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Review

Processing and characterization of natural cellulose fibers/thermoset polymer composites

Vijay Kumar Thakur[a,*], Manju Kumari Thakur[b]

[a] School of Mechanical and Materials Engineering, Washington State University, USA
[b] Division of Chemistry, Govt. Degree College Sarkaghat, Himachal Pradesh University, Shimla 171005, India

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ABSTRACT

Recently natural cellulose fibers from different biorenewable resources have attracted the considerable attraction of research community all around the globe owing to their unique intrinsic properties such as biodegradability, easy availability, environmental friendliness, flexibility, easy processing and impressive physico-mechanical properties. Natural cellulose fibers based materials are finding their applications in a number of fields ranging from automotive to biomedical. Natural cellulose fibers have been frequently used as the reinforcement component in polymers to add the specific properties in the final product. A variety of cellulose fibers based polymer composite materials have been developed using various synthetic strategies. Seeing the immense advantages of cellulose fibers, in this article we discuss the processing of biorenewable natural cellulose fibers; chemical functionalization of cellulose fibers; synthesis of polymer resins; different strategies to prepare cellulose based green polymer composites, and diverse applications of natural cellulose fibers/polymer composite materials. The article provides an in depth analysis and comprehensive knowledge to the beginners in the field of natural cellulose fibers/polymer composites. The prime aim of this review article is to demonstrate the recent development and emerging applications of natural cellulose fibers and their polymer materials.

Contents

1. Introduction

Polymers are playing an important role in the contemporary world for a number of applications starting from daily needs to biomedical and defense fields (Thakur & Singha, 2013; Thakur,

* Corresponding author. Tel.: +1 509 335 8491; fax: +1 509 335 4662.
E-mail addresses: vijayisu@hotmail.com, drvijay.kumar@wsu.edu (V.K. Thakur), shandilyamn@gmail.com (M.K. Thakur).

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2013; Yang, Yee, et al., 2012). Recently the field of polymer science has attracted greater attraction of the research community due to the enormous advantages offered by the polymer based materials and several polymers are appearing from the laboratories of scientist with unique and imperative properties for advanced applications (Banerjee et al., 2013; Thakur & Singha, 2013; Thakur, 2013; Yang, Kong, et al., 2012). Polymer based composite materials are playing an important role in niche applications since the last few decades ever since the discovery of Bakelite resin (Azwa, Yousif, Manalo, & Karunasena, 2013; Bharti, Mishra, & Sen, 2013; Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George, Sreekala, & Thomas, 2001; Guilbert-Garcia et al., 2012). These materials are emerging rapidly as the potential substitute to the metal or ceramic based materials in a number of applications including automotive, aerospace, marine, sporting goods and electronic industries to name a few (Abd-El-Messieh, Basta, & El-Saied, 2001). Among various composites materials, natural fibers reinforced polymer composites are dwindling under increasing scrutiny due to their easy process and enormous eco-friendly advantages (Bogoeva-Gaceva et al., 2007; Dhakal, Zhang, & Bennett, 2012; Eichhorn et al., 2010; George et al., 2001). Indeed the depletion of petro-chemical based materials have paved the way to switch toward biorenewable resources based materials (Banerjee et al., 2013). Biorenewable polymers such as natural cellulosic fibers have been the subject of study in both native and modified form for a variety of applications starting from biomedical to defense (Banerjee et al., 2013; Rangel-Vazquez & Leal-Garcia, 2010; Thakur, Thakur, & Gupta, 2013a). The increased environmental awareness appears to be reaching a new level with the emphasis on the usage of natural polymer based materials in place of commonly used synthetic materials (Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001; Mishra, Rani, & Sen, 2012). Natural polymers belong to the special

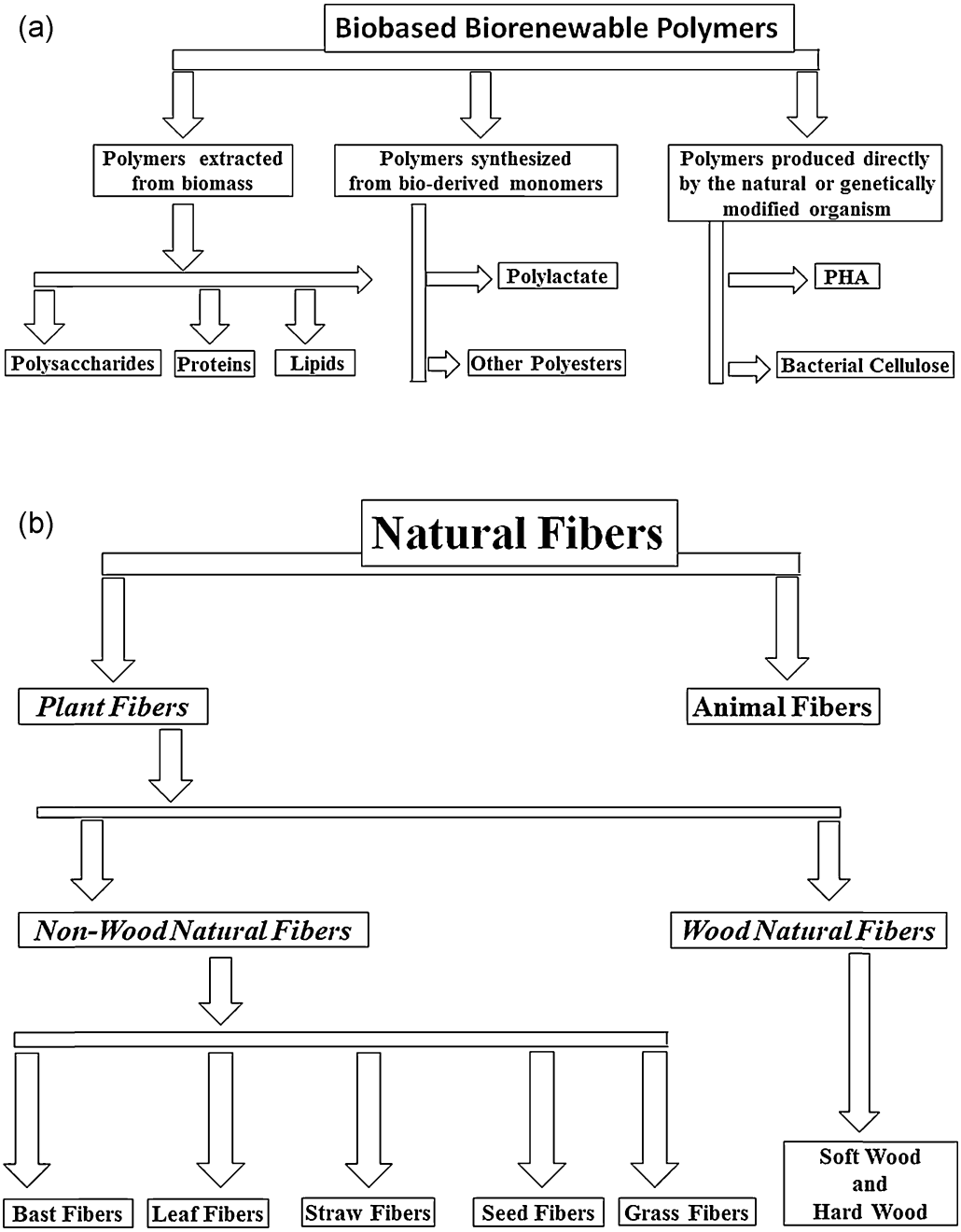

Fig. 1. (a) Classification of biobased polymers (Thakur & Singha, 2013; Thakur, 2013). (b) Classification of natural fibers (Thakur & Singha, 2013; Thakur, 2013).

class of polymers found in nature such as natural fibers, starch, proteins etc. (Thakur & Singha, 2013; Thakur, 2013) and possess a well-defined structure (Dhakal, Zhang, Guthrie, MacMullen, & Bennett, 2013). The use of natural polymers based materials by human beings is not new as these polymer materials have been used by people of earlier civilization for long back (many centuries ago) (Thakur, Thakur, & Gupta, 2013b). Polymers obtained from different biorenewable resources are generally refereed as biobased polymers. Fig. 1(a) shows the general classification of biobased polymers (Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001; Thakur & Singha, 2013; Thakur, 2013). Among these biorenewable polymers, polysaccharides are the most abundant natural polymers and are extracted from agricultural and biomass resources (Rani, Mishra, Sen, & Jha, 2012). These polymers are not only biorenewable resources, but also exhibit biodegradability, biocompatibility and antibacterial activity (Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001; Rani, Sen, Mishra, & Jha, 2012; Rani, Mishra, & Sen, 2013). Among different polysaccharides, natural fibers are frequently used as reinforcing materials for composites applications (Bajpai, Meena, Vatsa, & Singh, 2013).

Natural fibers reinforced polymer composite materials can be classified as special class of materials that seek to remedy most of the environmental and economic issues regarding synthetic fibers reinforced composites (Gomez Jimenez et al., 2009; Thakur & Singha, 2013; Thakur, Singha, & Mehta, 2010; Thakur, 2013). Biorenewable materials especially natural cellulosic polymers represent one of the most largest and renewable source of environmental friendly raw materials (Thakur, Thakur, & Gupta, 2013c). Indeed cellulose which is an important component of all natural fibers is the most abundant natural polymer available on the earth (Thakur, Singha, & Misra, 2011; Thakur & Singha, 2010b). Natural fibers reinforced polymer composites offer a number of advantages over their synthetic counterparts and traditional metal based materials (Jawaid, Khalil, & Abu Bakar, 2011a). These polymer composites offer a number of advantages over metal matrix and other materials such as considerable toughness, flexibility, easy processing, recyclability and eco-friendliness etc. (Khoathane, Vorster, & Sadiku, 2008). Particularly the light weight and superior mechanical properties of the natural fibers reinforced composite materials make them excellent candidates for automotive applications (Bajpai & Singh, 2013). In traditional polymer composite materials, there exists two or more distinct phases that include reinforcement (most frequently fibers are used as reinforcement) (Abdullah, Jawaid, Khalil, Zaidon, & Hadiyane, 2012). In natural fibers reinforced polymer composites, natural fibers are generally used as the reinforcement materials due to the higher volume fraction loading achievable and the possibility to tailor different properties by varying the load bearing capacity of the resulting composites (Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001; Khoathane, Sadiku, & Wambua, 2012).

The present review article is intended to provide an in depth analysis and comprehensive knowledge to the beginners in the field of natural fibers and their respective thermoset polymer composites. In this article different aspects of natural fibers reinforced thermoset polymer composites prepared using synthetic polymer as the matrix material are discussed including the interfacial characteristics. Furthermore the effect of surface modification of natural fibers on the properties of natural fibers reinforced composites is also explored.

2. Biorenewable natural fibers as novel materials

Different kinds of natural fibers are available all around the globe and common examples of these natural fibers include cellulosic fibers, wool and animal fibers (Thakur, Singha, & Thakur, 2012c). Natural fibers can be classified into different types depending upon their origin such as plant fibers and animal fibers (Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001). Fig. 1(b) shows the different classification of natural fibers (Thakur & Singha, 2013; Thakur, 2013). The plant fibers are generally subdivided into the following classes: bast; leaf straw; seed; grass and wood fibers (Fig. 1b).

In plant fibers, the bast and leaf fibers have been found to lend the mechanical support to the fibers (stems and leaf respectively) (Thakur, Singha, & Thakur, 2012a). Bast fibers are generally found in the bast of plants in which the plant core is surrounded by a stem (Faruk, Bledzki, Fink, & Sain, 2012,). These fibers are generated from the inner bark (phloem or bast) of the stems of dicotyledonous plants and are composed of several smaller cells termed ultimate fibers. Bast fibers have been used by people of earlier civilization for house hold applications and the shape/size of the stem of various bast fiber varies significantly depending upon the conditions from in which these are grown (Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001). Instead of different cultivation conditions these fibers contain varying amount of fiber cells in the phloem (Teaca, Bodirlau, Oprea, Tanase, & Colceru, 2008). Common examples of bast fibers include bagasse, hibiscus sabdariffa, flax, hemp, grewia optiva, jute, kenaf, and ramie (Teaca & Bodirlau, 2008). On the other hand leaf fibers have been found to run lengthwise through the leaves of most monocotyledonous plants (Akil et al., 2011). Common examples of leaf fibers are banana, sisal, henequen, abaca, pines and esparto. These fibers are generally used in the preparation of rugs, cordage, mats, carpet backings etc., and are much coarser than the bast fibers (Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001). Grasses fibers are generally procured from the stems of monocotyledonous plants. Common examples of grass fibers are bamboo, *Saccaharum cilliare*, esparto, sugar cane and sabai grass (Thakur & Singha, 2013; Thakur, 2013). Straw fibers are generally produced in large amount throughout the world as a result of by-product of cereal cultivation. Most of the time straw fibers are considered as waste and nearly half the straw is simply burned on the fields just to get rid of it. However, recently efforts are ongoing to use the straw fibers as reinforcing materials in polymer composites (Li, Cai, Winandy, & Basta, 2010). Compared to the bast and leaf fibers, seed hair fibers are single celled and one of the most common example of these is the cotton fiber (Thakur & Singha, 2013; Thakur, 2013). All natural cellulosic fibers primarily contain cellulose, hemicellulose and lignin as their indispensable constituents (Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001). In the following section we will be discussing different structural and chemical compositions of the natural fibers.

2.1. Constituent of natural fibers

2.1.1. Cellulose

Cellulose is primarily defined as the non-branched macromolecule containing chain of variable length of 1–4 linked β-d-anhydroglucopyranose units (Akil et al., 2011; Thakur & Singha, 2013; Thakur, 2013) (Fig. 2a). The length of different types of chains depends upon the source of cellulose (Sabo, Basta, & Winandy, 2013). A number of reviews have discussed in detail the structure and chemical composition of the cellulose so we will not be going in detail to avoid the duplication (Azwa et al., 2013; Akil et al., 2011; Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001). Generally most of natural cellulosic fibers contain 60–70% cellulose that is primarily composed of C, H, and O_2, having a general formula of $C_6H_{10}O_5$ (Akil et al., 2011; Thakur & Singha, 2013; Thakur, 2013).

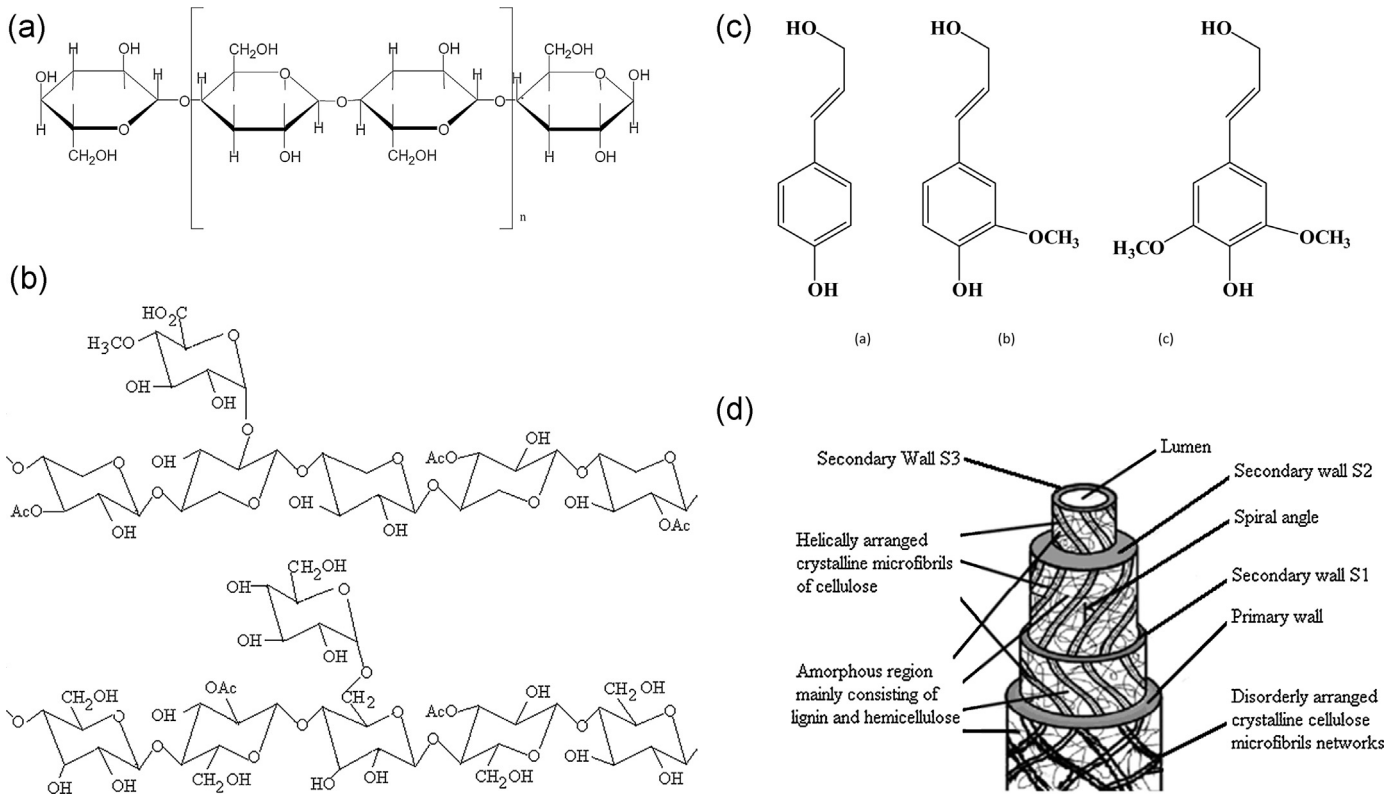

Fig. 2. (a) Chemical structure of cellulose. Reprinted with permission from Akil et al. (2011). Copy right 2011 Elsevier. (b) Structures of hemicelluloses. Adopted from Thakur and Singha (2013), Thakur (2013) and Meshitsuka and Isogai (1996). (c) Structure of Lignin. Adopted from Thakur and Singha (2013) and Thakur (2013). (d) Schematic picture of cell wall of the natural plants. Reprinted with permission from Akil et al. (2011). Copy right 2011 Elsevier.

2.1.2. Hemicellulose

Along with cellulose, one of the imperative constituents of natural cellulosic fibers is hemicellulose and is the second most abundant family of naturally occurring polymers (Thakur & Singha, 2013; Thakur, 2013). Hemicelluloses are buildup of a combination of 5- and 6-ring carbon ring sugars (Fig. 2b). Hemicelluloses comprise a group of polysaccharides (excluding pectin) having branched structure (Meshitsuka & Isogai, 1996; Sarkanen & Ludwig, 1971). These consist of mixtures of polysaccharides of much lower molecular weight than cellulose (Thakur & Singha, 2013; Thakur, 2013). Hemicellulose has been found to remain associated with cellulose after the removal of lignin. Hemicellulose is generally used as gelling agents, tablet binders viscosity modifiers etc. (Akil et al., 2011; Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001).

2.1.3. Lignin

Among all the components of cell wall, lignin is the highly branched polymers (Thakur & Singha, 2013; Thakur, 2013). It has been found to serve as the matrix materials along with hemicellulose to embed cellulose fibers. Lignin structure is very complex consisting of phenyl propane units organized in a three-dimensional structure (Akil et al., 2011; Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001). Different units in lignin are linked together through various types of carbon–carbon and ether bonds as opposed to linear or branched chains as in carbohydrates (Fig. 2c). Lignin has been found to play a major role in protecting the cellulose/hemicellulose from harsh environmental conditions such as water. Figures show the structure of lignin. All natural cellulosic fibers (wood/non-wood) have been found to contain different amount of cellulose, hemicellulose and lignin (Teaca, Rosu, Bodirilau, & Rosu, 2013). Table 1 shows the chemical composition of some of the cellulose containing materials (Khalil, Bhat, & Yusra, 2012). In all natural cellulosic fibers, the most important part is the plant cell wall (Thakur & Singha, 2013; Thakur, 2013). The schematic structure of natural plant cell wall shown in (Fig. 2d), demonstrates that the cell wall primarily consist of a hollow tube with four different layers (Akil et al., 2011; Thakur & Singha, 2013; Thakur, 2013). These are known as primary cell wall, secondary cell walls, and a lumen. There are three secondary walls and an open channel in the center of the microfibrils is

Table 1
Chemical composition of some typical cellulose-containing materials. Reprinted with permission from Khalil, Bhat, and Yusra (2012). Copy right 2012 Elsevier.

Type of bio fiber	Composition (%)			
	Source	Cellulose	Hemicellulose	Lignin	Extract
Wood	Hardwood	43–47	25–35	16–24	2–8
	Softwood	40–44	25–29	25–31	1–5
Non-wood	Bagasse	40	30	20	10
	Coir	32–43	10–20	43–49	4
	Corn cobs	45	35	15	5
	Corn stalks	35	25	35	5
	Cotton	95	2	1	0.4
	EFB	50	30	17	3
	Flax (retted)	71	21	2	6
	Flax (unretted)	63	12	3	13
	Hemp	70	22	6	2
	Henequen	78	4–8	13	4
	Istle	73	4–8	17	2
	Jute	71	14	13	2
	Ramie	76	17	1	6
	Sisal	73	14	11	2
	Sunn	80	10	6	3
	Wheat straw	30	50	15	5

Table 2
Factors effecting fiber quality at various stages of natural fiber production. Reprinted with permission from Dittenber and GangaRao (2012). Copy right 2012 Elsevier.

Stage	Factors effecting fiber quality
Plant growth	Species of plant Crop cultivation Crop location Fiber location in plant Local climate
Harvesting stage	Fiber ripeness, which effects: –Cell wall thickness –Coarseness of fibers –Adherence between fibers and surrounding structure
Fiber extraction stage	Decortication process Type of retting method
Supply stage	Transportation conditions Storage conditions Age of fiber

known as lumen (Akil et al., 2011). Each layer in the cell wall has been found to be composed of cellulose that embedded in a matrix of hemicellulose and lignin. During fiber production, several factors affect the overall quality of the natural cellulosic fibers depending upon the condition. Table 2 summarizes some of the factors affecting the overall quality of the fibers (Dittenber & GangaRao, 2012; Thakur & Singha, 2013; Thakur, 2013).

Natural fibers have found to exhibit a number of advantages in terms of specific modulus, cost per weight and cost per unit length along with the renewable and biodegradable nature (Dittenber & GangaRao, 2012). Although the mechanical properties of natural fibers have been found to be inferior to their synthetic counterparts, however the properties such as lower densities, economic than synthetic fibers, good specific modulus values, natural fibers can be highly preferable to synthetic fibers in automotive another applications where stiffness and weight are primary concerns (Dittenber & GangaRao, 2012; Thakur & Singha, 2013; Thakur, 2013).

3. Classification of polymer composites materials

Composites are frequently refereed as engineered materials composed of two or more different constituents (matrix and reinforcement) (Akil et al., 2011; Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001; Singha, Thakur, & Mishra, 2009). Each of these constituent generally contain different physical or chemical properties (Yan, Chouw, & Jayaraman, 2013). In a given composite material both the materials remain separate and distinct on a macroscopic level within the finished structure (Bajpai, Singh, & Madaan, 2012). Composite materials have been used by the people of earlier civilization since many centuries and one of finest example include the preparation of bricks for building construction using straw and mud (Akil et al., 2011; Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001). In polymer composite materials, the polymer act as the matrix while reinforcement can be of any type starting from organic to inorganic (Singh, Sharma, & Singh, 2013). In polymer composites materials, the reinforcing material (usually fibers) determines the overall properties and the matrix holds the reinforcement (Kumar, Gupta, Singh, & Sharma, 2010). The matrix also helps to transfer loads along the reinforcement. Polymer composite are divided into different categories depending upon the reinforcement and polymer matrix used (Akil et al., 2011; Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001). A number of different polymers are used as matrix materials depending upon the applications (Spiridon, Teaca, Bodirlau, & Bercea, 2013). Polymer composites are generally classified upon the bases of the reinforcement type and the matrix type. Polymer composites are generally classified upon the bases of the reinforcement type and the matrix type (Thakur & Singha, 2013; Thakur, 2013). On the basis of reinforcement type, polymer composites are classified into fibers reinforced polymer composites and particle reinforced polymer composites (Thakur & Singha, 2013; Thakur, 2013). In fibers reinforced composites, the reinforcement is used in the form of fibers and it may be natural/synthetic fiber or combination of both. While in particle reinforced composites, the reinforcement is converted into particle form of different dimension. Sometime both the particle and fiber reinforcement are used together depending upon the targeted application (Akil et al., 2011; Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001). Depending upon the renewable/non-renewable nature of the polymer matrix/reinforcement, polymer composites are also divided into three categories referred as (a) 100% Renewable composite (b) Partly renewable composite (c) Nonrenewable polymer composites. In 100% renewable polymer composites, both the matrix and the reinforcement are obtained from the biorenewable resources while in partly renewable polymer composites, either the matrix is obtained from renewable resources or the reinforcement (Akil et al., 2011; Teaca, Bodirlau, & Spiridon, 2012; Thakur & Singha, 2013; Thakur, 2013). However, in case of nonrenewable polymer composites, every component is obtained from non-renewable resources. Each of these composites materials have their own advantages and disadvantages (Thakur & Singha, 2013; Thakur, 2013). As discussed earlier, the present review article principally focuses on natural fibers reinforced synthetic thermoset polymer composites. So the polymer composites discussed in this article belong to the partly renewable polymer composites.

4. Processing and applications of natural cellulose fibers/polymer composites

The prime interest in natural cellulosic fibers arises due to their eco-friendly advantages, economical production and higher specific strength/stiffness compared to their traditional synthetic counterparts (El-Saied, El-Diwany, Basta, Atwa, & El-Ghwas, 2008; Shalwan & Yousif, 2013; Singha & Thakur, 2010). Furthermore for large scale industrial applications, the procurement process of these composites is healthier friendly and provides better working conditions (Singha & Thakur, 2008c). Although natural fibers offer a number of advantages over their synthetic counterparts, they have also few weakness (Singha & Thakur, 2009c). Some of the weaknesses of these fibers for some industrial applications include being sensitive to water/moisture absorption, polar and hydrophilic nature, and their less thermal stability (Akil et al., 2011; Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001). However on comparison of the overall properties, the advantages of natural cellulosic fibers outweigh the disadvantages (Singha & Thakur, 2009d). Most of the shortcomings have remedial measures in the form of chemical treatments depending upon the applications (Singha, Thakur, Mehta, et al., 2009; Thakur et al., 2012a). Different chemical surface modification techniques used to modify the surface of natural cellulosic fibers for polymer composites application have been recently reviewed (Azwa et al., 2013; Bledzki & Gassan, 1999; Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001; Mukherjee & Kao, 2011). In all these reviews, the effect of different surface modification techniques has been discussed in detail. Recently, gomuti fiber reinforced thermoset composites have been reviewed with particular emphasis on the use of gomuti fibers in different thermoset polymer matrices (Ticoalu, Aravinthan, & Cardona, 2013). So in the present section we will be mainly focusing on selected natural cellulosic fibers reinforced thermosetting polymer composites. Thermoset polymer

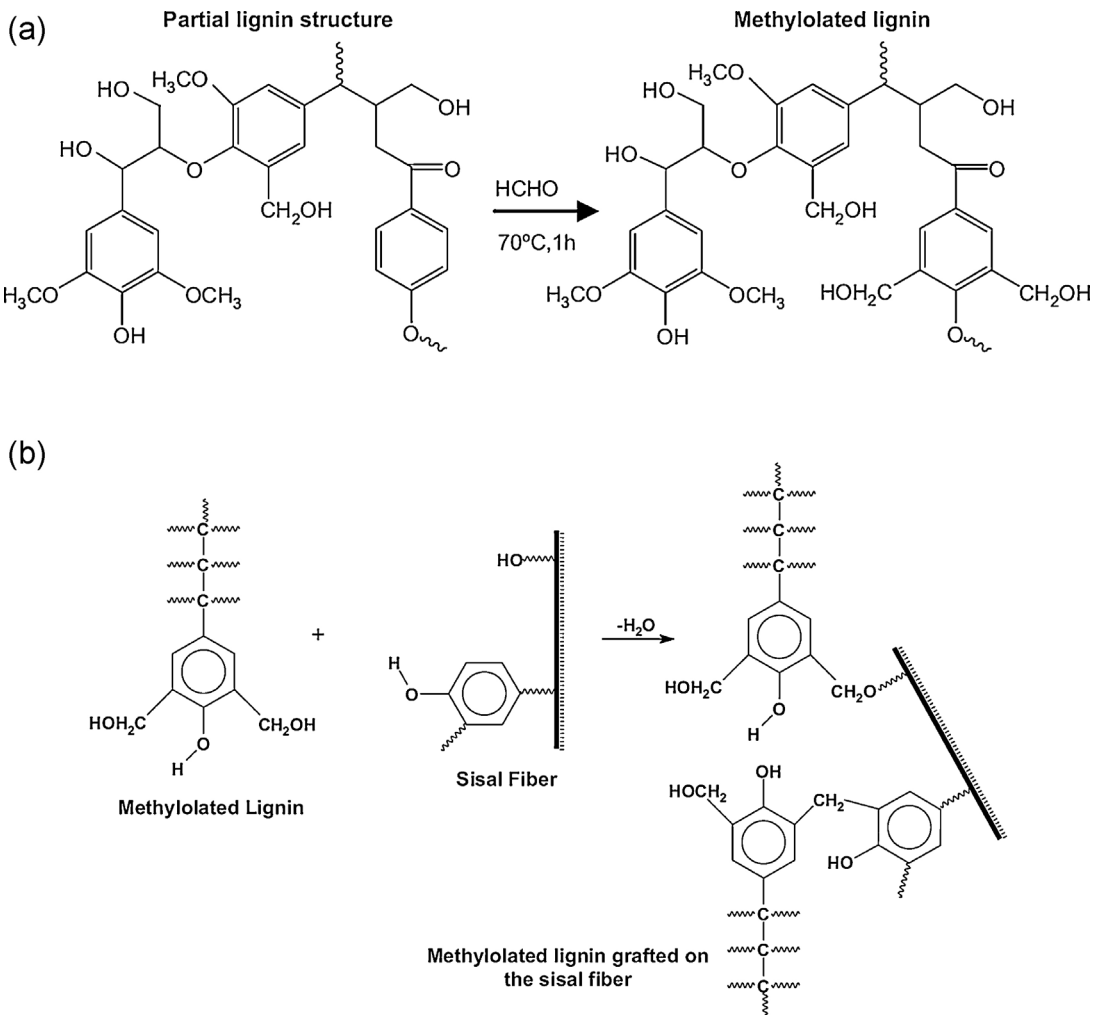

Fig. 3. (a) Schematic representation of methylation of lignin. Reprinted with permission from Megiatto et al. (2008). Copy right 2008 Elsevier. (b) Schematic representation of the reaction between methylated lignin and the sisal fiber surface. Reprinted with permission from Megiatto et al. (2008). Copy right 2008 Elsevier.

matrices offers the following advantages in the preparation of natural fibers reinforced composites (La Rosa et al., 2013; Liu, Song, Anderson, Chang, & Hua, 2012; Shahzad, 2012; Singha & Thakur, 2008b; Thakur & Singha, 2013; Thakur, 2013):

- Easy processing: The processing of natural fibers reinforced composites is easy as the initial resin system is in liquid form. So the fibers can be easily mixed with the resin.
- Less temperature is required for the preparation of composites compared to the thermoplastic composites.
- Self-made or simple low cost system can be used for the preparation of these composite systems.
- Pressure requirement is also low for these composites systems.
- Natural fibers can be easily wet depending the viscosity of the polymer resin
- Higher loading of the fibers can be easily achieved in the thermoset polymer matrix based composites.

Instead of the advantages, these thermoset polymer matrix composites also suffer from few shortcoming such as high curing time and non-recycling (Akil et al., 2011; Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001; Singha & Thakur, 2009a). However, instead of these disadvantages, thermoset polymers composites are frequently used for number of applications, thanks to their outstanding mechanical properties (Singha & Thakur, 2008a; Singha & Thakur, 2009b). In the following section we will be discussing some of the commercially important synthetic thermoset polymer matrix based composites.

4.1. Natural fibers/phenolic composites

Thermoset polymer composites have been most widely studied for a number of applications by researchers all around the globe due to their enormous advantages (Akil et al., 2011; Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001). In phenolic composites, phenol-formaldehyde is the most commonly used resin system (Singha & Thakur, 2008a,b,c; Singha & Thakur, 2009; Swamy, Kumar, Vrushabhendrappa, & Joseph, 2004). Lignocellulosic *Saccaharum cilliare* fiber-reinforced polymer biocomposites were prepared using compression-molding technique employing phenol-formaldehyde (PF) as a novel polymer matrix (Thakur, Singha, Kaur, Nagarajarao, & Liping, 2011). In this study, the effect of different fiber loading in terms of weight % was studied on the mechanical, morphological and thermal properties of the resulting composites. It was observed that different mechanical properties such as tensile strength, flexural strength, compressive strength and wear resistance increases up to 30%, and beyond this loading the properties decreased. Surface modification of these fibers was also carried out using silane treatment through aminopropyl triethoxy silane and subjected to evaluate the morphological and physicochemical properties (Thakur, Singha, Kaur, Nagarajarao, & Liping, 2010). The polymer composites prepared using these

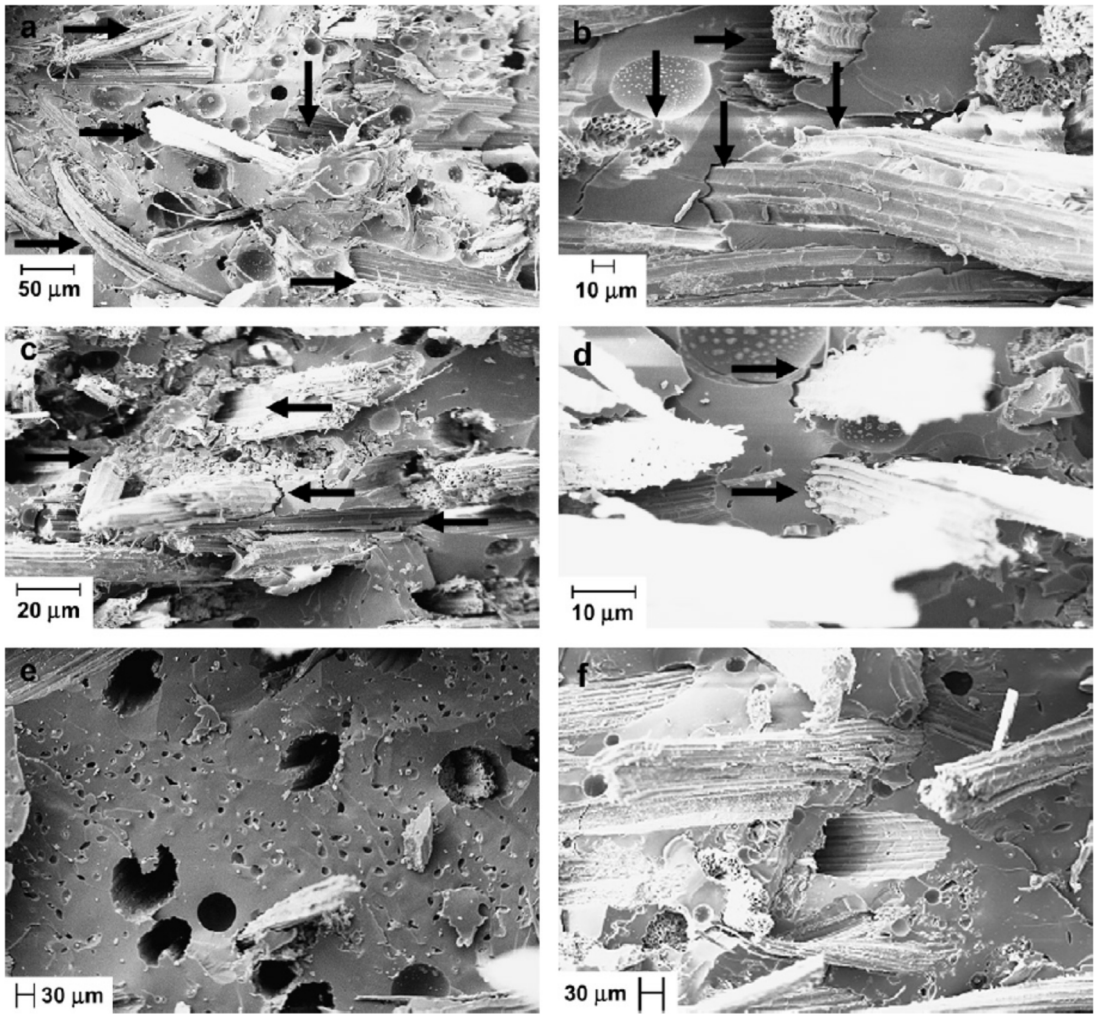

Fig. 4. SEM images of the impact fracture of phenolic composites reinforced with: (a), (b) sisal fibers chemically modified with methylated Indulin lignin for 30 and 60 min, respectively, (c), (d) sisal fibers chemically modified with methylated Organosolv lignin for 30 and 60 min, respectively, (e), (f) unmodified sisal fibers. Reprinted with permission from Megiatto et al. (2008). Copy right 2008 Elsevier.

fibers also demonstrated higher mechanical properties. Phenol formaldehyde matrix based composites were also prepared using raw and grafted grewia optiva fibers as reinforcement in the polymer matrix (Thakur, Singha, & Thakur, 2011). It was observed that grafted composites exhibit better mechanical properties compared to the un-grafted composites. Effect of different grewia optiva fiber loadings on the mechanical properties of the phenolic composites was also studied by the same authors (Singha & Thakur, 2009; Thakur & Singha, 2010a). Sisal fibers based phenolic composites using both the raw and modified fibers were studied in detail to understand the correlation between the different properties (Megiatto, Silva, Rosa, & Frollini, 2008). Sisal fibers were modified by sustainable technique using reaction with lignins. To further enhance the adhesion of the fibers with the polymer matrix these fibers were subsequently hydroxymethylated. In this study, lignins were extracted from pinus-type wood and sugarcane bagasse. Fig. 3(a) shows the scheme for the methylation of lignin and Fig. 3(b) shows the surface modification scheme by the methylated lignin. Changes in the surface morphology of the fibers were confirmed by the SEM analysis. It was demonstrated from the analysis that fibers modification with methylated lignin induced significant changes in the morphology of the fiber surface. The modified fibers reinforced composites also demonstrated higher impact strength due to the strong bonding between the fibers and the matrix. SEM micrographs of the composites reinforced with modified fibers also confirmed the adhesion improvement compared to the unmodified fibers (Fig. 4). Furthermore the surface modified fibers reinforced polymer composites also exhibit low water absorption as the phenolic resin penetrated very well into the modified fibers. This process resulted in the blocking of water passage through their channels (Megiatto et al., 2008).

Pine needles were also used as the reinforcement in polymer composites preparation using phenol-formaldehyde (PF) as a novel polymer matrix (Singha & Thakur, 2009). The polymer composites were prepared using compression molding technique with the reinforcement in the form of particles. It was revealed from the study that mechanical properties such as: tensile strength, compressive strength, flexural strength, and wear resistance of the PF resin increases up to 30% fiber loading. Higher loading beyond this value decreased the mechanical properties due to agglomeration of the fibers. The physico-chemical properties of the pine needles reinforced composites with different dimension were also studied by the same research group (Thakur & Singha, 2010b). Phenolic composites based on phenolic matrices were prepared using raw and surface modified sugar cane bagasse/curaua fibers (Trindade et al., 2005). Surface modification of the fibers was carried out by oxidization method by chlorine dioxide, mainly phenolic syringyl and guaiacyl units of the lignin polymer. After the oxidation, the

fibers were modified by grafting with furfuryl alcohol (FA). Furfuryl alcohol was used in the grafting because it is obtained from a renewable source. The fibers characterization was accomplished with different techniques namely chemical composition analysis, SEM, DSC, UV–vis diffuse reflectance spectroscopy crystallinity, TG, tensile strength, and 13 C CP-MAS NMR. All the techniques successfully confirmed the modification of the fibers. Polymer composites prepared using the modified fibers also demonstrated higher mechanical properties. Banana fibers reinforced phenolic composites were also prepared using phenolic resoles for light structural applications (Joseph, Sreekala, Koshy, & Thomas, 2008). Banana fibers were chose in this study due to their richness in cellulose content as well as being inexpensive, and abundantly available. In this study banana fibers was combined with glass fibers to develop lightweight, high-performance, cost-effective, hybrid composites. Subsequently the effect of different layering patterns of both the fibers banana/glass on the mechanical properties namely tensile, flexural, and impact was studied. From the experimental investigation, it was concluded that an intimate mixture of both fibers exhibit highest tensile strength while the maximum flexural/impact strength was obtained for the composite specimen prepared using interleaving layers of banana fiber and glass fiber. Furthermore the water uptake behavior of the composites samples was found to decrease with the incorporation of glass fiber into banana fiber in the polymer matrix.

The effect of different chemical modifications on the thermal stability and degradation of banana fiber and banana fiber-reinforced phenol formaldehyde composites was also studied by the same research group in detail (Joseph, Sreekala, & Thomas, 2008). In this study, the modification of the banana fibers was carried out by employing latex treatment, sodium hydroxide, heat treatment, silanes, and cyanoethylation. The thermal degradation behavior of both the fiber in treated/untreated fibers showed two-stage decomposition and all the surface treatments increased the thermal stability of the fibers as a result of physical and chemical changes induced by the treatments. These fibers were then used as the reinforcement in the phenol formaldehyde polymer matrix and thermal behavior showed that phenol formaldehyde composites were thermally more stable than the fibers. However, thermal stability was lesser than the parent PF resin matrix. All the composite samples exhibited four-stage degradation with treated fiber-reinforced composites showing significant improvement in thermal stability. The potential of banana fibers for electrical properties applications had also been studied (Joseph & Thomas, 2008). In this study, the effect of different fiber loading/fiber treatments, and hybridization of glass fibers with banana fibers on the electrical properties was investigated in detail. It was observed that thee dielectric constant of the resulting composites decreased with frequency and fiber loading. Furthermore, the surface modification of the fibers carried out using different treatments with silanes/NaOH/acetylation/latex treatment/heat treatment/cyanoethylation negatively affected the dielectric constant as the number of hydroxyl groups in the fibers were considerably decreased after the modification of fibers. In case of banana/glass hybrid composites, increase in glass fiber loading decreased the dielectric constant.

Banana fibers were also used in the micro/nano form in the preparation of polymer composites (Neelamana, Thomas, & Parameswaranpillai, 2013). Banana based microfibers and nanofibers in this study were prepared using a steam explosion process and the fiber surface of chemically modified and unmodified banana fibers were investigated by different techniques including atomic force microscopy, Zeta potential measurements etc. It was observed that the thermal stability of the fibers increased from macroscale to nanoscale. Furthermore, the polymer composites prepared using the nanofibers showed enhanced mechanical properties compared to the microfibers. Phenol formaldehyde resin (PF) polymer composites were also prepared using short sisal fibers (SF) as the potential reinforcement (Mu, Wei, & Feng, 2009). In this work, polymer composites were prepared by using two methods, direct-mixing and polymerization filling and their impact and bending properties were extensively investigated. It was observed that under the same compression molding conditions, polymer composites prepared using the polymerization methods displayed higher mechanical properties compared to the simply mixed composites. The effect of different fiber treatments was also studied and it was found that the treated-SF-reinforced composites exhibit better mechanical properties compared to that of untreated-SF-reinforced composites. Sisal fibers reinforced polymer composites were also prepared using Phenol–furfural resins as the matrix materials (X. Li et al., 2010; Oliveira, Gardrat, Enjalbal, Frollini, & Castellan, 2008). In this study, the polymer resins were prepared in alkaline conditions (potassium hydroxide or potassium carbonate) using furfural. It was concluded from that polymer composites can be prepared with decent mechanical properties avoiding the use of formaldehyde.

4.2. Natural fibers/epoxy composites

Epoxy, matrix based composites have been studied by a number of researchers for different applications using different types of natural cellulosic fibers (e.g. bacterial cellulose; electrospun cellulose fibers; recycled cellulose fibers; cellulose whisker; nanocrystal) (Chiciudean, Stoica-Guzun, Dobre, & Van Tooren, 2011). Natural fibers based epoxy composites have been reported to a be novel material for different applications (Jawaid, Khalil, & Abu Bakar, 2010; Jawaid, Khalil, & Abu Bakar, 2011b; Lu, Askeland, & Drzal, 2008). Different types of surface modification of natural fibers (micro/nano) have been carried out for further enhancing their use in epoxy based polymer composites (Lu et al., 2008). Natural fibers reinforced structural composite material was prepared by Ben Amor et al. (2010) using palm tree fiber as the reinforcement and the epoxy resin as the polymer matrix. Different dielectric properties of the thermoset epoxy composite were studied in detail. It was observed that at low frequency, the dielectric constant increases with the increase in the temperature. It was concluded from the study that in addition to the relaxation associated to the glass transition of the polymer resin, and ionic relaxation, the palm tree fiber also gives rise to the other relaxation associated to the MWS interfacial polarization. Short date palm tree fibers reinforced polyepoxy composites were also prepared and studied for different mechanical properties analysis using resin transfer molding (RTM) (Sbiai, Maazouz, Fleury, Sautereau, & Kaddami, 2010). The interaction between the fibers and the matrix was enhanced by treating the fibers with chemical modification. The modification was carried out using TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) catalyst mediation. It was observed that the surface modification facilitated the fabrication of composites using RTM as well as increased the mechanical properties. Natural fiber-reinforced epoxy polymer composite face/honeycomb core sandwich panels were also studied in detail for creep properties (Du, Yan, & Kortschot, 2013). The sandwich panel creep properties were studied in a period of 30 days. The properties were studied in ambient conditions at 65% relative humidity. It was observed that at ambient conditions (relative humidity (RH) at 20–50%), sandwich panels showed linear viscoelastic properties (stress level <30% of their failure stress). However higher relative humidity (65%) produced a significant acceleration of creep strain (Du, Yan, et al., 2013).

Palm fibers reinforced polyester and epoxy matrices were also prepared (Kaddami et al., 2006). In this study, the fibers were used in the short fiber form. Surface modification of the fibers was carried out to improve interfacial adhesion between the fibers and

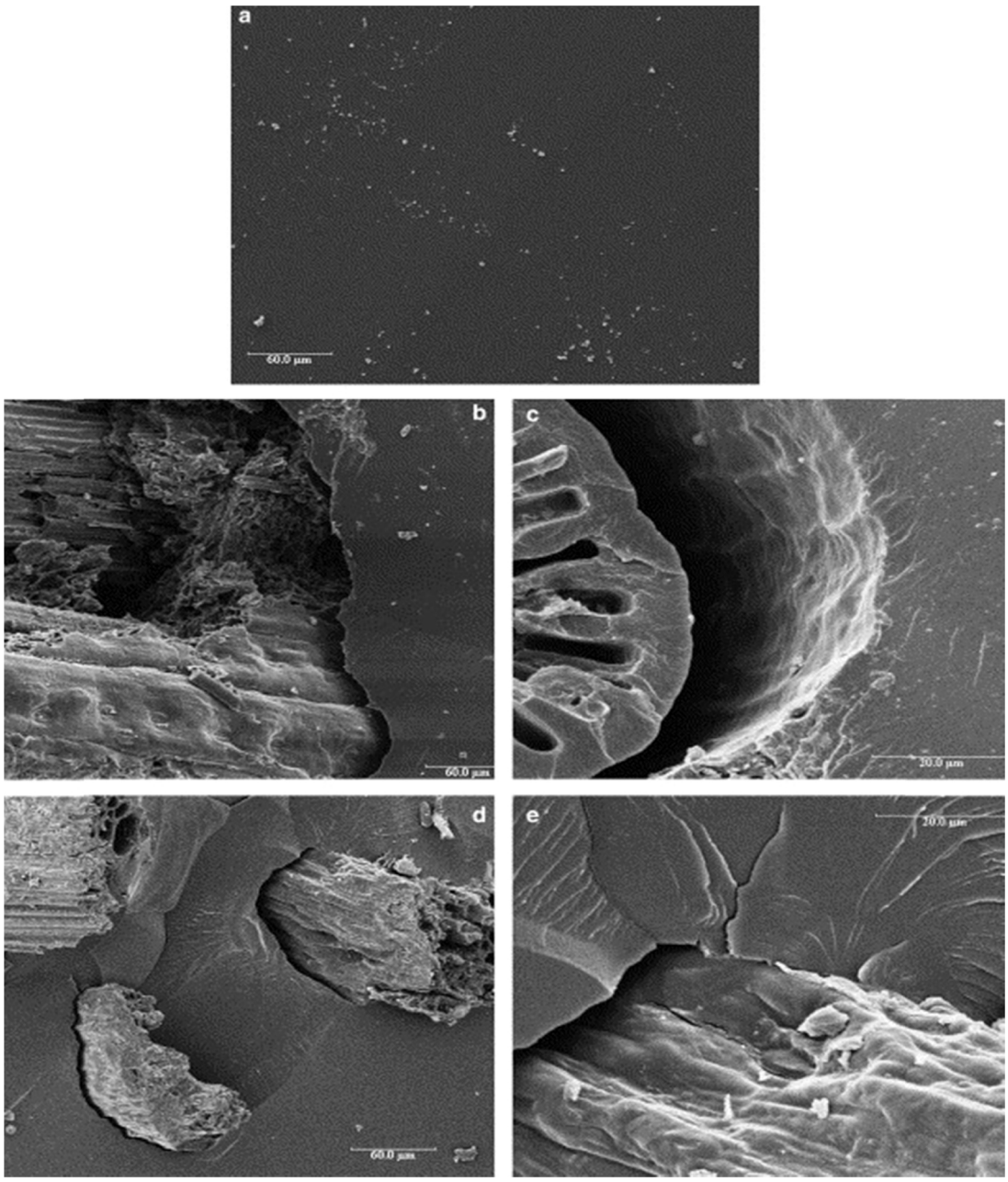

Fig. 5. Scanning electron micrograph of freshly fractured surface for an unsaturated polyester film filled with (a) 0 wt%, (b, c) 17 wt% of unmodified and (d, e) 17 wt% of acetate modified palm tree fibers. Reprinted with permission from Kaddami et al. (2006). Copy right 2006 Elsevier.

the resin using the esterification reaction. The surface modified fibers were then used as reinforcement in the polymer resin and tested for their mechanical properties. Fig. 5 shows the SEM images of the prepared composites with and without fracture. It was concluded from the study that epoxy-based composites exhibit higher properties due to better interfacial adhesion in comparison to the unsaturated polyester. In order to determine the real potential of natural fibers reinforced composites, water absorption behavior of the carpet waste jute yarns reinforced thermoset polymer matrices i.e. epoxy and polyester was also studied (Karaduman & Onal, 2011). Along with the water absorption behavior, mechanical properties (flexural and impact) of the fibers reinforced composites were also studied after aging in distilled water. In order to improve the adhesion of the fibers with the matrix, alkali treatment of the fibers was carried out and it was observed that alkali treatment increases the mechanical properties as well as reduces water absorption of the resulting composites. This behavior was attributed to strong interface improvement between the reinforcement and the fibers (Karaduman & Onal, 2011). Hybrid polymer composites using Jute/Bagasse as the reinforcement and epoxy polymer as the matrix were also prepared (Saw & Datta, 2009). These fibers were then treated with furfuryl alcohol to increase the adhesion between the matrix and the fibers. It was confirmed through different techniques that the surface modification reduces the hydrophilicity of the composites and significantly increased the overall mechanical pretties of the composites.

Recycled cellulose fiber (RCF) reinforced epoxy composites were prepared with different fiber loadings (19, 28, 40 and 46 wt%) to determine the reinforcing potential of these fibers (Alamri & Low, 2012b). The investigated results showed that the mechanical

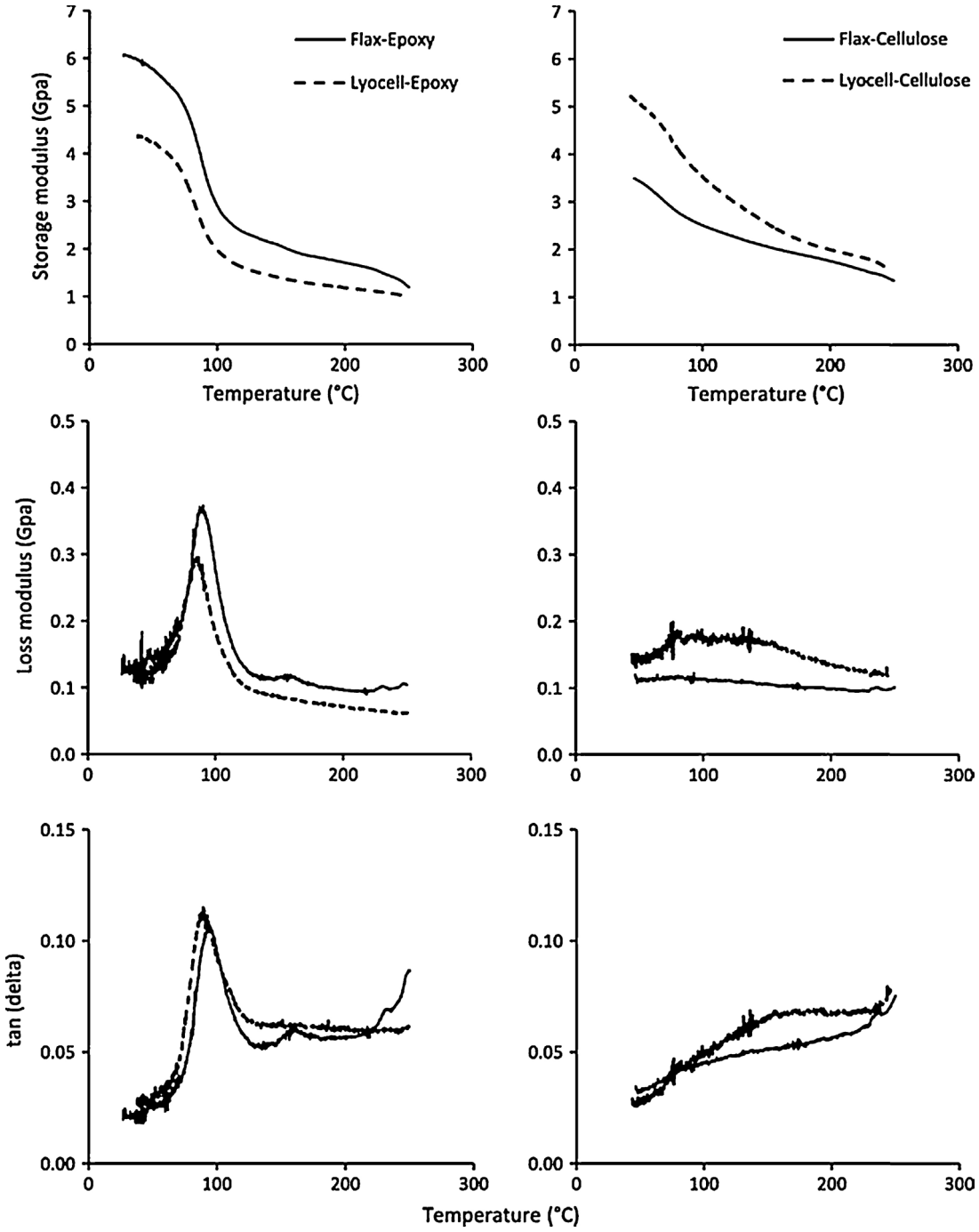

Fig. 6. Results from dynamic mechanical analysis of flax and lyocell composites with epoxy matrix and all-cellulose composites, respectively. Reprinted with permission from Gindl-Altmutter et al. (2012). Copy right 2012 Elsevier.

properties such as flexural strength/flexural modulus/fracture toughness and impact strength increased with the increase in the fiber content and maximum mechanical properties were achieved for a fiber content of 46 wt%. Furthermore, maximum water uptake and diffusion coefficient study of the composites was also studied and it was found that water absorption increases with an increase in fiber content. The SEM micrographs show the significant effect of fiber content on the fracture surface. It was observed that the composites samples filled with lower fiber content (19 and 28 wt%) exhibit an increase in matrix rich regions compared to composites filled with higher fiber content (Alamri & Low, 2012b). Same authors have also prepared hybrid epoxy composites using recycled cellulose fibers (RCF) and nanosilicon carbide (n-SiC) particles as reinforcement and the results were compared to the individual reinforcement (Alamri & Low, 2012a). The mechanical and thermal properties of these composites were found to increase with the incorporation of RCF/n-SiC. All-cellulose composites (ACCs) were prepared and compared to composites with epoxy matrix (Gindl-Altmutter et al., 2012). In this study, all cellulosic composites were prepared by partial dissolution in ionic liquid and characterized with different techniques including wide-angle X-ray diffraction and scanning electron microscopy. Table 3 summarizes the tensile strength results of the prepared composites (Gindl-Altmutter et al., 2012). It was observed from the

Table 3
Tensile mechanical properties and density of flax and lyocell fiber-reinforced composites (E: modulus of elasticity, σ_{max}: tensile strength, ε_{max}: failure strain, ρ: density). Reprinted with permission from Gindl-Altmutter et al. (2012). Copy right 2012 Elsevier.

Type of material	E (GPa)	σ_{max} (MPa)	ε_{max} (%)	ρ (g cm^{-3})
Flax-epoxy	8.6 ± 0.8	79 ± 5	1.4 ± 0.1	1.15
Lyocell-epoxy	6.5 ± 0.6	64 ± 7	1.2 ± 0.2	1.25
Flax-cellulose	4.6 ± 0.5	34 ± 2	0.8 ± 0.1	0.95
Lyocell-cellulose	7.2 ± 1.0	78 ± 4	5.2 ± 2.6	1.27

table that lyocell-fiber based ACCs showed similar strength and stiffness, however in comparison to flax fibers, tensile properties inferior to flax-epoxy were observed. Dynamic-mechanical and thermogravimetric analysis revealed a favorable behavior for ACC in terms of more diffuse thermal softening and increased resistance to thermal degradation. SEM images of fracture surfaces of the composite revealed that both epoxy-based variants show common features. These images demonstrated a similarity in the failure mechanism of these composites. The dynamic mechanical analysis also supported the tensile results of the composites (Fig. 6).

4.3. Natural fibers/polyester composites

Along with phenolic and epoxy polymer matrix, polyester is another polymer matrix that is frequently used for the preparation of natural fibers reinforced polymer composites (Akil et al., 2011; Bogoeva-Gaceva et al., 2007; Eichhorn et al., 2010; George et al., 2001; Li, Flodin, & Ronnhult, 1987). Roselle fibers reinforced polyester composites have been discussed in detail in a comprehensive review with particular emphasis on tailoring the polyester properties (Thiruchitrambalam, Athijayamani, Sathiyamurthy, & Abu Thaheer, 2010). Polyester matrix based composites had been prepared and studied for flexural properties (Boynard, Monteiro, & d'Almeida, 2003). In this study Sponge gourd (*Luffa cylindrica*) fiber was used as the reinforcement. To improve the fiber–matrix interface, Luffa fibers were alkali-treated at two temperatures, with varying alkali concentrations. It was observed that similar to other natural fibers treatments, the mercerization also strongly influenced the morphological changes on the surface of luffa fibers. The outer surface of the fibers was completely removed and fiber with 5% NaOH treatment exhibited the best flexural mechanical properties that were attributed to mechanical interlock due to the increase of fiber roughness and the increase of the contact area of the fibers. Sugarcane bagasse reinforced polyester polymer composites were also prepared and examined for tribological applications (El-Tayeb, 2008). In this study, compression molding along with hand-lay-up techniques were used to prepare the sugarcane fiber/polyester (SCRP) and glass fiber/polyester (GRP) composites (with chopped fibers of 1, 5, 10 mm length randomly distributed and unidirectional mat fibers). Fig. 7 shows the process for the preparation of polymer composites (El-Tayeb, 2008). After the preparation of the composites, these were subjected to adhesive and wear friction studies. The variation of friction coefficient and wear resistance for chopped (C-SCRP) polymer composite with different fibers lengths (1, 5 and 10 mm) tested at 2.5 m/s sliding velocity and 2.25 km sliding distance. The SEM micrographs for SCRP composite show that the SCF formed a fairly good bonding with the polyester matrix and can served as the replacement to the glass fibers reinforced composites.

Effect of chemical treatments on the mechanical and water absorption properties of the bamboos fibers reinforced polymer composites was also studied (Kushwaha & Kumar, 2011). The chemical modification of the fibers was carried out using bamboo fibers in mat form with maleic anhydride, permanganate, benzoyl chloride, benzyl chloride, and pre-impregnation. After the surface modification these fibers were used as the reinforcement in the polymer matrices and the effect of chemical pretreatment on the tensile, flexural, impact, and water absorption properties of the composites was investigated in detail. It was summarized in this study that all these pretreatments significantly improved the mechanical and water absorption properties of the resulting composites. Brazilian sisal fibers reinforced polyester composites were also prepared and studied for mechanical properties and pullout analysis (Sydenstricker, Mochnaz, & Amico, 2003). Surface functionalization of these fibers was subsequently carried out to get the polyester composites with optimum mechanical properties. The modification of the fibers in this study was carried out using NaOH or N-isopropyl-acrylamide pretreatment in the selected solutions. Table 4 shows the tensile strength results of fibers with different treatments. Changes in surface morphology of the fibers were ascertained by different characterization techniques including FTIR and SEM. All the characterization techniques successfully confirmed the modification of the fiber surface. Polyester composites were prepared using the treated fibers (with different concentration of NaOH and N-isopropyl-acrylamide) and untreated fibers. Table 5 demonstrates the shear strength measured by pull-out tests (Sydenstricker et al., 2003). It is quite obvious from the table that the different chemical treatments increased the adhesion between the polymer matrix and the fibers. Lignin content and density of fibers were reduced with the chemical treatment and the N-isopropyl-acrylamide treatment caused a significant reduction in moisture absorption. Tensile tests of NaOH (0.25, 0.5, 1, 2, 5, and 10% (w/w)) and N-isopropyl-acrylamide (1, 2, and 3% (w/w)) treated fibers were carried out and a reinforcement effect of the sisal treated with 2% solutions was observed. TGA measurements showed that with the NaOH treatment the fiber becomes more thermally resistant. SEM micrographs and crystallinity index of sisal indicated how different treatments altered the fiber surface. Pull-out tests in polyester resin were performed, evidencing that all treatments were effective in improving interfacial adhesion. The best results were obtained with the 2% N-isopropyl-acrylamide treatment.

Table 4
Fiber tensile strength (MPa). Reprinted with permission from Sydenstricker et al. (2003). Copy right 2003 Elsevier.

Treatment	Mean	Standard deviation
None	324.2	173.9
0.25% NaOH	350.0	179.9
0.50% NaOH	372.8	150.5
1.0% NaOH	366.2	217.9
2.0% NaOH	375.4	209.7
5.0% NaOH	328.0	155.1
10.0% NaOH	296.9	171.2
1.0% N-isopropyl acrylamide	331.2	172.2
2.0% N-isopropyl acrylamide	347.8	170.6
3.0% N-isopropyl acrylamide	256.4	121.6

Table 5
Fiber/polyester shear strength measured by pull-out tests. Reprinted with permission from Sydenstricker et al. (2003). Copy right 2003 Elsevier.

Treatment	Adhesion (MPa)	Standard deviation
None	2.6	173.9
0.25% NaOH	4.5	179.9
0.50% NaOH	5.2	150.5
1.0% NaOH	5.9	217.9
2.0% NaOH	6.9	209.7
5.0% NaOH	6.7	155.1
10.0% NaOH	6.3	171.2
1.0% N-isopropyl acrylamide	5.9	172.2
2.0% N-isopropyl acrylamide	6.8	170.6
3.0% N-isopropyl acrylamide	5.8	121.6

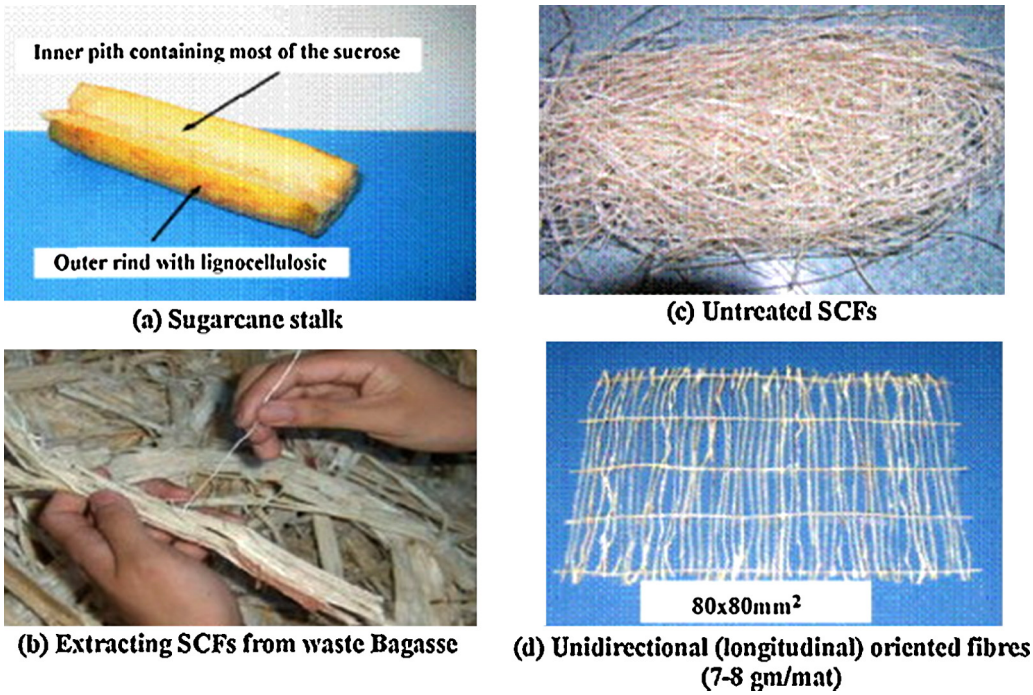

Fig. 7. Steps and process of preparing SCFs. (a) Sugarcane stalk. (b) Extracting SCFs from waste Bagasse. (c) Untreated SCFs. (d) Unidirectional (longitudinal) oriented fibers (7–8 g/mat). Reprinted with permission from El-Tayeb (2008). Copy right 2008 Elsevier.

4.4. Natural fibers/polyester composites

Unsaturated polyesters have also been used as the potential polymer matrix for polymer composites applications (Dhakal, Zhang, & Richardson, 2007; Dhakal, Zhang, Bennett, & Reis, 2012; Dhakal, Zhang, Reis, Surip, & Bennett, 2012). Unsaturated polyester reinforced biocomposites were prepared using nonwoven hemp mats as the reinforcing material and the unsaturated polyester resin (UPE) as the matrix (Mehta, Drzal, Mohanty, & Misra, 2006). The optimization of different fiber loading was also carried out along with surface treatments (alkali treatment, silane treatment, UPE (matrix) treatment, and acrylonitrile treatment) to get the composites with desired high mechanical and thermal properties. From the different mechanical and thermal study, it was observed that mechanical properties of the UPE matrix significantly increased with the increase in treatment of hemp fibers. Kapok fibers based thermoset polymer composites were also prepared and subjected to different mechanical properties study (Reddy, Naidu, & Rani, 2008). In this study Kapok fabric were used as a reinforcement in raw or surface modified form. The surface modification of these fibers was carried out using alkali treatment. Furthermore these fibers were hybridized with glass and sisal fabrics in polyester matrix to study the impact of hybridization on the properties. From the mechanical and other characterizations, it was observed that the impact properties of the composites significantly increased with the loading of fibers (kapok/glass fabrics/sisal fibers). It was observed that the polymer composites prepared using 9 vol% of total fabrics loading in kapok/glass and at 5 vol% fabrics loading in kapok/sisal composites demonstrated higher mechanical properties compared to other loadings. The enhanced mechanical properties were attributed to the excellent dispersion of the reinforcement in the composites along with the good load distribution at these compositions (Reddy et al., 2008).

Henequen reinforced unsaturated polyester composites were also prepared and studied for different properties including the influence of water (Cho, Yoon, & Drzal, 2009). In this study, the effect of different surface modification techniques on the henequen fiber topography along with the interfacial shear strength of henequen/unsaturated polyester composites was ascertained. It was found that each treatment strongly changed the topography of henequen fiber surfaces and significantly improved the mechanical properties. Bacterial cellulose (BC) reinforced unsaturated polyester (UPE) composites prepared using resin transfer molding method were also studied for different physico-chemical properties analysis (Gao et al., 2011). To improve the adhesion between the matrix and BC, silane functionalization of the fibers was carried out. From the studied mechanical properties, it was revealed that silane modified fibers reinforced composites exhibit higher fiber–resin adhesion strength in comparison to original BC. Cellulose fibers reinforced unsaturated polyesters composites were prepared using the raw and trichloro-s-triazine coupling agents modified fibers. In this study different types of trichloro-s-triazine coupling agents were used to modify the surface characteristics of the fibers. It was observed from the functionalization using these coupling agents that the treatment containing double bonds resulted in the formation of covalent bonds between fiber and matrix. The tensile properties of composites prepared using treated/untreated fibers were studied and treated fiber composites were found to exhibit the higher mechanical properties followed by low water absorption (Zadorecki & Flodin, 1985)

4.5. Natural fibers/vinyl ester composites

Along with the other esters used in polymer composites preparation, vinyl ester has also been considerably investigated. Table 6 shows some of the properties of the vinyl ester resin (Khalil, Kang, Khairul, Ridzuan, & Adawi, 2009). Bast fibers and various other types of natural fibers reinforced vinyl ester polymer composites have also been prepared for automotive applications (Kim et al., 2012; Sadasivam, Cherng, & Mallick, 2000). Natural flax fibers reinforced vinyl ester and modified acrylic resin composites were manufactured by resin transfer molding (Andersons, Sparnins, & Joffe, 2006). In this study, the fibers were used in the form of mat. In addition to these thermoset composites, thermoplastic composites

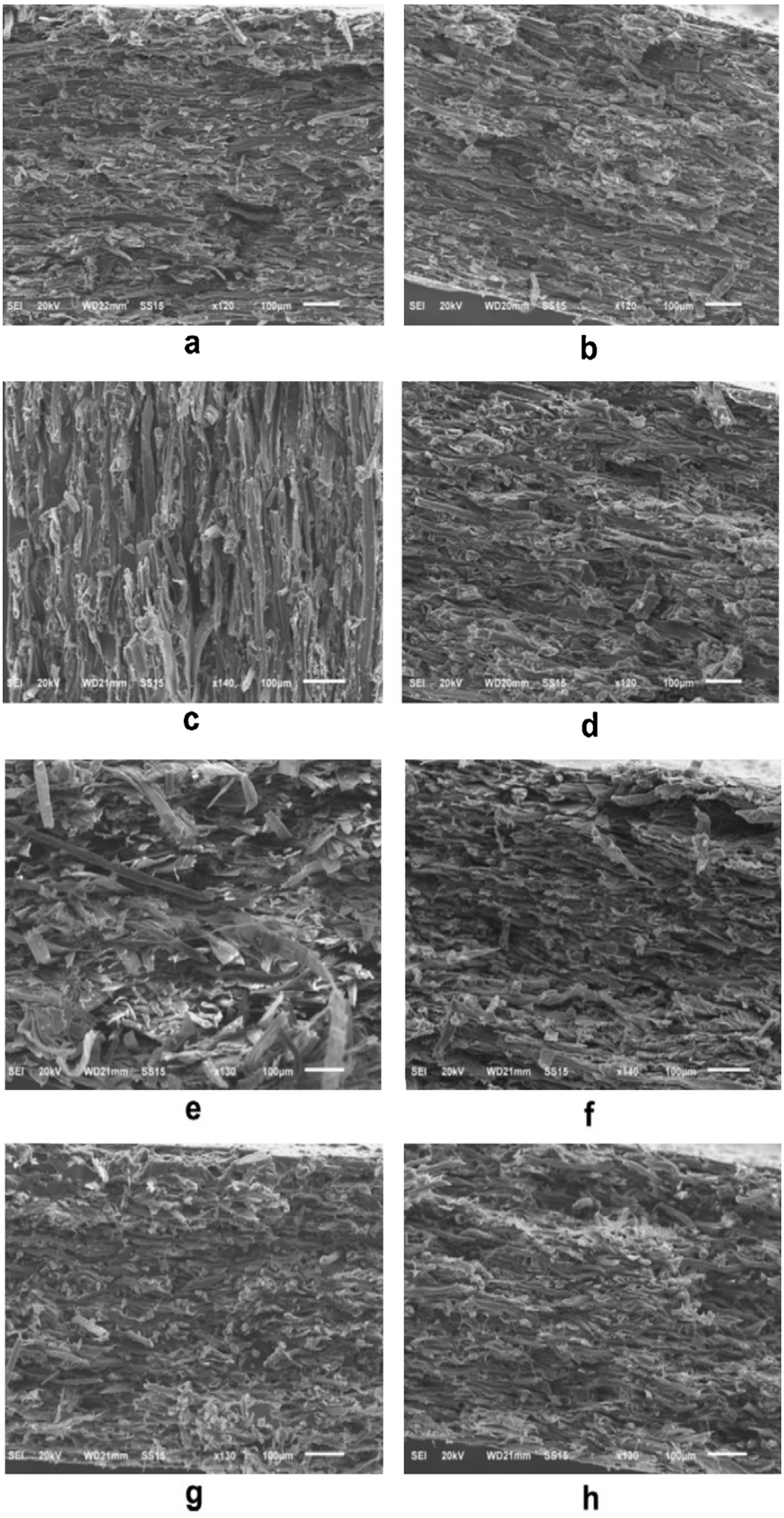

Fig. 8. Fracture surfaces of eight composites fabricated with four pulp fibers and two resins: (a) HW–UPE; (b) HW–VE; (c) SW–UPE; (d) SW–VE; (e) Kraft–UPE; (f) Kraft–VE; (g) WM–UPE; and (h) WM–VE. Reprinted with permission from Du et al. (2013a). Copy right 2013 Elsevier.

Table 6
The physical and chemical properties of vinyl ester matrix. Reprinted with permission from Khalil et al. (2009). Copy right Sage 2009.

Appearance	Brownish, viscous liquid
Odor	Aromatic odor
Solubility	Insoluble in water, soluble in most organic solvents
Boiling point	145 °C
Melting point	N/A
Vapor pressure	5 mmHg
Percent volatiles	44–48%
Vapor density	Heavier than air
Specific gravity	1.10 at 25 °C
Other properties	Viscosity at 25 °C: 450–650 cps
pH	N/A

were also prepared in this study using polypropylene and maleic anhydride grafted polypropylene. Different theoretical models and rule of mixtures were applied to develop the fiber composites. It was observed that the rule of mixture yield acceptable stiffness prediction of both types of composites, while the sensitivity of a rule-of-mixtures model of strength to the matrix and adhesion properties was found to depend on the relative ineffective fiber length (Andersons et al., 2006). A simulation procedure was also developed by Behzad & Sain, 2007 to predict the temperature profile and the curing behavior of the hemp fiber/thermoset (acrylic resin) composite during the molding process (Behzad & Sain, 2007). It was observed from the experimental data that the simulation procedure is numerically valid and stable for the studied composite systems. Furthermore the analysis provided the reasonably accurate predictions. Natural *L. cylindrica* fruit fiber reinforced vinyl ester polymer composites were also prepared after modification treatments (Botaro, Novack, & Siqueira, 2012). Different extraction treatments along with mercerization, and esterification with BTDA dianhydrides were used to modify the natural fibers. It was observed from the study that the polymer composite prepared using Luffa fibers as reinforcement showed improvements in mechanical and thermal properties compared to the vinyl ester matrix. Pulp fibers reinforced unsaturated polyester (UPE) and vinyl ester (VE) composites were also studied for different thermal and mechanical properties (Du, Wu, Yan, Kortschot, & Farnood, 2013). In this study, four different types of pulp fibers namely hardwood and softwood high-yield pulp (HYP), Kraft pulp, and Whatman cellulose fibers were used. Fig. 8 shows the SEM images of these fibers as well as their respective polymer composites (Du, Wu, et al., 2013). From the experimental investigation it was observed that the HYP fibers were more compatible to the UPE resin. It was observed that the residue lignin on the HYP fibers acted as a natural coupling agent and resulted in improved fiber–matrix interfacial bonding by reducing the hydrophilicity of the pulp fiber. On the other hand, the Kraft and Whatman cellulose fibers were more compatible to the VE resin. These results were also confirmed by the tensile properties. The DMA study of the composites also indicated that the incorporation of pulp fibers considerably improved the composites' storage moduli compared to the pristine UPE and VE resins.

Hybrid polymer composites of oil palm empty fruit bunch fibers (EFB) along with glass fibers were prepared using vinyl ester as the polymer matrix (Khalil et al., 2009). In this study, the oil palm of empty fruit bunch fibers (EFB) was laminated at different layer arrangements with glass fiber (CSM). These polymer composites were then subjected to the tensile, flexural, and impact test along with their physical properties (water absorption, dimension stability, and density). The mechanical properties, water absorption, and density of hybrid composites exhibited higher properties than control composites (chemical and mechanical fibers). It was observed that the mechanical properties of hybrid EFB/glass fiber with vinyl ester hybrid composites were significantly better than the mechanical board and chemical board (Khalil et al., 2009). The SEM micrographs of the failure impact surface of the EFB/vinyl ester clearly showed that fiber fracture and matrix cracking were observed. From the different mechanical investigations, it was observed that the hybrid composites displayed comparable mechanical properties to the pristine glass fiber composites. Flax fibers reinforced thermoset, vinyl ester and polyester resins composites were also studied for determining the competitive potential of these fibers for automotive applications (Joffe, Andersons, & Wallstrom, 2003). In this study single fiber fragmentation test was used to characterize the strength distribution of flax fibers in polymer matrices. To improve the adhesion of the fibers with the matrices, surface functionalization of the flax fibers was also carried out. It was observed from the experimental study through various characterizations that surface pretreatments of flax fibers significantly improved the interfacial strength of the resulting composites compared to the raw flax fibers reinforced composites.

5. Conclusion

Natural cellulosic fibers are playing an important role in a number of applications due to their inherent eco-friendly advantages since the last few decades. These fibers are being explored as the potential alternatives to traditional synthetic fibers for diverse applications with particular emphasis as green reinforcement. Indeed natural fibers reinforced composites are emerging very rapidly as the potential substitute to the metal or ceramic based materials in applications that also include automotive, aerospace, marine, sporting goods and electronic industries to name a few. Natural cellulosic fibers and their respective polymer composites offers a number of advantages over conventional materials such as considerable toughness, flexibility, easy processing, recyclability and eco-friendliness etc. In the present article, we have discussed the different natural fibers with particular emphasis on their use as reinforcement in thermoset polymer matrix based composites. Furthermore, the effect of different processing conditions and different surface modification techniques on the cellulose fibers as well their composites have been discussed in detail. The present review article provide an in depth analysis and comprehensive knowledge to the beginners in the field of natural fibers/thermoset polymer composites.

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