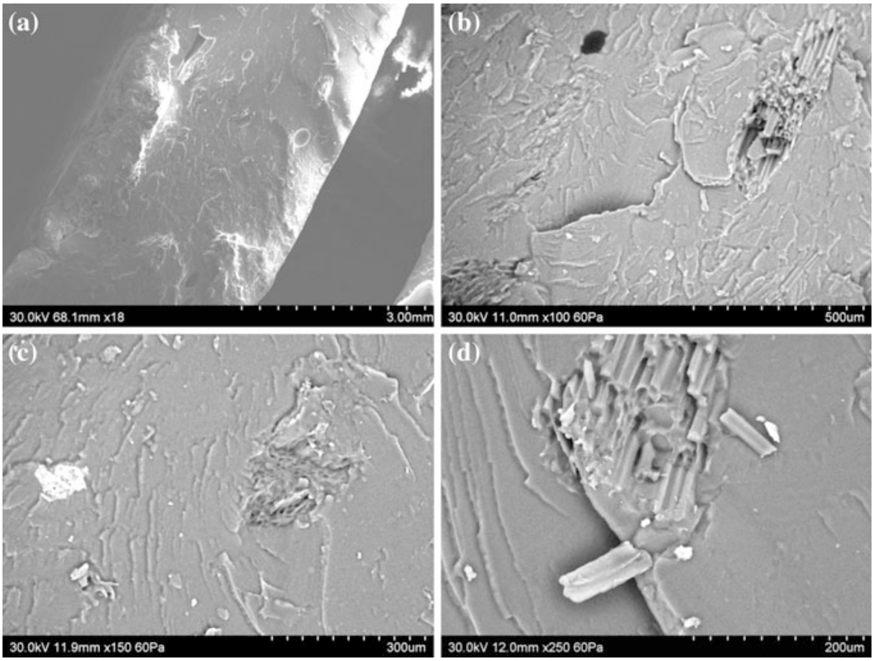


Fig. 9 SEM image of tensile tested compounded PLA-SBP composite specimen

4 Conclusions

SBP fibre is successfully synthesized using mechanical mixer. Particulate fibre is dispersed in PLA matrix about uniformly when MCM technique is employed for composite lamina preparation effectively. The thickness of the specimens had given a confidence that the technique of MCM is useful for preparation of lamina. Out of all the biodegradable composites studied in this work, compounding cum MCM result in good bond between reinforcement and matrix. The mechanical properties of SBP-PLA composites are reasonably good, but a thorough investigation is needed to enhance their performance and other working conditions of environment.

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