Progress in Green Polymer Composites from Lignin for Multifunctional Applications: A Review

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ABSTRACT: Rising environmental concerns and depletion of petro-chemical resources has resulted in an increased interest in biorenewable polymer-based environmentally friendly materials. Among biorenewable polymers, lignin is the second most abundant and fascinating natural polymer next to cellulose. Lignin is one of the three major components found in the cell walls of natural lignocellulosic materials. Lignin is widely available as a major byproduct of a number of industries involved in retrieving the polysaccharide components of plants for industrial applications, such as in paper making, ethanol production from biomass, etc. The impressive properties of lignin, such as its high abundance, low weight, environmentally friendliness and its antioxidant, antimicrobial, and biodegradable nature, along with its CO_2 neutrality and reinforcing capability, make it an ideal candidate for the development of novel polymer composite materials. Considerable efforts are now being made to effectively utilize waste lignin as one of the components in polymer matrices for high performance composite applications. This article is intended to summarize the recent advances and issues involving the use of lignin in the development of new polymer composite materials. In this review, we have made an attempt to classify different types of lignin-reinforced polymer composites starting from synthetic to biodegradable polymer matrices and highlight recent advances in multifunctional applications of lignin. The structural features and functions of the lignin/polymer composite systems are discussed in each section. The current research trends in lignin-based materials for engineering applications, including strategies for modification of lignin, fabrication of thermoset/thermoplastic/biodegradable/rubber/foam composites, and the use of lignin as a compatibilizer are presented. This study will increase the interest of researchers all around the globe in lignin-based polymer composites and the development of new ideas in this field.

KEYWORDS: Sustainable materials, Green composites, Chemical composition, Surface treatments, Processing, Multifunctional applications
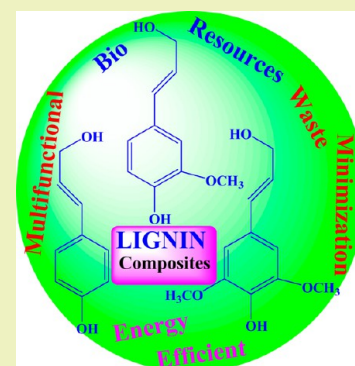
INTRODUCTION

During the last few decades, compared to synthetic materials, the use of polymer-based materials in a number of applications has increased very rapidly.[1−3] Polymers have simplified human lives and influenced every aspect of modern civilization. Today, different kinds of polymers are available for household to aerospace applications and can be easily seen in everyday use.[4,5] Different kinds of materials such as artificial fibers, elastomers, plastic, and polymer composites have been developed using polymers, and these materials are being tailored frequently to meet the desired industrial applications.[6] Polymers have even replaced traditional metals and glass-based materials for a number of applications due to their ease of processing, low cost, and availability.[7−9] However, due to rising environmental awareness, depletion of petroleum resources, and health concerns, the past few years have seen a dramatic shift in the development of novel materials derived from biorenewable resources.[10,11] Biopolymers that include polysaccharides, such as starch, chitin/chitosan, cellulose, alginate, and carbohydrate polymers, and animal protein-based biopolymers, such as gelatin, wool, silk, and collagen, are some well-known examples

of biorenewable resource-based environmentally friendly polymeric materials.[12] Biobased materials procured from different natural resources are presently being used in a number of fields especially in the automotive and biomedical fields.[13,14] A number of properties of biorenewable materials such as biodegradability, acceptable specific strength, low density, recyclability, ease of separation, high toughness, good thermal properties, no health risk, reduced tool wear, nonirritation to the skin, and enhanced energy recovery have made them a material of choice.[15−17] Biobased materials are readily available from renewable feedstocks in large quantities at very low cost and meet the industrial demand for renewable content.[18,19] Among various materials, biobased polymer composites are important for the automotive industry.[20,21] Diverse efforts are being made to incorporate biorenewable materials such as natural fibers/agriculture residue in polymer
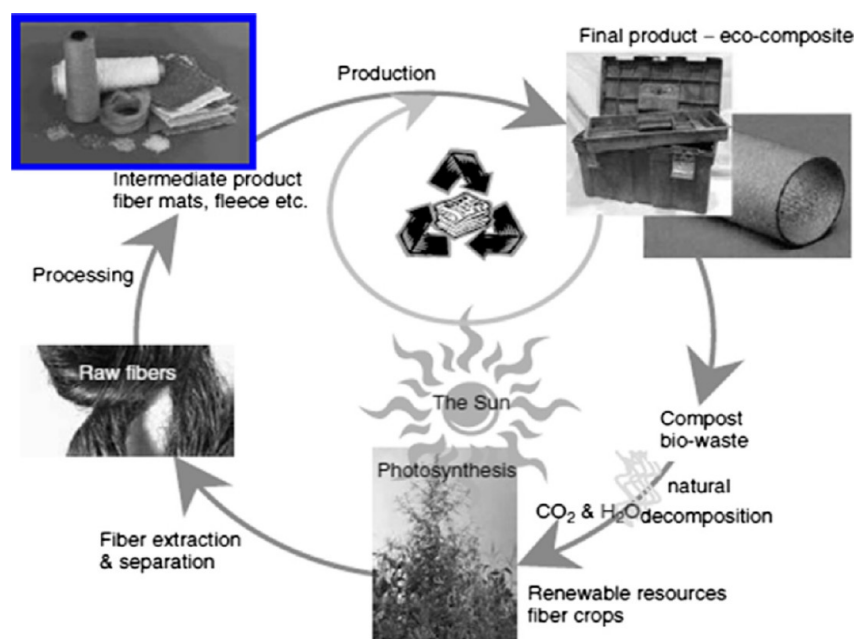
Figure 1. Life cycle of biorenewable lignocellulosic polymer biocomposites. Reprinted with permission.[50] Copyright 2011 Elsevier.

(natural/synthetic) matrices to make the final product completely/partially biodegradable and eco-friendly.[22,23]

For polymer composite applications, an intensifying focus has been directed toward the use of natural fibers (wood/non-wood) for high-end applications to efficiently reduce the dependence on petrochemical-based plastics.[24,25] Natural fibers as such or in the form of extracted cellulose have been frequently used for the preparation of high performance composites. Flax, hemp, pine needles, coir, jute, *Hibiscus sabdariffa*, kenaf, *Grewia optiva*, *Saccaharum cilliare*, sisal, ramie etc. are some of the natural fibers commonly used as reinforcement in the preparation of composite materials.[26,27] The incorporation of these natural fibers in polymer results in new materials with a number of advantages such as being lightweight, no/lower impact on the environment, low cost, reduced wear on processing equipment, biodegradability, biocompatibility, etc.[28−32] Previous research has been primarily focused on the use of natural fiber-based materials as reinforcement in polymers, and limited research has been carried out on the preparation of lignin-based polymer composites. Very recently, lignin has emerged as a potential component for various polymer composite applications, e.g., stabilizing agents, lubricants, coatings, plasticizers, surfactants, and superabsorbent hydrogels in place of the commercially used ones.[24,33−38] It has been reported that all over the world the chemical pulp industries generate nearly 50 million tons of lignin every year.[39,40] This lignin is produced as a byproduct of the paper/pulp industry and is considered a waste.[40] The waste lignin from industries offers a number of advantages, such as sufficient reactive functional groups, film-forming ability, high carbon content, compatibility with diverse industrial chemicals, good stability, mechanical properties due the presence of aromatic rings, good rheological and viscoelastic properties, tailored ability for chemical transformations, continuous production during paper making, high volumes, etc., making it a potential candidate to be used as reinforcing material in polymer composites.[24,33−38,41,42] The preparation of novel materials from lignin/lignin-derived products will improve the economics of polymer composite materials as well as possibly address the problem of its waste disposal.[41−43]

Lignin is the second most available polymer next to cellulose and comprises 25−30% of the nonfossil organic molecules on earth.[44−46] Several review articles have been published on natural fiber-reinforced polymer composites.[27,47] However, inadequate information is available in the existing literature that summarizes the lignin-reinforced polymer composites.[48,49] So, the present article intends to review the feasibility of using lignin as an indispensable component in the polymer matrices to prepare environmentally friendly, low cost, polymer composites. The main focus of the present article is on the development of polymer composite materials formulated with lignin within the previously described field of eco-friendly materials applications. This review intends to show that polymer composite materials can be efficiently prepared and executed in industrial applications using lignin as a potential reinforcement. The overall characteristics of lignin used in polymer composites, type, structure, chemical composition, along with different modification methods applied to functionalize lignin will be reviewed and discussed in detail. Different processing technologies for lignin-reinforced composites are also discussed based on different polymer matrices. Finally, the review will conclude with recent developments and future trends of lignin-reinforced polymer composites

Structure and Chemistry of Lignin. Diverse lignocellulosic materials are available all around the globe and primarily composed of cellulose, hemicellulose and lignin along with small fractions of waxes, and several water-soluble compounds.[13,27,47,50] Due to their eco-friendly advantages, lignocellulosic materials are now easily found in all life cycle of life (Figure 1).[50] Each of these constituent of lignocellulosic natural fibers play an important role in determining the overall properties of natural fibrous materials. At all levels, cellulose, hemicellulose and lignin are combined together and determine the properties (materials/biological) of lignocellulosic polymers.[50,51] The schematic structure of the cell wall of lignocellulosic natural plants is commonly known as the

microfibrils/microfiber.[50] The cell wall has been found to consist of a hollow tube with four different layers (one primary wall and there secondary walls). The cell wall also consist of an open channel in the center of microfibrils known as lumen. Each of these layers in the cell wall contains cellulose that is embedded in the matrix of lignin and hemicellulose.[50,51] In other words, the microfibrils consisting of celulose are glued by lignin and hemicellulose. Figure 2(a) shows the embedment of
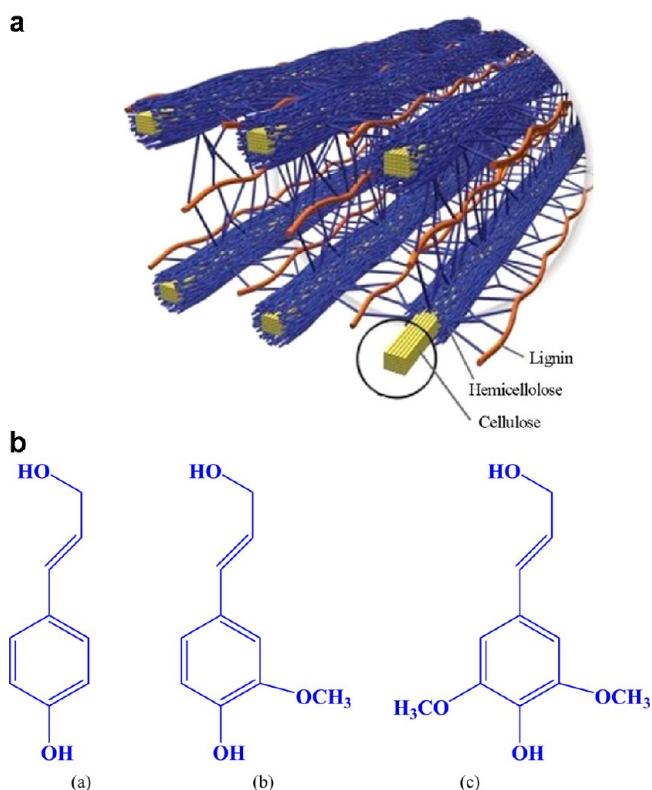
Figure 2. (a) Cellulose strands surrounded by hemicellulose and lignin. Reprinted with permission.[52] Copyright 2011 Elsevier. (b) Monolignol monomer species: (a) p-coumaryl alcohol (4-hydroxyl phenyl, H), (b) coniferyl alcohol (guaiacyl, G), (c) sinapyl alcohol (syringyl, S). Adopted with permission.[52] Copyright 2011 Elsevier.

cellulose within a matrix of lignin and hemicellulose.[52] Hemicellulose is formed from different highly branched polysaccharides such as glucose, galactose, mannose, xylose and others, while lignin is composed of aliphatic and aromatic hydrocarbons.[52] In a given lignocellulosic material (e.g., natural fibers), cellulose provide the strength to the materials and hemicellulose on the other hand is responsible for thermal degradation, biodegradation and moisture absorption.[53,54] Among these three constituents, lignin is thermally stable but it is responsible for the ultraviolet (UV) biodegradation of the materials.[55,56] It has been reported that the bonds between lignin and carbohydrate are of covalent nature and primarily composed of benzyl ethers benzyl esters, and phenyl glycosides.[52]

Lignin is hydrophobic in nature, thus making the cell wall impermeable to water and ensuring an efficient water and nutrition transport in the cells.[57] It is known as a cross-linked macromolecular material based on a phenylpropanoid monomer structure (Figure 2(b)).[52] The monomer structure has been reported to consist of the same phenyl propenoid skeleton.[58] However, these structures differ in the degree of

oxygen substitution on the phenyl ring.[52] In lignin, both the carbon−carbon and carbon−oxygen bond occurs between the monomers. The carbon−oxygen link between a p-hydroxy moiety and the β-end of the propenyl group (β−O−4) accounts for most of the bonds between monomer units in lignin from most of the resources.[52] Figure 3 shows the
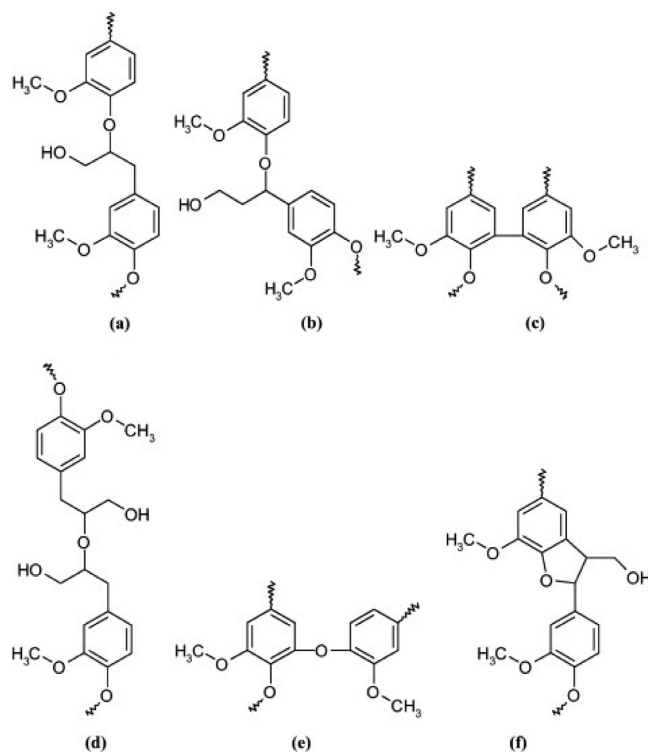
Figure 3. Monolignol monomer species: (a) p-coumaryl alcohol (4-hydroxyl phenyl, H), (b) coniferyl alcohol (guaiacyl, G), and (c) sinapyl alcohol (syringyl, S). Reprinted with permission.[52] Copyright 2011 Elsevier.

carbon−carbon and carbon−oxygen bonds formed between different monomers units in lignin.[52] Depending upon the type of lignin (whether it is procured from soft wood/hard wood), the degree of cross-linking is possible in lignin, and depending upon the degree of substitution, the rigidity of the structure varies.[52] As an example, in softwoods, the G structure has been found to be dominant, and in hardwood, lignins with a mixture of S and G structures with S in the majority dominates.[59] In the case of lignin obtained from grasses, the H structures dominate.[60] In brief, lignin obtained from soft wood is easily branched and cross-linked, while that obtained from hard wood is more linear.[52] As shown in the structure, the prime reason for this is that hard wood lignin contains a syringyl unit as well as guaiacyl that facilitate retaining the linear structure of lignin. Generally, the molecular masses of lignin isolated from different resources have been reported to be in the range of 1000−20,000 g/mol.[52] However, it is very difficult to measure the degree of polymerization because lignin is invariably fragmented during extraction and consists of several types of substructures that repeat in an apparently haphazard manner.

Properties of Lignin. Lignin-based materials offer a number of advantages over synthetic materials such as being biodegradable, CO_2 neutral, available abundantly in industrial waste, low in cost, and environmentally friendly, and having antioxidant, antimicrobial, and stabilizer properties.[5244,61,62]

The properties of lignin determine its potential applications in different fields.[63] Primarily, the source from which the lignin is extracted (hard wood/soft wood/grass) and the process of extraction determines the overall physicochemical properties of the lignin.[64,69] Although most of the properties of lignin can be determined, the difficulty rises in accurately determining the molecular weight due to varying functionality and high cross-linking. Different properties (molecular weight/functional groups) of some selected lignin are summarized in Table 1.[52]

Table 1. Molecular Weight and Functional Groups of Lignins[a]

lignin type	M_n (g mol^{-1})	COOH (%)	OH phenolic (%)	methoxy (%)
soda (bagasse)	2160	13.6	5.1	10.0
soda (wheat straw)	1700	7.2	2.6	16.0
kraft (softwood)	3000	4.1	2.6	14.0
organosolv (hardwood)	800	3.6	3.7	19.0
organosolv (bagasse)	2000	7.7	3.4	15.1

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The reactivity and functionality of these groups has been found to determine the final properties of the end product.[65] It has been demonstrated by Mahendran et al. in their pioneer work on lignins that the processing methods of the lignin have a strong impact on the adhesive properties of the synthesized phenol-formaldehyde adhesive.[66] The authors observed that the properties of kraft lignin-derived phenol-formaldehyde resin were more superior than the steam-exploded lignin-based phenol-formaldehyde resin.[66] Along with the molecular weight and functionality, the glass transition temperature (T_g) is another imperative property that affects the properties of the final product. Table 2 shows the T_g of some of the lignins

Table 2. T_g of Different Lignin Processed Using Different Techniques[67]

types of lignin	T_g (°C)
milled wood lignin	
steam explosion lignin	113−139
hardwood	110−130
softwood	138−160
organosolv lignin	91−97
kraft lignin	124−174

derived from different resources.[67] Baumberger et al. have also carried out an extensive study on determining the relationships between the molecular structure and the thermal behavior of lignins using different techniques such as thermomechanical analyses.[68] The lignin used in their study was procured from milled wood and enzyme poplar lignin fractions that were prepared from genetically modified and control woods (referred to as series A and B in the study). The genetically modified counterparts of each series were grown in the same conditions. It was observed that the transgenic trees obtained were either deficient in OMT (O-methyl transferase) activity (ASOMT), in CAD (cinnamyl alcohol dehydrogenase) activity (ASCAD samples), or in both activities (ASCAD × ASOMT). Table 3 shows the structural characteristics of the investigated lignins.[68] Thermal properties of these lignin were also investigated. It was observed that all the lignin samples displayed similar thermal profiles. For all the samples, a clear inflection point was assigned to the glass transition point. T_g for the tested samples was found to vary between 170 and 190 °C depending upon the sources of the lignin, and this behavior was attributed to the condensation degree of lignins that was evaluated by thioacidolysis. It was also reported that along with the molecular weight and functionalities present in the lignins, T_g depends upon the amount of polysaccharides and water in the lignin.[68]

Processing of Lignin. Lignin is processed using different chemical processes, and each process has its own advantages/disadvantages.[62] During the processing of lignin, it is broken down into low molecular weight fractions, and its physico-chemical properties are affected by these processes.[69] Most of the processing methods for extraction of lignin from different resources follow either an acid- or base-catalyzed mechanism.[52] Different processes used to extract lignin from diverse lignocellulosic resources include three major processes, namely, sulfite, kraft, and soda, along with many others. Recently, William et al. in their excellent review have summarized the different techniques used in the processing of lignin.[52] In the following section, we will be giving an overview of these techniques.

The sulfite process has been traditionally used in pulping technology, and this process is also a source of lignin that is produced as a byproduct during this process.[52] It is an acid-catalyzed process that involves the cleavage of the α-ether linkages and β-ether linkages of lignin. In the pulping process, three main reactions have been found to take place that involved (1) reaction between free sulphurous acid and lignin leading to the formation of lignosulfonic acid, (2) soluble lignosulfonates formation with cations (e.g., Mg, Na, or NH4$^+$), and (3) lignosulfonates fragmentation. In addition to the formation of lignosulfonates in the sulfite process, degraded carbohydrates are also produced in this reaction.[52,70] On the

Table 3. Structural Characteristics and Molecular Weight Distribution[a]

	control A	ASCAD A	ASOMT A	ASCAD × ASOMT	control B	ASCAD B
isolation yield (%)	37	50	43	59	54	83
β−O−4 (μmol g^{-1} lignin)	2500	2250	1900	1550	1550	1400
condensation degree (%)	50	55	62	69	56	72
M_w (Da × 10^3)	36	26	32	28	28	16
M_n (Da × 10^3)	8.7	6.7	7.5	7.2	5.5	4.3
M_w/M_n	4.1	3.8	4.2	3.8	5.6	3.8

[a]Weight-average molecular weight, M_w; number-average molecular weight, Mn; and polydispersity, M_w/M_n) of MWEL (milled wood and enzyme lignins). Fractions isolated from two year old (series A) and six month old (series B) control and transgenic poplar trees. Reprinted with permission.[68] Copyright 2002 American Chemical Society.

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dx.doi.org/10.1021/sc500087z | ACS Sustainable Chem. Eng. 2014, 2, 1072−1092

other hand, kraft lignin produced using craft pulping has been found to exhibit a dark color and is insoluble in water and solvent.[71] However, it has been found to be dissolved in alkali solutions owing to the high concentration of phenolic hydroxyl groups present in it. During craft pulping, which is frequently used for the preparation of lignin, it is most of the time degraded and dissolved into black liquor. Compared to other types of lignins, kraft lignin contains the highest quantity of the phenolic hydroxyl groups. The degradation of lignin results in an increment in the number of hydroxyl groups with a decrease in the molecular mass of lignin as a result of the cleavage of $\beta-$O$-4'$ bonds. The cooking condition used during craft pulping has been found to control the amount of free hydroxy groups. Due to the cleavage of the bonds, the solvency of kraft lignin in aqueous system has been found to be influenced by the ionic strength, temperature, and pH of the solution.[52] Most of the kraft lignins are generally used in low added value applications.[52] Soda lignin is produced during the soda pulping process and is one of the major components of the black liquor. Soda lignin obtained from different resources generally exhibit similar properties such as low molecular weight, high phenolic hydroxyl content, and relatively low glass transition temperature.[52,70,72] The soda pulping process involves the use of sodium hydroxide as the cooking chemical to produce wood pulp. Compared to the kraft pulping process, this process has been found to yield pulp with lower tear strength. Due to environmental concerns, the soda lignin is recovered so as to avoid pollution. However, a very small quantity (<1%) of lignin is used for industrial applications. Other techniques presently being used in the processing of lignin involves organsolv pulping and the combination of chemical, biochemical, physical, and thermal methods.[52] In organsolv pulping, different organic solvents, namely, ethanol, methanol, formic acid, acetic acid, etc. are used to produce lignin, while physical methods involve hydrothermolysis, pulverizing, and steam explosion.[72] Recently, ionic liquids are also being explored in fractionation lignocellulosic materials due to their environmentally friendly advantages.[52,72]

Fabrication and Applications of Lignin-Based Polymer Composites. Polymer composites are materials that are obtained by reinforcing the polymer matrix with suitable reinforcement (fibers/particulate).[73−76] These are generally defined in different ways.[77] Depending upon the applications, the nature of the matrix varies from a synthetic to natural polymer.[78] For most of the applications, the matrix is obtained from synthetic polymers, and very recently, biopolymers are being used as the matrix material.[75] The reinforcing materials in general are fibers, either synthetic (e.g., carbon, glass, etc.) or natural (e.g., sisal, hemp, flax, pine needles, coir, bagasse, etc.). Both the polymer matrix and the reinforcement have been found to play an important role in determining the overall physicochemical properties of the composites.[57,79−82] An extensive study has been carried out on natural fiber-reinforced polymer composites, and several reviews have also been published. However, very recently, the lignin-based polymer composites have received the interest of the research community all over the world.[83−85] Intense efforts are being made to use lignin as a low cost eco-friendly reinforcement to prepare high performance composites.[86−88] In the following section, we describe the study carried out on lignin-based polymer composites.

Thermoplastic Polymer Composites from Lignin. Lignin-reinforced thermoplastic composites have been prepared by a number of researchers.[89−92] Barzegar et al. have reported their study on the mechanical and rheological behavior of lignin-reinforced polystyrene (PS) composites.[90] Different PS/lignin polymer composites were prepared with and without the addition of a linear triblock copolymer based on styrene, ethylene, and butylene (SEBS). The composites were prepared by compounding in an internal batch mixer. The loading of lignin in the composites significantly affected the overall mechanical properties of the studied system. However, each property varied differently with respect to lignin content.[90] As an example, the flexural and torsion moduli increased with an increase in lignin loading, while the tensile properties decreased. However, the compatibilizer used in this study significantly improved the tensile modulus and flexural modulus of the lignin/PS composites. The increase in the modulus was attributed to the improved interfacial adhesion between lignin and PS.[90] Polystyrene matrix-based polymer composites were also prepared using lignin modified with the transition metals for packaging applications.[92] The lignin used in this study was modified using different transition metal cations such as Fe (III), Ni (II), and Co (II). After the modification, the modified samples were characterized by UV spectra, gas chromatography (GC) mass spectra, and scanning electron microscopy (SEM) to confirm the changes in the structure of the lignin filler particles along with vanillin-transition metal ions. To better understand the mechanism/interaction between the lignin and the metal ions, vanillin was also used as a model for the lignin because of its similarity in the chemical structure with the lignin.[92] From the UV study, it was observed that the lignin fraction, AL, exhibits the basic UV spectra typical of lignins, having an absorption maxima at 282 nm, while other peaks also successfully demonstrated the appearance of AL−metal complexes. The interaction between the lignin and transitional metal was further confirmed by fluorescent microscopy (as lignin is brown in color and it is difficult for the appearance of a color change due to the complex formation) followed by a SEM study. Figure 4(a) and (b) show the UV−fluorescent microscope and scanning electron microscope images of different lignin/vanillin metal complexes, respectively.[92] Both the images confirm a change in the morphological structure of lignin after complex formation with the transition metal ions. The glass transition (T_g) for various blends prepared using 5% loading was also studied It was observed that T_g of the composite decreases, and this behavior was attributed to the immiscibility between the polymer matrix and both the vanillin and lignin.[92] It was also observed from the T_g that complexation results in a slightly better compatibility with PS compared to the unmodified form. The mechanical properties analysis of the composites prepared using unmodified/modified lignin/vanillin shows that the tensile strength decreases with the addition of the vanillin and lignin, while it increases with the incorporation of both Co (II)-vanillin and Co (II)-lignin complexes. The increment in the tensile strength with the addition of the complexes was attributed to the better compatibility of these complexes with the PS.[92] Stiubianu et al. have prepared polydimethylsiloxane-α, ω-diol (PDMS) polymeric matrix-based composites using silica aerogel as reinforcement and lignin powder as bulking filler.[88] The polymer matrix used in this study was synthetized using cationic polymerization. Different properties of the composites were investigated using tensile strength tests, dynamic mechanical analysis, scanning electron microscopy, X-ray diffraction analysis, thermogravimetric analysis, and differential
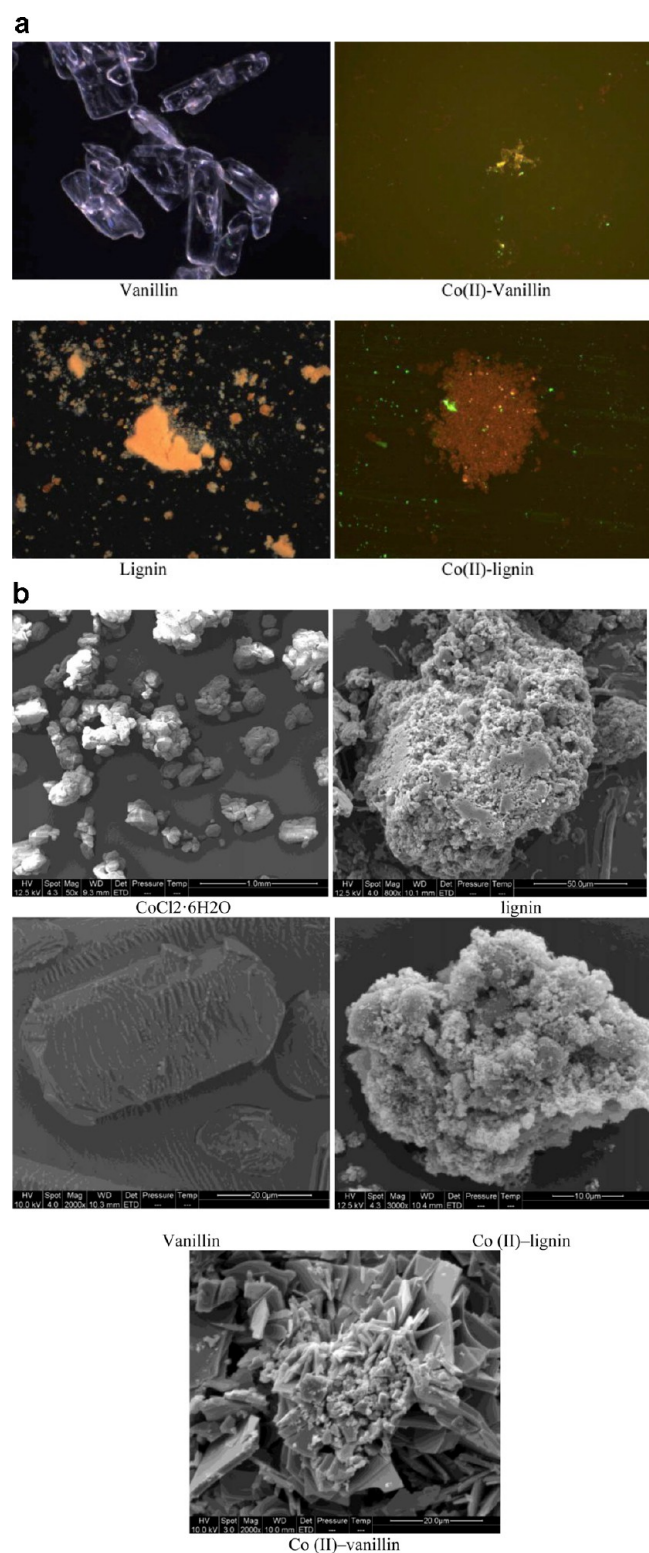
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dx.doi.org/10.1021/sc500087z | ACS Sustainable Chem. Eng. 2014, 2, 1072−1092

a

b

Figure 4. (a) UV–fluorescent microscope for vanillin, lignin, and their Co²⁺ complexes, indicating the presence of green fluorescent spots for the complexes. Reprinted with permission.[92] Copyright 2011 Elsevier. (b) SEM for CoCl₂·6H₂O, lignin, vanillin, Co (II)-lignin, and Co (II)-vanillin. Reprinted with permission.[92] Copyright 2011 Elsevier.

scanning calorimetry. It was observed that incorporation of lignin in the matrix slight improves the mechanical properties, hypothesizing that lignin can be used as an extender for silicones. The particular benefits of using lignin in this study

were mainly related to the material's cost, which decreases considerably using lignin.[88] Poly(ethylene terephthalate) (PET) matrix-based composites reinforced with lignin (L) were prepared using a single-screw extruder.[93] The influence of the concentration of lignin on thermal stability and melting behavior was studied in detail using thermogravimetric analysis.[93] It was observed that the lignin amount in the composites strongly influenced the thermal stability. The experiments carried out in an air atmosphere demonstrated that lignin incorporation in the polymer composites favors the formation of a protective surface shield. This shield was found to be able to reduce the oxygen diffusion toward the polymer bulk. The incorporation of lignin in the composites also strongly influenced the melting behavior of annealed samples and promoted the crystallization that resulted in a faster crystalline reorganization than that of the pure PET.[93] Same authors have also studied the supermolecular structure and thermal properties of poly(ethylene terephthalate)/lignin composites. In particular, effect of lignin content on the crystalline structure of PET was studied in detail.[94] The polymer composites were subsequently characterized using polarizing optical microscopy (POM) and wide-angle X-ray diffraction (WAXD) to study the dispersion and crystallization behavior of the resulting composites. The morphological analysis clearly demonstrated a good dispersion of the lignin particles in the polymer for all the investigated composites.[94]

The compatibility of different types of polymer blends using kraft lignin as the reinforcing material and a number of polymers (e.g., polypropylene (PP); PS; polyacrylonitrile (PAN); polyvinylchloride (PVC); polyvinyl alcohol (PVA), etc.) as the matrix was also studied.[95] The compatibility of different ligands was studied using the blend morphology, and it was demonstrated that the compatibility of the blends could be easily improved by selecting a suitable structure of the polymer matrix.[95] Poly(ethylene oxide) (PEO) and kraft lignin-based blends were also prepared by Kadla and Kubo using thermal mixing.[96] All the blends were found to be miscible over the studied range. The miscibility in these blends was attributed to the hydrogen-bonding interactions between the hydroxyl protons of lignin and the proton accepting sites of PEO. The strength of the hydrogen-bonding interactions in the blends was found to be varied for the aromatic and aliphatic hydroxyl groups in lignin.[96]

Thermosetting Polymer Composites from Lignin. Thermosetting polymer matrix-based composites prepared using lignin as reinforcement have also been reported.[97−99] Yin et al. have reported their study on the preparation of lignin-reinforced epoxy composites.[97] Lignin with different loadings (as high as 60%) was used to prepare the composites. The composites were prepared using the hot press molding technique. The effect of different parameters such as molding temperature/pressure and curing agent was studied on the mechanical and microstructure properties. It was observed that the mechanical properties along with thermal properties were affected considerably by the molding process. Due to strong interactions between the polymer resin and the lignin, a strong interfacial interaction was formed between the two components that resulted in higher mechanical properties. Furthermore, the properties were found to increase with the increment in molding temperature (up to 130 °C) and pressure.[97] Doherty et al. have also prepared lignin-reinforced phenol formaldehyde (PF) polymer composites for coating applications along with bagasse fibers as reinforcement.[98] The wettability study

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dx.doi.org/10.1021/sc500087z | *ACS Sustainable Chem. Eng.* 2014, 2, 1072−1092

demonstrated that the lignin and lignin-PF resin films are effective water barrier coatings. However, the contact angles of the lignin-PF resin films was found to be considerably lower than the commercially used wax films. Stanzione et al. have prepared lignin-based bio-oils for the development of biobased vinyl ester resins according to ref 99. In their study, a methacrylated lignin-based bio-oil mimic (MBO) was synthesized and used as a low viscosity vinyl ester resin (30.3 cP at 25 °C). The thermo-gravimetric and thermo-mechanical properties of the thermoset were found to be comparable to that of the commercial petroleum-based and vinyl ester-based thermosets.[99]

Rubber Composites from Lignin. A number of polymer composite systems have been prepared using rubber as the matrix and lignin as reinforcement.[70,100−104] Xiao et al. have prepared lignin-reinforced styrene-butadiene rubber (SBR)/lignin-LDH (layered double hydroxide) composites by the melt compounding method.[105] In this study, first of all, the layered double hydroxide (lignin-LDH) complex was synthesized using an in situ method, and then the composites were prepared. The synthesized lignin-LDH complexes were named according to the lignin content present in the samples (30LDH-3Lignin, 30LDH-9Lignin, 30LDH-15Lignin, respectively). As an example, in this study, 30LDH-3Lignin referred to a lignin-LDH complex whose ratio of LDH to lignin was 10 to 1, while pristine LDH was referred as LDH due to no lignin amount. These composites were characterized using X-ray diffraction analysis to study the crystalline nature of lignin-LDH and transmission electron microscopy analysis to study the dispersion of lignin-LDH in the SBR matrix. Both the crystalline nature and well dispersion were verified using these techniques. Furthermore, mechanical properties such as tensile strength, elongation at break, modulus, and hardness of the composites were also studied. It was observed that compared to LDH/SBR composite samples, the properties of lignin-LDH/SBR were significantly improved.[105] Nanocomposites using nanolignin and natural rubber were also prepared.[106] The nanocomposites were prepared using co-precipitation of colloidal lignin−cationic polyelectrolyte complexes and rubber latex. The nanolignin in this study was synthesized by fabricating colloidal lignin-poly(diallyldimethylammonium chloride) (PDADMAC) complexes (LPCs) employing the self-assembly technology. LPCs were subsequently characterized by dynamic light scattering (DLS), zeta potential, transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and ultraviolet−visible (UV−vis) absorption measurements to study the interaction of PDADMAC with lignin cation. Polymer nanocomposites were then prepared using natural rubber as the matrix. The LPCs were found to homogenously distribute in the natural rubber (NR) matrix (as confirmed by SEM and dynamic mechanical analysis (DMA) study). The prepared nanocomposites show enhanced thermal and mechanical properties.[106] Khalil et al. have prepared epoxy matrix-based composites using empty fruit bunch as the reinforcement.[107] In this study, lignin obtained from the black liquor was used as the curing agent in different ratios (15%, 20%, 25%, and 30%). It was found that polymer composites prepared using 25% lignin as the curing agent exhibit higher mechanical properties compared to the composites prepared using a commercial curing agent[107]

Lignin-Reinforced Biodegradable Polymer Matrix-Based Composites. Lignin-reinforced biodegradable polymer matrix-based composites have also been studied.[40,108−110] Biodegrad-able polymer matrix-based hybrid composites were developed by Sahoo et al. using polybutylene succinate (PBS) as the biodegradable polymer matrix and lignin as reinforcement.[111] Polymer composites were prepared using a melt mixing process employing an injection molding technique. In this study, the effects of both lignin and polymeric methylene diphenyl diisocyanate (PMDI) compatibilizer with different loadings on the properties of the pristine polymer were studied. Figure 5
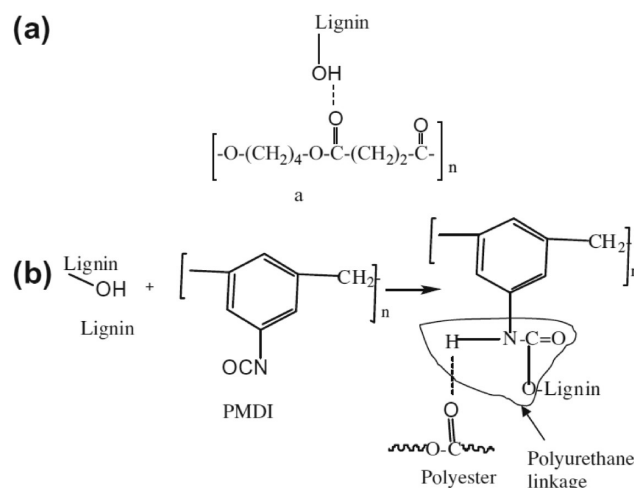

Figure 5. Schematics of the reaction between lignin, PBS, and PMDI. (a) Interaction between lignin and PBS through hydrogen bonding. (b) Polyurethane linkage formation. Reprinted with permission.[111] Copyright 2011 Elsevier.

shows the schematics of the possible interactions between the lignin, compatibilizer, and the matrix. Successful lignin loading up to 65% was achieved in this work. The polymer composites were subjected to the evaluation of their mechanical, thermal, dynamic mechanical, and morphological properties. Table 4 shows the different mechanical properties of the polymer composites. The mechanical properties results are the average values of five replications represented with error bars. Both the lignin content and compatibilizer were found to control the overall mechanical properties of the composites. In the case of thermal degradation behavior, degradation onset of the composites was found to gradually decrease with an increase in the amount of lignin. The enhancement in the mechanical properties were attributed to better interfacial interaction between the polymer matrix and the lignin and was confirmed by the SEM images of the fractured surface of the polymer composites with different loadings. The dynamic mechanical properties of the polymer composites (storage modulus, loss modulus, and tan delta) as a function of temperature were also studied. It was observed that storage modulus of the polymer and composites decreased with increasing temperature, and this behavior was attributed to the softening of the polymer as a result of the increase in the chain mobility of the polymer matrix at high temperatures. However, compared to pristine PBS, the storage modulus of the composites was found to be significantly enhanced at room temperature (25 °C) with lignin loading varying from 30−65 wt %.

PBS polymer matrix-based hybrid composites were also developed by the same research group in combination with switch grass.[112] The composites were prepared using an extrusion technique followed by injection molding. The composites were prepared using lignin and switch grass as

Table 4. Tensile, Flexural, HDT, and Impact Properties of Composites[a]

specimen label	tensile strength (MPa)	tensile modulus (GPa)	elongation At break (%)	flexural strength (MPa)	flexural modulus (GPa)	impact strength (J/M)	HDT (°C)
PBS	35 ± 1.5	0.6 ± 0.01	122 ± 21	28 ± 0.4	0.6 ± 0.01	40 ± 8.4	78 ± 1.9
30% lignin-PBS	26 ± 1.8	1.1 ± 0.03	4.6 ± 0.3	40 ± 0.5	1.1 ± 0.01	29 ± 1.0	83 ± 3.0
50% lignin-PBS	29 ± 3.4	2.3 ± 0.35	2.0 ± 0.8	46 ± 0.3	2.2 ± 0.0	15 ± 0.9	86 ± 3.1
65% lignin-PBS	39 ± 1.1	3.3 ± 0.04	1.5 ± 0.1	52 ± 1.1	3.8 ± 0.15	11 ± 0.9	85 ± 0.6
50% lignin-PBS-1% PMD	37 ± 6.1	2.0 ± 0.03	3.1 ± 1.3	68 ± 1.8	2.3 ± 0.07	29 ± 2.3	90 ± 1.9
50% lignin-PBS-2% PMDI	42 ± 4.7	1.9 ± 0.19	4.3 ± 0.7	66 ± 0.7	2.1 ± 0.03	24 ± 3.7	94 ± 1.6

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reinforcement, polymeric methylene diphenyl diisocyanate (PMDI) as compatibilizer, and poly(butylene succinate) (PBS) as the biodegradable polymer matrix. The effect of individual/hybrid loading was studied on different physicomechanical and thermal properties of the composites. It was concluded from the study that hybrid filler improves the properties of the resulting composites to a greater extent as compared to the individual filler. Furthermore, the PMDI used as compatibilizer positively affected the properties and improved the mechanical and thermomechanical properties to a significant extent.[112] Camargo et al. have reported their study on the biodegradable polymer matrix-based composites prepared using lignin as the reinforcement and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) as the matrix.[113] The lignin in this study was obtained from sugar cane bagasse and loaded up to 80 wt %. The composites were then characterized in terms of their morphological, thermal, and mechanical properties. It was confirmed from the images that no physical contact exists between filler and matrix. On the other hand, the residual mass of the composites was found to increase with an increase in the amount of lignin, and crystallinity remains unaffected with the incorporation of lignin. It was also observed that higher temperatures were necessary to promote PHBV crystallization in the presence of lignin. Tables 5(a) and 5(b)) show the mechanical properties of the different

Table 5(a). Average results of the Tensile Stress vs Strain Test for Extruded and Not Extruded PHBV and the 50:50 (w/w) Lignin/PHBV Composites[113]

samples	maximum tensile stress (MPa)	elongation at break (%)	Young's modulus (MPa)	tensile stress at break (MPa)
PHBV (not extruded)	23.4 ± 0.6	5.5 ± 0.4	853.3 ± 42.3	23.1 ± 0.7
PHBV (extruded)	24.1 ± 0.7	5.1 ± 0.4	900.4 ± 47.3	24.0 ± 0.7
50:50 (w/w) lignin/PHBV	7.6 ± 0.8	2.1 ± 0.2	753.7 ± 61.7	7.6 ± 0.7

Table 5(b). Average Results of the Flexural Stress vs Strain Test for Extruded and Not Extruded PHBV and the 50:50 (w/w) Lignin/PHBV Composites[113]

samples	maximum flexural stress (MPa)	flexural modulus (MPa)
PHBV (not extruded)	30.1 ± 1.8	1779.0 ± 101
PHBV (extruded)	35.0 ± 1.4	2107.0 ± 100
50:50 (w/w) lignin/PHBV	15.2 ± 2.0	2344.0 ± 169

processes polymers/composites. It had been found that the incorporation of lignin negatively affected the mechanical properties of the resulting composites. The decrease in mechanical properties was attributed to the noninteraction between lignin and PHBV. Thus, the absence of physical contact between filler and polymeric matrix prevented the stress transfer in the filler/matrix interface resulting in lowering the mechanical properties. Çalgeris et al. have also prepared lignin reinforced starch-based biocomposites.[114] Lignin was extracted from hazelnut shells and used as a potential additive in different ratios in the preparation of starch composites biofilms. Prior to use, lignin was characterized using UV spectroscopy and Fourier transform infrared (FTIR) spectroscopy. It was observed that the lignin content in the starch-based films improves the mechanical and thermal properties to a considerable extent depending upon the loading. Furthermore, the drug release mechanism of starch/lignin biofilms was also studied, and it was concluded that these films have potential to be used in a number of fields such as in coatings, food packaging, and drug delivery systems.[114] Spiridon et al. have also reported their study on the preparation of lignin-reinforced starch-based composites.[115] In this study, glycerol-plasticized corn starch (GCS) prepared using a casting process was used as the polymer matrix, while adipic acid (AA)-modified starch microparticles (AASM) were used as the reinforcing materials. Subsequently, the effect of two different types of lignin on the morphology, mechanical, thermal, and surface properties, along with water sorption, was investigated. It was observed that the thermal stability and surface water resistance of the composite materials was significantly improved through the addition of lignin.[115]

Lignin as Reinforcement in Foam-Based Composites. Lignin has been reported to be used as potential reinforcement in foam-based polymer composites. Saz-Orozco et al. have prepared lignin-reinforced phenolic foams.[116] Different formulations of the phenolic foams prepared using unreinforced and lignin nanoparticle-reinforced foams were optimized using an analysis of the variance approach. It was observed that the incorporation of nanolignin significantly improved the mechanical properties of the foams. As an example, the compressive modulus and compressive strength were found to increase up to 128% and 174%, respectively, compared to the unreinforced foams. Furthermore, during the preparation of these foams, the amount of blowing agent was also found to be saved (up to 31% of the amount necessary to produce an unreinforced foam having the same density).[116] Water-blown rigid biofoam-based composites from soy oil-based polyurethane were also prepared using lignin as reinforcement.[117] The lignin in this study was procured from bioethanol production, while biofoam (BioPU) was prepared from two polyols

(soybean oil-derived polyol SOPEP and petrochemical polyol Jeffol A-630) and poly(diphenylmethane diisocyanate) (pMDI). Subsequently the BioPU samples were reinforced with lignin and evaluated for different properties such as morphological, mechanical, thermal, and density. The biofoam composites were prepared using lignin concentrations of 0%, 5%, 10%, and 15% (w/w), with respect to the total polyol mass. Figure 6 shows the SEM images of the neat and biofoam
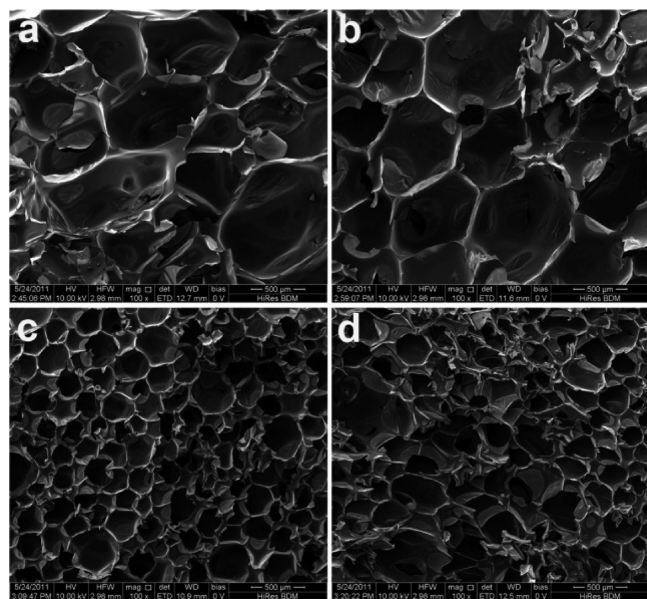

Figure 6. SEM images of neat biofoam and biofoam composites (100×; scale bar, 1 mm): (a) BioPULignin0, (b) BioPULignin5, (c) BioPULignin10, and (d) BioPUlignin15. Reprinted with permission.[117] Copyright 2013 Elsevier.

composites. As evident from the images, with the addition of lignin, the overall cell structure became more uniform. In biofoam composites, the density is an imperative parameter that affects the mechanical and thermal properties of foams. Table 6(a) shows the density and cell size of the neat foam and foam composites. For each data point, five neat/composite foam specimens were tested, and average values with the standard deviation were reported.[117] Densities of the resultant composites had been found to increase with an increase in the amount of lignin. Table 6(b) shows the different mechanical properties of the foam.[117] With variation in lignin content from 5% to 10 wt %, the mechanical properties were found to increase, and there was a decrease for samples with 15 wt % of lignin content. This behavior was attributed to the lignin—polyurethane interactions that determine the incorporation of urethane—urethane- and ester—urethane-ordered structures. With the addition of excess lignin (15%), the urethane structures could not crystallize, and the mechanical properties decreased. The dynamic mechanical properties were

also analyzed using a thermal analysis technique. The increase in the storage modulus of the rigid BioPU foam composites was attributed to the high mechanical modulus of lignin and cross-linking introduced by lignin in the foam. Thermal stability of the BioPU/BioPU composites was also studied using thermogravimetric analysis (TGA) under a nitrogen atmosphere. From the thermogravimetric study of the prepared pristine biofoam/composites, it was observed that the lignin improves improve the thermal stability of the composites. Water absorbent polyurethane (PU) rigid composite foams were also prepared using polyurethane and lignin filled with microcrystalline cellulose (MCC).[118] The polyurethanes in this work were prepared using polyols derived from molasses, and lignin filled with MCC was used in different particle sizes. Different water absorption and mechanical properties were also studied. Starch-based foams have also been prepared by Stevens et al. using lignin as one of the essential components.[119] In their study, replacement of 20% of the starch with lignin produced no deleterious effects on density or morphology of the foams. The addition of lignin was found to stabilize the residual starch structure resulting in a decrease in water absorption diffusion constants for the starch and starch—lignin foams. Furthermore the flexural strength of the starch—lignin foam was found to be similar to that of foamed polystyrene.[119]

Lignin Modification for Composites Applications. Lignin is used for application in polymer composites as a reinforcement. However, for some applications, it is often difficult to blend lignin with other systems such as biopolymers. Some researchers have made efforts to modify lignin with different techniques in order to make it compatible with the polymer matrices.[120−123] Researchers from Stanford University have recently reported their study on the modification of lignin via a catalytic and solvent-free method.[124] In this study, lignin was modified using a graft copolymerization reaction by graft polymerization of lactide onto lignin, and the reaction was catalyzed by triazabicyclodecene (TBD). The chain length of the polylactic acid (PLA) in the lignin-g-poly(lactic acid) copolymer was controlled by varying the lignin/lactide ratio and preacetylation treatment. Polymer composites were subsequently prepared using the raw/modified lignin and were subjected to mechanical/optical studies. It was observed that the incorporation of lignin-g-PLA copolymers resulted in a modest increase in the tensile strength (+16%) and strain (+9%) without a sacrifice in the tensile modulus.[124]

In order to reuse lignin, lignophenol (LP) was graft copolymerized with poly(2-ethyl-2-oxazoline) (POZO) and used in the preparation of polymer blends with poly(vinyl chloride) (PVC), poly(bisphenol A carbonate) (PC), polyvinylpyrrolidone (PVP), and polystyrene (PSt) as commodity polymers.[125] Compared to the pristine lignin, the grafted lignin was found to be soluble in common organic solvents such as chloroform, acetone, tetrahydrofuran (THF), and methanol. The miscibility of LP-graft-POZO with commodity polymers was confirmed by differential scanning calorimetry (DSC).[125]

Table 6(a). Density and Cell Size of Neat Biofoam and Biofoam Composites[a]

sample	BioPULignin0	BioPULignin5	BioPUlignin10	BioPUlignin15
lignin content (wt %)	0	5	10	15
density (g/cm³)	0.062 ± 0.007	0.065 ± 0.001	0.076 ± 0.008	0.086 ± 0.011
cell size (μm)	587.3 ± 115.5	513.5 ± 119.9	270.2 ± 56.3	298.8 ± 57.5

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Table 6(b). Mechanical Properties of Neat Biofoam and Biofoam Composites[a]

sample	compressive strength (MPa)	compressive modulus (MPa)	flexural strength (MPa)	flexural modulus (MPa)	impact strength (J/M)
BioPULignin0	0.39 ± 0.05	6.76 ± 0.88	0.54 ± 0.12	12.14 ± 4.09	1.33 ± 0.02
BioPULignin5	0.40 ± 0.04	9.19 ± 1.94	0.74 ± 0.12	21.12 ± 5.42	1.29 ± 0.03
BioPULignin10	0.46 ± 0.02	11.66 ± 1.38	0.87 ± 0.17	26.97 ± 5.0	1.28 ± 0.05
BioPULignin15	0.32 ± 0.02	9.19 ± 1.99	0.67 ± 0.07	19.70 ± 1.32	1.32 ± 0.05

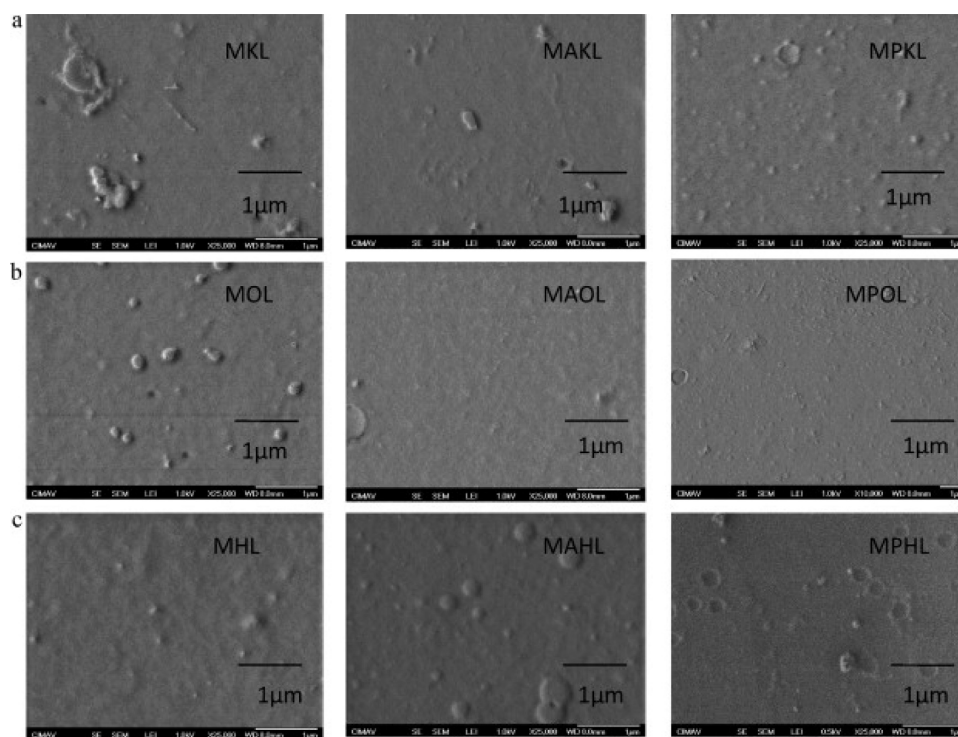[a]Reprinted with permission. Copyright 2013 Elsevier.

Figure 7. FE-SEM micrographs of nanocomposites membranes (M) based on cellulose triacetate and 1 wt % of propionated lignin (PKL, POL, or PHL) and prepared at 35 °C and 70% relative humidity. Reprinted with permission.[126] Copyright 2011 Elsevier.

Biopolymers-based nanocomposites membranes for water purification applications have also been prepared by Nevarez et al. using propionated lignin and cellulose triacetate (CTA).[126] In the preparation of nanocomposite membranes, three kinds of lignin, namely, kraft (KL), organosolv (OL), and hydrolytic (HL), were used. In order to make these different lignins compatible with CTA, these were modified using propionation reaction. The nanocomposites were then characterized for different mechanical properties (DMA), and the interaction between the membranes was further confirmed by morphology (through FE-SEM and atomic force microscopy). It was observed that among all the nanocomposite membranes, the propionated kraft lignin-reinforced membrane showed the highest Young's modulus as well as tensile strength. Elongation at break decreased, as expected. Figure 7 shows the SEM images of the polymer nanocomposites membranes. The strong interaction between the modified lignin-based membranes was confirmed by the different images. For all membranes obtained, the homogeneity was clearly improved in the presence of chemically modified lignin as the modified lignin groups improved their incorporation into the matrix due to a correspondingly higher solubility. Surface roughness of the nanocomposite membranes was also studied using atomic force microscopy (AFM) (Figure 8). It was obvious from the images that significant smoothing occurred in the nanocomposite

membranes after esterification. In order to make the lignin compatible with polypropylene, Maldhure et al. have modified lignin using esterification and alkylation techniques.[127] The influence of these modifications was also studied on the mechanical properties followed by a processing study. The polymer blends were prepared using polypropylene as the matrix and different types of unmodified and modified lignin as the reinforcement. The reinforcement was used in terms of different loadings, and the maximum loading applied was 25 wt %. The mechanical properties such as tensile strength, elongation at break, Young's modulus, and impact strength were found to be significantly affected when modified lignin was used as the reinforcement compared to blends arising out of unmodified lignin. It was observed that a polymer blend with a loading ranging up to 10 wt % of modified lignin exhibits better properties compared to those with higher proportions. However, among the two modification techniques for modified lignins, lignin modified (esterified) with maleic anhydride was found to exhibit better properties as compared to the lignin modified with alkylation.[127] Rosin polymer-grafted lignin composites were also prepared by Wang et al. via "grafting from" the atom transfer radical polymerization (ATRP) technique.[128] For carrying out the polymerization, 2-bromoisobutyryl ester-modified lignin was used as the macroinitiator. The grafted polymers were prepared by two different
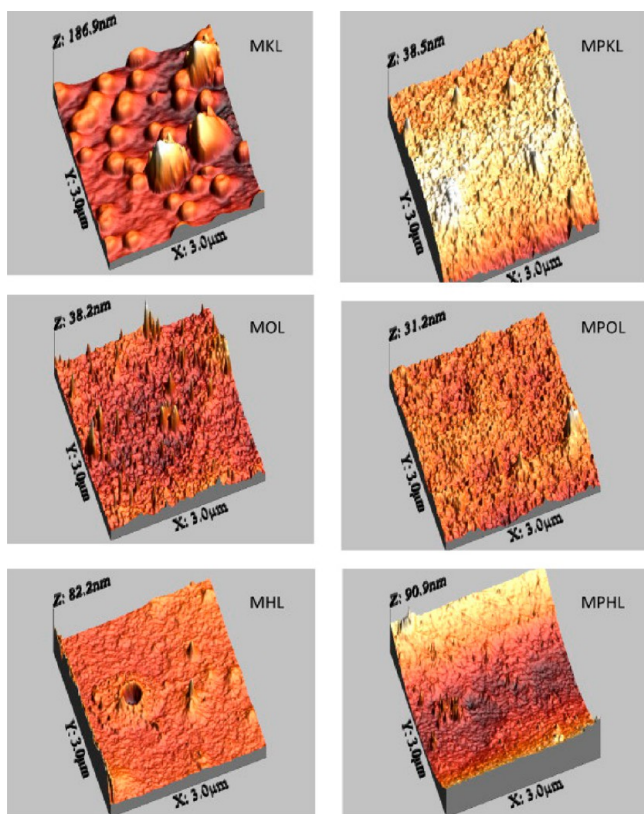
Figure 8. Topographic images obtained by AFM for raw and propionated lignin nanocomposites. Reprinted with permission.[126] Copyright 2011 Elsevier.

techniques. The first technique involved the molecular attachment of dehydroabietic ester onto lignin (lignin-g-DA) through an esterification reaction that was carried out between lignin and DA. The second technique involved grafting from ATRP of a series of rosin-derived (meth) acrylates from lignin macroinitiators. The controlled and "living" polymerizations reactions were confirmed by kinetic studies. From the different experiments, it was revealed that the incorporation of rosin moiety (dehydroabietic group) into lignin increased the hydrophobicity of the rosin−lignin composites.[128] Sailaja and Deepthi have also modified lignin using phthalic anhydride and prepared polymer composites with different loadings (up to 40 wt %) of raw and unmodified lignin using low density polyethylene (LDPE) as the matrix material.[129] The modification of lignin was confirmed by different techniques. The peak at 1710 cm^{-1} successfully confirmed the esterification of lignin. In this study, maleic anhydride-grafted LDPE was also used as a compatibilizer to enhance the mechanical properties of the composites. Different mechanical and thermal properties of the resulting polymer blends were then studied. The maleic anhydride-grafted LDPE facilitated the enhancement in the mechanical properties due to improved adhesion between the polymer matrix and esterified lignin. The strong interfacial bonding between the matrix and the modified lignin was further confirmed by the blend morphology that showed a highly deformed surface. The SEM images demonstrated the good interfacial adhesion and resistance to the removal of modified lignin from the blend. Lignin obtained from rice husk using the acidolytic (AL) or alkaline enzymatic extraction (AEL) methods was modified by acetylation using acetic anhydride.[44] It was then used to prepare the poly(3-hydroxybutyrate)

(PHB) matrix-based composites. After successful acetylation, biocomposites were prepared usingthe solvent-casting method employing chloroform solution with 15 wt % loading of pristine/modified lignin. These polymer composites samples were extensively studied using morphological, structural, and thermal characterizations. Acetylated AL lignin was found to demonstrate higher thermal stability and was used for further preparation of the composites with different loading. It was observed that the AL sample has a strong interference on the crystallization behavior and thermo-oxidative degradation of the PHB. The PHB-AL biocomposite demonstrated enhanced thermal stability as a function of the lignin amount in the PHB-AL biocomposite series. On the other hand, it also caused a decrease in the overall crystallization rate and the spherulite radial growth of the PHB.[44] Teramoto et al. have carried out the acetylation of organosolv lignin (OSL) to prepare miscible blends with different polymers such as poly(vinyl acetate) (PVAc), poly(N-vinyl pyrrolidone) (PVP), and poly(N-vinyl pyrrolidone-co-vinyl acetate) (P (VP-co-VAc)).[130] The blends of the pristine or modified lignin were prepared using a solvent casting method using N,N-dimethylformamide as a good solvent. Miscibility of the blends was confirmed by differential scanning calorimetry and Fourier transform infrared spectra measurements. It was found that acetylated organosolv lignin was miscible with all the polymers, while pristine lignin showed no interaction.[130] Soda lignin has also been modified by Yue et al. to be used in the improvement of interfacial binding between the PVC (poly vinyl chloride) and wood flour composites.[131] The modification of lignin was carried out using the Mannich reaction to prepare lignin amine. The synthesized lignin amine was then used to modify the wood flour, and subsequently, polymer composites were prepared using the pristine wood flour and wood flour modified with the lignin amine. The polymer composites prepared using lignin amine were found to exhibit properties comparable to the traditional silane treatment-prepared composites.[131] Semi-interpenetrating polymer networks (semi-IPNs) were also prepared using ammonium lignosulfonate (ALS) with vinyl ester resin (VER).[132] These IPNs were characterized using Fourier transform infrared (FT-IR) spectroscopy, optical microscopy (OM), and differential scanning calorimetry (DSC) techniques. Figure 9(a) and (b) show the schematics for the preparation of VER and VER-ALS semi-IPNs formulations, respectively. From all the characterizations carried out, it was clear that the synthesized networks revealed decent compatibility due to possible interactions between the functional groups from VER and ALS components, respectively. Yu et al. have modified lignin through grafting with flame retardant polymers to improve the thermal stability and flame retardancy.[133] In this work, modification was carried out on alkali lignin by chemical grafting of flame retardant elements, phosphorus and nitrogen, via a three-step reaction, and the grafted lignin was further used for the preparation of polypropylene matrix-based composites. Figure 10 shows the schematic for the functionalization of lignin.[133] Thermal stability of functionalized lignin was found to be much higher than the pristine one as well as for the PP composite prepared with modified lignin. It was observed that compared to pristine lignin, the modified lignin (PN-lignin) exhibits a higher char-forming ability with a char of 61.4 wt % (40.7 wt % for lignin) at 600 °C in N$_2$. In PP composites also, PN-lignin was found to induce a much higher thermal stability and amount of char residue on polypropylene relative to lignin. Flame retardancy of the composites was further conformed by
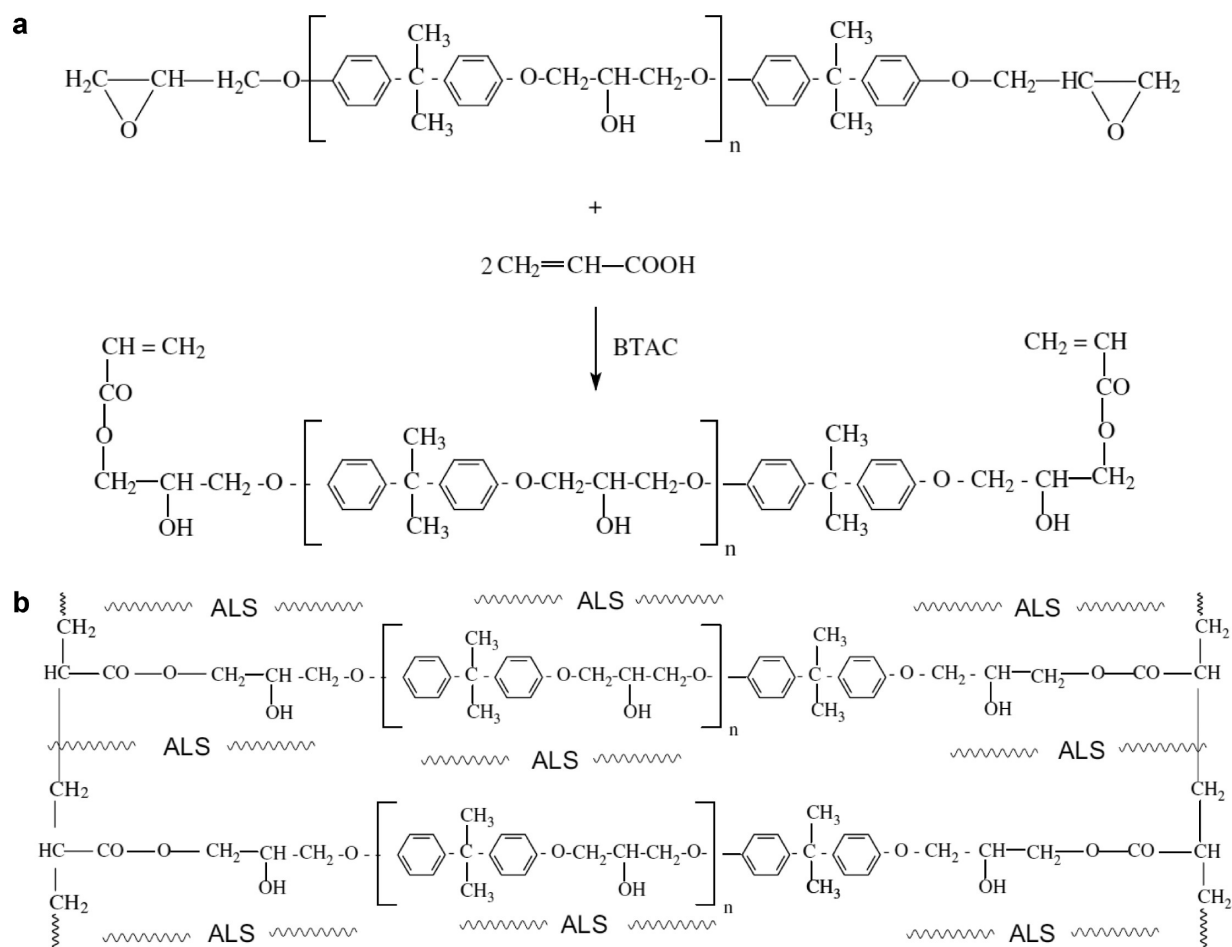
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dx.doi.org/10.1021/sc500087z | ACS Sustainable Chem. Eng. 2014, 2, 1072−1092

Figure 9. (a) Synthesis of VER. Reprinted with permission.[132] Copyright 2009 Elsevier. (b) VER-ALS semi-IPNs formulation. Reprinted with permission.[132] Copyright 2009 Elsevier.
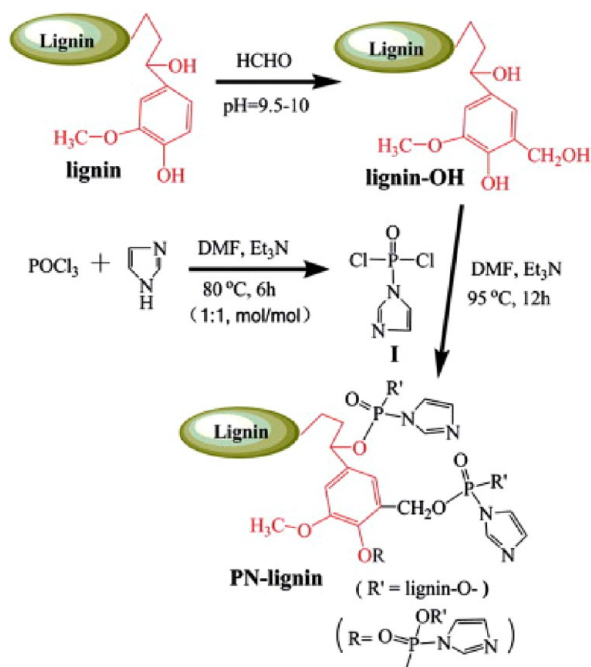

Figure 10. Illustration of the typical synthetic route to the functionalized lignin, namely, PN-lignin. Reprinted with permission.[133] Copyright 2012 Elsevier.

the cone calorimeter tests (Figure 11). It is evident from the figure, that PN-lignin significantly reduced the heat release rate and slows the combustion process, confirming flame retardancy. These results were further supported by the SEM analysis (Figure 12). It was concluded from the study that the continuous and intact char layer was the prime contributor in improving flame retardancy. These authors have also studied the effect of incorporation of nickel (cobalt or zinc) acetates on the thermal and flammability properties of PP/PN-lignin systems.[134] Figure 13 shows the possible reaction mechanisms for char forming during combustion of PP/PN-lignin/metal acetates systems. It was observed that in the case of thermogravimetric analysis, addition of 2 wt % nickel acetate (Ni (Ac)$_2$) catalytically degrades PP/PN-lignin but significantly increased the char residues in different thermal conditions (N$_2$ and air). On the other hand, the addition of cobalt and zinc salts have a slight effect on the thermal stability. The nickel acetate was also found to considerably increase the char residue due to its strong catalytic carbonization action on PP and functionalized lignin; thus contributing to the improved flame retardancy.[134] Compared to the nickel acetate-based composites, cobalt (and/or zinc) acetate displayed no obvious effects on the flame retardancy. Depending upon the extensive thermal and morphological characterizations, a possible char-forming mechanism for the PN-lignin/Ni (Ac)$_2$ system was proposed (Figure 13).
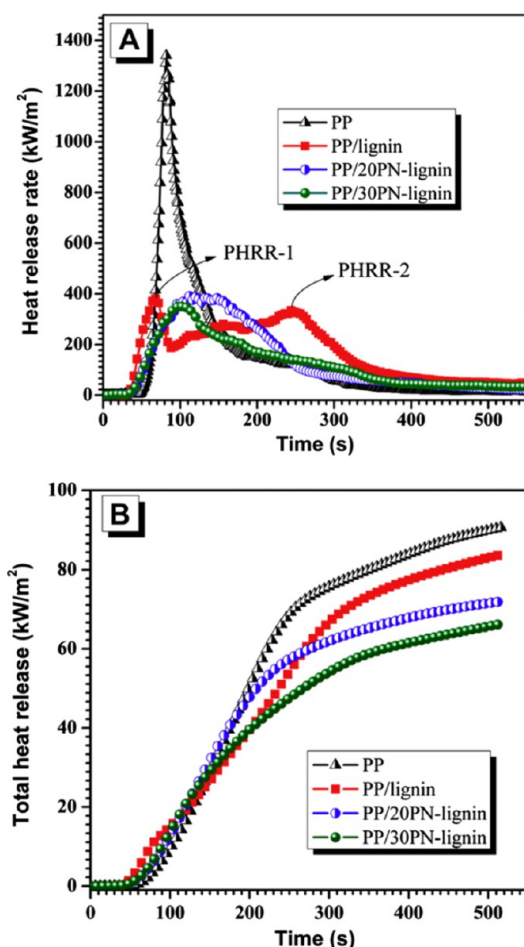
Figure 11. (A) Heat release rate and (B) total heat release curves of PP and its composites at a heat flux of 35 kW/m2. Reprinted with permission.[133] Copyright 2012 Elsevier.
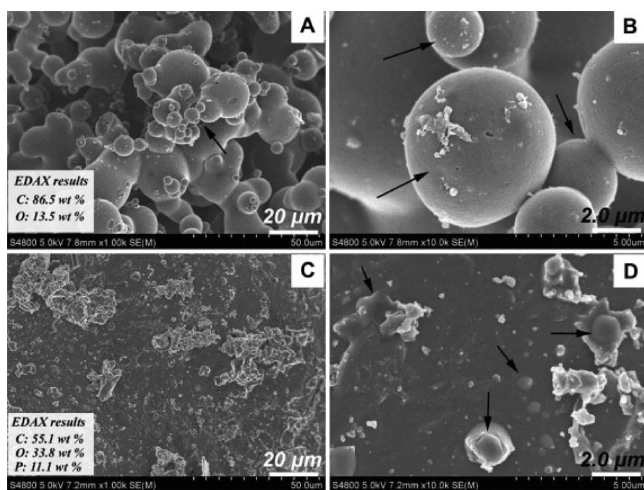

Figure 12. SEM images of the residue char (A, B) from PP/lignin and (C, D) from PP/30PN-lignin after cone calorimeter measurements. Reprinted with permission.[133] Copyright 2012 Elsevier.

Lignin as Compatibilizer in Polymer Composites. In addition to its use as reinforcement and a coupling agent, the use of lignin has also been explored as a compatibilizer in polymer composites.[135−138] Thielemans and Wool have used butyrated kraft lignin as the compatibilizing agent in the
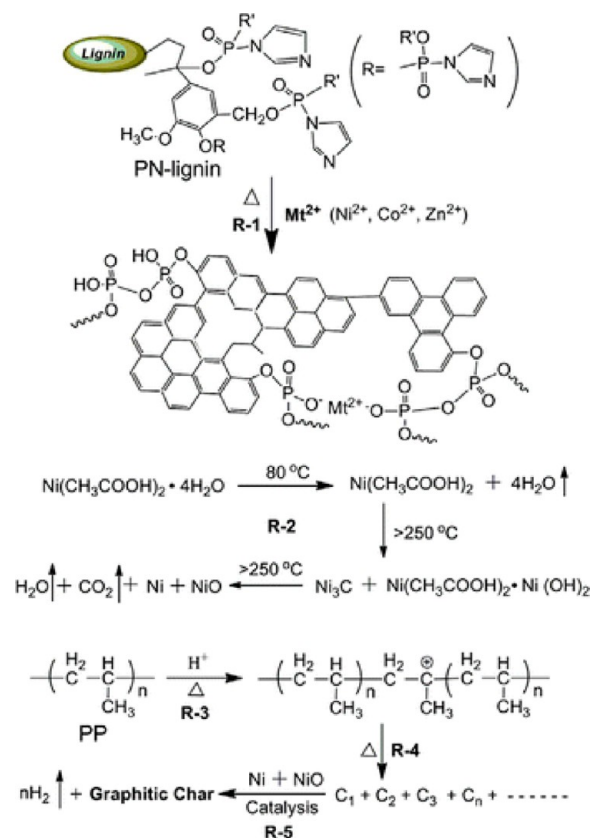

Figure 13. Possible reaction mechanisms for char forming during combustion of PP/PN-lignin/metals acetates systems. Reprinted with permission.[134] Copyright 2012 American Chemical Society.

unsaturated thermosetting resin (used as the matrix).[135] The polymer resin was prepared using a mixture of acrylated epoxidized soybean oil and styrene. In the preparation of the composites, flax fibers were used as the reinforcement. The vacuum assisted transfer molding (VARTM) process was used to prepare the composites with varying amounts of butyrated kraft lignin that was dissolved in the unsaturated resin system. It was observed from the experimental study that the butyrated kraft lignin improved the interface between the resin and reinforcing flax fibers.[135] Wood et al. have also reported their study on the addition of lignin as a compatibilizer in hemp-reinforced epoxy composites.[139] Polymer composites with varying loading of lignin (0−10%) were prepared using the vacuum-assisted resin transfer molding (VARTM) process. The mechanical properties were found to be significantly improved with the amount of lignin in the polymer. It was observed that these properties varied upon the lignin content in the composites. As an example, tensile and flexural properties decreased after certain loading, and this behavior was attributed to the prevention of complete resin infusion across the hemp mat by lignin particles that reduces the physical properties.[139] Tay et al. have also used chemically treated lignin (Alcell lignin) as a compatibilizer to prepare polypropylene−oil palm empty fruit bunch (PP-EFB) composites.[140,141] The Alcell lignin was initially modified by glycidyl methacrylate (GMA) and allyl glycidyl ether (AGE) using different ratios (1:1, 1:2, and 1:3) based on equivalent weight. Subsequently, after modification, it was used as a compatibilizer in different loadings (1%, 3%, and 5%, based on the weight of EFB filler) for the preparation of oil palm empty fruit thermoplastic composites.[141] During the

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dx.doi.org/10.1021/sc500087z | ACS Sustainable Chem. Eng. 2014, 2, 1072−1092

Table 7(a). Mechanical Properties of Composites[a]

samples	tensile strength (MPa)	tensile modulus (GPa)	energy at break (J)	flexural strength (MPa)	flexural modulus (GPa)	impact strength (kJ/m2)
EPAC	20.85	1.37	0.52	59.55	2.75	18.54
EP-L15	8.56	0.18	0.27	19.29	0.28	4.41
EP-L20	10.36	0.38	0.25	36.00	0.92	7.21
EP-L25	13.60	0.45	1.21	74.09	3.02	12.77
EP-L30	9.95	0.62	0.50	49.32	2.85	6.94

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preparation of the composites, an EFB filler with dimensions of 53−180 mm was used, while the ratio of PP to EFB filler was fixed at 40%:60% (wt %). The prepared composites were subjected to the study of mechanical and water absorption behavior analysis. From the experimental results, it was evident that modified lignin (GMA/AGE-treated lignin) exhibits enhanced mechanical properties and increased hydrophobicity. The enhanced properties were attributed to the strong interfacial attraction between the different components. Among the two modified lignins, GMA-treated lignin exhibited enhanced mechanical properties compared to those with AGE-treated lignin.[141] Lignin was also modified using phenolization followed by a quaternizing reagent (monomeric quaternary ammonium salt) to make it compatible with poly(vinyl alcohol) (PVA) to prepare composites for absorbent applications.[142] During the preparation of the composites, glutaraldehyde was also used as a cross-linker. The absorbent was characterized using FTIR, DSC, SEM, BET, DMA, and mechanical studies. The composite absorbent prepared using modified lignin exhibited a remarkable network structure with large numbers of connected holes. The mechanical strength of the absorbent was also significantly enhanced by using modified lignin and cross-linkage of glutaraldehyde. The composite absorbents with modified lignin also exhibit effectiveness in the removal of nitrate from aqueous solutions demonstrating that modified lignin has great potential in the fabrication of new composite absorbents from economical and efficiency point of views.[142] Khalil et al. have explored the use of lignin as a curing agent in the preparation of green epoxy composites.[143] Lignin was procured from oil palm biomass empty fruit bunch (EFB) fibers. Subsequently epoxy−lignin polymer composites were prepared with varying lignin content (15%, 20%, 25%, and 30%) using EFB fiber as reinforcement. The effect of lignin on the mechanical, thermal, and morphology properties of the epoxy composites was studied in detail and compared with the composites cured using an isophorone diamine curing agent.[143] Tables 7(a) and 7(b) summarize the different mechanical and thermal properties of EFB/epoxy−lignin green composites with various lignin contents (15%, 20%, 25%, and 30%) used as hardener along with amine-cured EFB/epoxy composites. The mechanical properties of the epoxy composites were found to be strongly influenced by adhesion between the polymer matrix and fibers. The tensile properties of the EFB/epoxy−lignin composites were found to increase with an increase in lignin content, with a slight decrease in tensile strength at 30% lignin content. The SEM micrographs of the fractured surface of the composites also provided an insight into the bonding interaction between the constituent of the polymer composites and showed regions with good adhesion at the interface. The improved thermal stability of the polymer composites was attributed to good fiber−matrix interaction, induced by the curing agent (lignin). The epoxy composites cured with 25% lignin content had been found to exhibit optimum interfacial

Table 7(b). Thermal Properties of the Different Composites Studied[a]

composite samples	degradation temperatures (°C)				DTG peak temperatures (°C)		
	T_{on}	$T_{10\%}$	$T_{50\%}$	residual weight at 800 °C	T_{1max}	T_{2max}	T_{3max}
EFB fiber	253	271	364	13.7	317	379	−
EFB-lignin	253	264	429	33.0	308	393	−
EPA	253	267	353	4.61	332	464	−
EPAC	152	266	389	10.0	328	384	−
EP-L15	239	266	346	21.7	272	301	384
EP-L2	257	284	364	20.0	295	331	397
EP-L25	266	284	363	16.7	301	341	394
EP-L30	248	275	354	16.5	295	331	386

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interaction compared to other formulations. The results suggested that these composites have high potential to be used in load bearing applications.

Excellent physicochemical and mechanical properties of lignin have resulted in its potential use in a number of applications from automotive to energy storage.[144−146] Milczarek and Nowicki have recently explored the use of kraft lignin in the surface functionalization of multi-walled carbon nanotubes (CNTs) for energy storage applications.[147] The surface functionalization of MWCNT was confirmed by X-ray photoelectron spectroscopy (XPS), FT-IR spectroscopy, and AFM analysis. Figure 14 shows the AFM images of the functionalized CNT.[147] All the characterization techniques successfully demonstrated the functionalization of CNT by kraft lignin, especially XPS and FTIR studies showed an increase in oxygen content and the appearance of spectral features characteristic of highly oxidized polyphenolic compounds with the attachment of kraft lignin on the MWCNT. The KL-functionalized CNTs were found to be easily dispersible in organic (DMSO) and aqueous (0.1 M ammonia) solutions. The functionalized CNT were easily deposited on the surface of a gold electrode and were electrochemically characterized. The results suggested that the reversible redox activity of the lignin adsorbate can be efficiently utilized for charge storage. Figure 15 shows the galvanostatic charging/discharging experiments carried out to explore the potential of the modified CNT in energy storage. It had been observed that there was more than a 100% increase in the capacitance of KL-modified carbon nanotubes compared with unmodified ones. Convincing evidence for a dense KL wrapping onto CNTs had been obtained from spectroscopic studies and AFM imaging.[147]

■ CONCLUSIONS AND FUTURE PERSPECTIVES

Biorenewable materials have been frequently used as low cost reinforcement for polymer composite applications. The
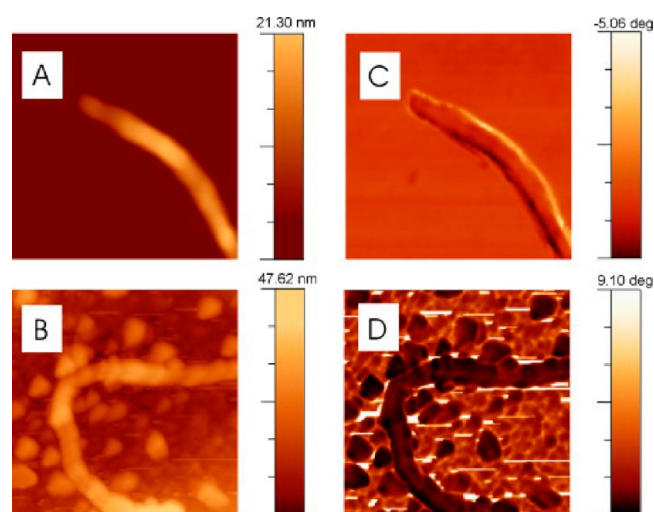
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Figure 14. AFM images of individual unmodified carbon nanotubes (A) and (C) and KL-functionalized carbon nanotubes (B) and (D). Images (A) and (B) are topographic, and images (C) and (D) are phase contrast. Image size −0.6 μm × 0.6 μm in all cases. Reprinted with permission.[147] Copyright 2013 Elsevier.

polymer composites designed for different applications are mostly based on natural cellulosic fibers. Along with these cellulosic fibers, lignin is a promising alternative to traditional

petrochemical-based reinforcement. Lignin along with cellulose and hemicellulose is one of the major components of natural polymers that provide strength and rigidity to plant stems. Lignin is the most abundant byproduct of the paper industry as well as the second most abundant natural polymer on earth next to cellulose. Industrially, lignin usually plays a negative role and is considered a waste material because it is produced during the processes aimed at retrieving the polysaccharide component of plants for use in industrial applications. Several problems lie in the disposal of lignin, which is produced in huge amounts in several paper or other industries. Recently, researchers have started exploring the use of lignin as potential reinforcement in polymer composites. The inherent properties of lignin being biodegradable, CO_2 neutral, available abundantly in industrial waste, low in cost, and environmentally friendly, and having antioxidant, antimicrobial, and stabilizer properties make lignin a promising low cost reinforcement. Due to the above-stated advantages, lignin-based polymer composites are promising as a new class of environmentally friendly, low cost, composite materials. There has not been much literature on lignin-reinforced polymer composites as the research on lignin-based polymer composites is still in its infancy. On the basis of the existing literature, the applications of lignin-reinforced polymer composites are highly plausible as alternatives to traditional synthetic fiber-reinforced composites. Indeed, lignin-based polymer composites display a bright future for the numerous reasons highlighted in the previous discussion. Although lignin
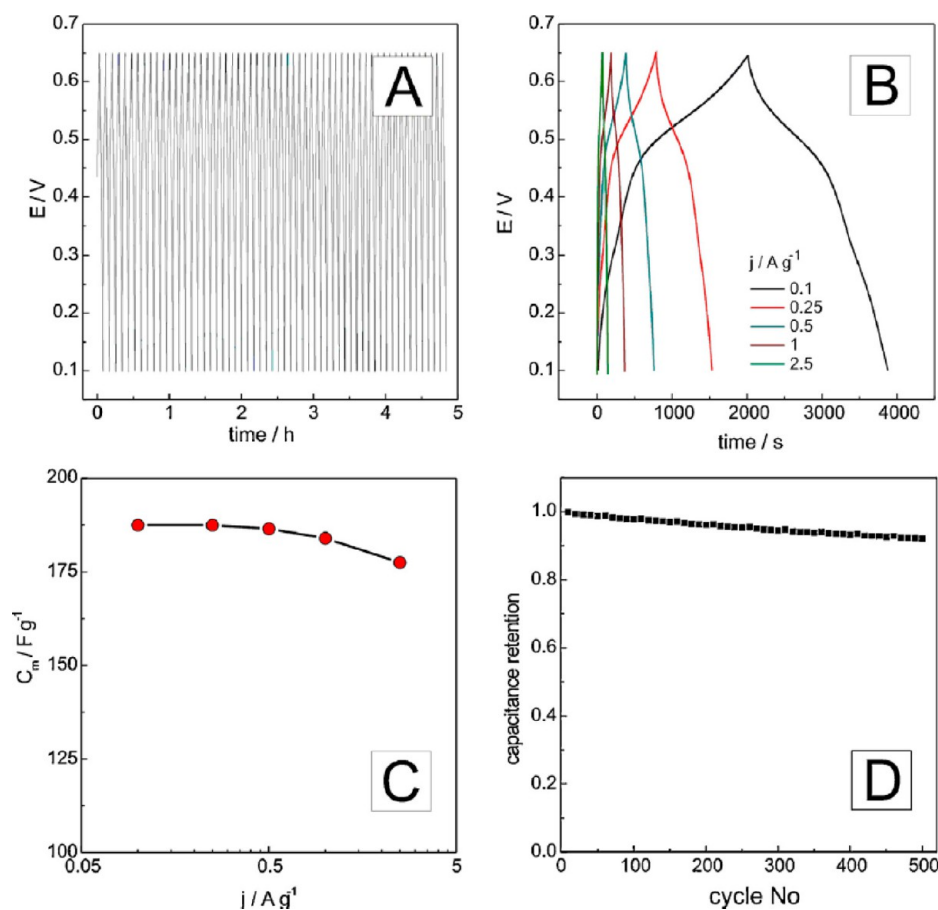

Figure 15. Charge storage properties of the CNT/KL composite: (A) multiple charging/discharging at current density of 1 A g^{-1}, (B) galvanostatic charge and discharge curves at various current densities, (C) dependence of mass-specific capacitance on the current density, and (D) capacitance retention vs cycle number for charging/discharging at 1 A g^{-1}. The electrolyte was 0.5 M H_2SO_4.[147] Copyright 2013 Elsevier.

offers a number of benefits over other presently available reinforcements, the vastly variable and complex nature of lignin limits its successful applications. Due to these hindrances, so far limited success has been achieved in moving lignin utilization from a laboratory scale to an industrial scale. From a technological point of view, some hindrance in the use of lignin as reinforcement, especially the incompatibility with polymer matrices and other factors, should be taken into account. Considerable efforts should be devoted to the surface modification of lignins through suitable techniques to make it compatible with other polymer matrices/materials. Graft copolymerization is one of the techniques that may be used to alter the surface characteristics of the lignin to make it compatible for the targeted applications. In addition to this, considerable attention should be given to the development of a better understanding of the physics and chemistry of the lignin molecule. The structural aspects, physicochemical and mechanical properties of lignin/different polymers matrices, and recent development in polymer composites as discussed in this article might be used for the commercialization of lignin-based, low cost, environmental friendly materials for numerous applications.

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■ ACKNOWLEDGMENTS

■ ABBREVIATIONS

UV, ultraviolet; T_g, glass transition temperature; OMT, O-methyl transferase; CAD, cinnamyl alcohol dehydrogenase; PS, polystyrene; SEBS, styrene, ethylene, and butylene; GC, gas chromatography; SEM, scanning electron microscopy; PDMS, polydimethylsiloxane-α, ω-diol; PET, poly(ethylene terephthalate); L, lignin; POM, polarizing optical microscopy; WAXD, wide-angle X-ray diffraction; PP, polypropylene; PAN, polyacrylonitrile; PVC, polyvinylchloride; PVA, polyvinyl alcohol; PEO, poly(ethylene oxide); PF, phenol formaldehyde; MBO, methacrylated lignin-based bio-oil mimic; SBR, styrene-butadiene rubber; LDH, layered double hydroxide; PDAD-MAC, polydiallyldimethylammonium chloride; DLS, dynamic light scattering; TEM, transmission electron microscopy; FTIR,

Fourier transform infrared spectroscopy; UV–vis, ultraviolet–visible; NR, natural rubber; DMA, dynamic mechanical analysis; PBS, polybutylene succinate; PMDI, polymeric methylene diphenyl diisocyanate; PHBV, poly(3-hydroxybutyrate-co-3-hydroxyvalerate); GCS, glycerol plasticized-corn starch; AA, adipic acid; SM, starch microparticles; PU, polyurethane; TGA, thermogravimetric analysis; MCC, microcrystalline cellulose; TBD, triazabicyclodecene; PLA, polylactic acid; LP, lignophenol; POZO, poly(2-ethyl-2-oxazoline); PC, poly(bisphenol A carbonate); PVP, polyvinylpyrrolidone; THF, tetrahydrofuran; DSC, differential scanning calorimetry; CTA, cellulose triacetate; KL, kraft lignin; OL, organosolv lignin; HL, hydrolytic lignin; AFM, atomic force microscopy; ATRP, atom transfer radical polymerization; LDPE, low density polyethylene; PHB, poly(3-hydroxybutyrate); PVAc, poly(vinyl acetate); P(VP-co-VAc, poly(N-vinyl pyrrolidone-co-vinyl acetate); ALS, ammonium lignosulfonate; OM, optical microscopy; VER, vinyl ester resin; VARTM, vacuum assisted transfer molding; GMA, glycidyl methacrylate; CNT, carbon nanotubes; XPS, X-ray photoelectron spectroscopy

■ REFERENCES

(1) Zhang, C.; Subramanian, H.; Grailer, J. J.; Tiwari, A.; Pilla, S.; Steeber, D. A.; Gong, S. Fabrication of biodegradable poly-(trimethylene carbonate) networks for potential tissue engineering scaffold applications. *Polym. Adv. Technol.* **2009**, *20*, 742−747.

(2) Pilla, S.; Gong, S.; O'Neill, E.; Yang, L.; Rowell, R. M. Polylactide-recycled wood fiber composites. *J. Appl. Polym. Sci.* **2009**, *111*, 37−47.

(3) Pilla, S.; Kramschuster, A.; Yang, L.; Lee, J.; Gong, S.; Turng, L.-S. Microcellular injection-molding of polylactide with chain-extender. *Mater. Sci. Eng., C* **2009**, *29*, 1258−1265.

(4) Chalivendra, V. B.; Shukla, A.; Bose, A.; Parameswaran, V. Processing and mechanical characterization of lightweight polyurethane composites. *J. Mater. Sci.* **2003**, *38*, 1631−1643.

(5) Gao, C.; Yu, L.; Liu, H.; Chen, L. Development of self-reinforced polymer composites. *Prog. Polym. Sci.* **2012**, *37*, 767−780.

(6) Cardoso, S. M.; Chalivendra, V. B.; Shukla, A.; Yang, S. Damage detection of rubber toughened nanocomposites in the fracture process zone using carbon nanotubes. *Eng. Fract. Mech.* **2012**, *96*, 380−391.

(7) Pinto, M. A.; Chalivendra, V. B.; Kim, Y. K.; Lewis, A. F. Evaluation of surface treatment and fabrication methods for jute fiber/epoxy laminar composites. *Polym. Compos.* **2014**, *35*, 310−317.

(8) Dhakal, H. N.; Zhang, Z. Y.; Richardson, M. O. W. Nanoindentation behaviour of layered silicate reinforced unsaturated polyester nanocomposites. *Polym. Test.* **2006**, *25*, 846−852.

(9) Volkova, N.; Ibrahim, V.; Hatti-Kaul, R.; Wadso, L. Water sorption isotherms of kraft lignin and its composites. *Carbohydr. Polym.* **2012**, *87*, 1817−1821.

(10) Faruk, O.; Bledzki, A. K.; Fink, H.-P.; Sain, M. Biocomposites reinforced with natural fibers: 2000−2010. *Prog. Polym. Sci.* **2012**, *37*, 1552−1596.

(11) Fernandes, E. M.; Pires, R. A.; Mano, J. F.; Reis, R. L. Bionanocomposites from lignocellulosic resources: Properties, applications and future trends for their use in the biomedical field. *Prog. Polym. Sci.* **2013**, *38*, 1415−1441.

(12) Pinto, M. A.; Chalivendra, V. B.; Kim, Y. K.; Lewis, A. F. Effect of surface treatment and Z-axis reinforcement on the interlaminar fracture of jute/epoxy laminated composites. *Eng. Fract. Mech.* **2013**, *114*, 104−114.

(13) Ojijo, V.; Ray, S. S. Processing strategies in bionanocomposites. *Prog. Polym. Sci.* **2013**, *38*, 1543−1589.

(14) Cosutchi, A. I.; Hulubei, C.; Stoica, I.; Ioan, S. Morphological and structural-rheological relationship in Epiclon-based polyimide/hydroxypropylcellulose blend systems. *J. Polym. Res.* **2010**, *17*, 541−550.

(15) Dobos, A. M.; Onofrei, M.-D.; Stoica, I.; Olaru, N.; Olaru, L.; Ioan, S. Rheological properties and microstructures of cellulose acetate

phthalate/hydroxypropyl cellulose blends. *Polym. Compos.* **2012**, *33*, 2072−2083.

(16) Dobos, A. M.; Stoica, I.; Olaru, N.; Olaru, L.; Ioanid, E. G.; Ioan, S. Surface properties and biocompatibility of cellulose acetates. *J. Appl. Polym. Sci.* **2012**, *125*, 2521−2528.

(17) Necula, A. M.; Olaru, N.; Olaru, L.; Homocianu, M.; Ioan, S. Influence of the substitution degrees on the optical properties of cellulose acetates. *J. Appl. Polym. Sci.* **2010**, *115*, 1751−1757.

(18) De Rosa, I. M.; Dhakal, H. N.; Santulli, C.; Sarasini, F.; Zhang, Z. Y. Post-impact static and cyclic flexural characterisation of hemp fibre reinforced laminates. *Compos. Part B* **2012**, *43*, 1382−1396.

(19) Dhakal, H. N.; Zhang, Z. Y.; Bennett, N. Influence of fibre treatment and glass fibre hybridisation on thermal degradation and surface energy characteristics of hemp/unsaturated polyester composites. *Compos. Part B* **2012**, *43*, 2757−2761.

(20) Dhakal, H. N.; Zhang, Z. Y.; Guthrie, R.; MacMullen, J.; Bennett, N. Development of flax/carbon fibre hybrid composites for enhanced properties. *Carbohydr. Polym.* **2013**, *96*, 1−8.

(21) Thakur, V. K.; Singha, A. S.; Mehta, I. K. Renewable resource-based green polymer composites: Analysis and characterization. *Int. J. Polym. Anal. Charact.* **2010**, *15*, 137−146.

(22) Thakur, V. K.; Thakur, M. K.; Gupta, R. K. Graft copolymers from cellulose: Synthesis, characterization and evaluation. *Carbohydr. Polym.* **2013**, *97*, 18−25.

(23) Thakur, V. K.; Thakur, M. K.; Gupta, R. K. Synthesis of lignocellulosic polymer with improved chemical resistance through free radical polymerization. *Int. J. Biol. Macromol.* **2013**, *61*, 121−126.

(24) Le Digabel, F.; Avérous, L. Effects of lignin content on the properties of lignocellulose-based biocomposites. *Carbohydr. Polym.* **2006**, *66*, 537−545.

(25) Uraki, Y.; Nemoto, J.; Yanaga, K.; Koizumi, A.; Hirai, T. Preparation of board-like moldings from composites of isolated lignins and waste paper II: Effect of inorganic salt addition on board performance and evaluation of practical use of MDF. *J. Wood Sci.* **2005**, *51*, 589−594.

(26) Singha, A. S.; Thakur, V. K. Chemical resistance, mechanical and physical properties of biofibers-based polymer composites. *Polym.-Plast. Technol. Eng.* **2009**, *48*, 736−744.

(27) Azwa, Z. N.; Yousif, B. F.; Manalo, A. C.; Karunasena, W. A review on the degradability of polymeric composites based on natural fibres. *Mater. Des.* **2013**, *47*, 424−442.

(28) Singha, A. S.; Thakur, V. K. Mechanical, morphological and thermal properties of pine needle-reinforced polymer composites. *Int. J. Polym. Mater.* **2008**, *58*, 21−31.

(29) Singha, A. S.; Thakur, V. K. Synthesis and characterization of short *Grewia optiva* fiber-based polymer composites. *Polym. Compos.* **2009**, NA−NA.

(30) Thakur, V. K.; Singha, A. S. Physicochemical and mechanical behavior of cellulosic pine needle-based biocomposites. *Int. J. Polym. Anal. Charact.* **2011**, *16*, 390−398.

(31) Thakur, V. K.; Singha, A. S.; Thakur, M. K. Green composites from natural fibers: Mechanical and chemical aging properties. *Int. J. Polym. Anal. Charact.* **2012**, *17*, 401−407.

(32) Thakur, V. K.; Singha, A. S.; Thakur, M. K. Natural cellulosic polymers as potential reinforcement in composites: Physicochemical and mechanical studies. *Adv. Polym. Technol.* **2013**, *32*, E427−E435.

(33) Wang, H.; Zou, J.; Shen, Y.; Fei, G.; Mou, J. Preparation and colloidal properties of an aqueous acetic acid lignin containing polyurethane surfactant. *J. Appl. Polym. Sci.* **2013**, *130*, 1855−1862.

(34) Faria, F. A.; Evtuguin, D. V.; Rudnitskaya, A.; Gomes, M. T.; Oliveira, J. A.; Graça, M. P. F.; Costa, L. C. Lignin-based polyurethane doped with carbon nanotubes for sensor applications. *Polym. Int.* **2012**, *61*, 788−794.

(35) Cerrutti, B. M.; de Souza, C. S.; Castellan, A.; Ruggiero, R.; Frollini, E. Carboxymethyl lignin as stabilizing agent in aqueous ceramic suspensions. *Ind. Crops Prod.* **2012**, *36*, 108−115.

(36) Erakovic, S.; Veljovic, D.; Diouf, P. N.; Stevanovic, T.; Mitric, M.; Milonjic, S.; Miskovic-Stankovic, V. B. Electrophoretic deposition of biocomposite lignin/hydroxyapatite coatings on titanium. *Int. J. Chem. React. Eng.* **2009**, *7*.

(37) Raschip, I. E.; Hitruc, E. G.; Vasile, C. Semi-interpenetrating polymer networks containing polysaccharides. II. Xanthan/lignin networks: a spectral and thermal characterization. *High Perform. Polym.* **2011**, *23*, 219−229.

(38) Feldman, D.; Banu, D.; Manley, R. S. J.; Zhu, H. Highly filled blends of a vinylic copolymer with plasticized lignin: Thermal and mechanical properties. *J. Appl. Polym. Sci.* **2003**, *89*, 2000−2010.

(39) F. Graça, M. P.; Rudnitskaya, A.; C. Faria, F. A.; Evtuguin, D. V.; S.R. Gomes, M. T.; B.P. Oliveira, J. A.; C. Costa, L. Electrochemical impedance study of the lignin-derived conducting polymer. *Electrochim. Acta* **2012**, *76*, 69−76.

(40) Rozite, L.; Varna, J.; Joffe, R.; Pupurs, A. Nonlinear behavior of PLA and lignin-based flax composites subjected to tensile loading. *J. Thermoplast. Compos. Mater.* **2013**, *26*, 476−496.

(41) Li, Y.; Cao, X.; Qian, X.; Chen, Y.; Liu, S. Immobilization of laccase in N-doped carbon hollow spheres/chitosan composite film for electrochemical detection of kraft lignin. *J. Electroanal. Chem.* **2012**, *686*, 7−11.

(42) Raschip, I. E.; Hitruc, G. E.; Vasile, C.; Popescu, M.-C. Effect of the lignin type on the morphology and thermal properties of the xanthan/lignin hydrogels. *Int. J. Biol. Macromol.* **2013**, *54*, 230−237.

(43) Wu, R.-L.; Wang, X.-L.; Li, F.; Li, H.-Z.; Wang, Y.-Z. Green composite films prepared from cellulose, starch and lignin in room-temperature ionic liquid. *Bioresour. Technol.* **2009**, *100*, 2569−2574.

(44) Bertini, F.; Canetti, M.; Cacciamani, A.; Elegir, G.; Orlandi, M.; Zoia, L. Effect of ligno-derivatives on thermal properties and degradation behavior of poly(3-hydroxybutyrate)-based biocomposites. *Polym. Degrad. Stab.* **2012**, *97*, 1979−1987.

(45) Stiubianu, G.; Nistor, A.; Vlad, A.; Cazacu, M. Modification of water sorption capacity of polydimethylsiloxane based composites by incorporation of lignin. *Mater. Plast.* **2011**, *48*, 289−294.

(46) Notley, S. M.; Norgren, M. Surface energy and wettability of spin-coated thin films of lignin isolated from wood. *Langmuir* **2010**, *26*, 5484−5490.

(47) Chapple, S.; Anandjiwala, R. Flammability of natural fiber-reinforced composites and strategies for fire retardancy: A review. *J. Thermoplast. Compos. Mater.* **2010**, *23*, 871−893.

(48) Yelle, D.; Goodell, B.; Gardner, D. J.; Amirbahman, A.; Winistorfer, P.; Shaler, S. Bonding of wood fiber composites using a synthetic chelator-lignin activation system. *For. Prod. J.* **2004**, *54*, 73−78.

(49) Zhong, L.; Fu, S.; Li, F.; Zhan, H. Chlorine dioxide treatment of sisal fibre: Surface lignin and its influences on fibre surface characteristics and interfacial behaviour of sisal fibre/phenolic resin composites. *Bioresources* **2010**, *5*, 2431−2446.

(50) Akil, H. M.; Omar, M. F.; Mazuki, A. A. M.; Safiee, S.; Ishak, Z. A. M.; Abu Bakar, A. Kenaf fiber reinforced composites: A review. *Mater. Des.* **2011**, *32*, 4107−4121.

(51) Singha, A. S.; Thakur, V. K. Physical, chemical and mechanical properties of *Hibiscus sabdariffa* fiber/polymer composite. *Int. J. Polym. Mater.* **2009**, *58*, 217−228.

(52) Doherty, W. O. S.; Mousavioun, P.; Fellows, C. M. Value-adding to cellulosic ethanol: Lignin polymers. *Ind. Crops Prod.* **2011**, *33*, 259−276.

(53) Singha, A. S.; Thakur, V. K. Mechanical, morphological, and thermal characterization of compression-molded polymer biocomposites. *Int. J. Polym. Anal. Charact.* **2010**, *15*, 87−97.

(54) Singha, A. S.; Vijay Kumar, T. Synthesis, characterization and study of pine needles reinforced polymer matrix based composites. *J. Reinf. Plast. Compos.* **2009**, *29*, 700−709.

(55) Singha, A. S.; Thakur, V. K.; Mehta, I. K.; Shama, A.; Khanna, A. J.; Rana, R. K.; Rana, A. K. Surface-modified *Hibiscus sabdariffa* fibers: Physicochemical, thermal, and morphological properties evaluation. *Int. J. Polym. Anal. Charact.* **2009**, *14*, 695−711.

(56) Constantino, C. J. L.; Dhanabalan, A.; Curvelo, A.; Oliveira, O. N. Preparation and characterization of composite LB films of lignin and cadmium stearate. *Thin Solid Films* **1998**, *327*, 47−51.

(57) Nordström, Y.; Norberg, I.; Sjöholm, E.; Drougge, R. A new softening agent for melt spinning of softwood kraft lignin. *J. Appl. Polym. Sci.* **2013**, *129*, 1274−1279.

(58) Erakovic, S.; Veljovic, D.; Diouf, P. N.; Stevanovic, T.; Mitric, M.; Janackovic, D.; Matic, I. Z.; Juranic, Z. D.; Miskovic-Stankovic, V. The effect of lignin on the structure and characteristics of composite coatings electrodeposited on titanium. *Prog. Org. Coat.* **2012**, *75*, 275−283.

(59) Gravitis, J.; Abolins, J.; Tupciauskas, R.; Veveris, A. Lignin from steam-exploded wood as binder in wood composites. *J. Environ. Eng. Landsc. Manag.* **2010**, *18*, 75−84.

(60) Hanjie, W.; Frits, P.; de, V.; Yongcan, J. A win-win technique of stabilizing sand dune and purifying paper mill black-liquor. *J. Environ. Sci. China* **2009**, *21*, 488−493.

(61) Uraki, Y.; Sugiyama, Y.; Koda, K.; Kubo, S.; Kishimoto, T.; Kadla, J. F. Thermal mobility of β-O-−4-type artificial lignin. *Biomacromolecules* **2012**, *13*, 867−872.

(62) Pinkert, A.; Goeke, D. F.; Marsh, K. N.; Pang, S. Extracting wood lignin without dissolving or degrading cellulose: investigations on the use of food additive-derived ionic liquids. *Green Chem.* **2011**, *13*, 3124.

(63) He, Z.-W.; Lu, Q.-F.; Zhang, J.-Y. Facile preparation of hierarchical polyaniline-lignin composite with a reactive silver-ion adsorbability. *ACS Appl. Mater. Interfaces* **2012**, *4*, 369−374.

(64) He, Z.-W.; Yang, J.; Lu, Q.-F.; Lin, Q. Effect of structure on the electrochemical performance of nitrogen- and oxygen-containing carbon micro/nanospheres prepared from lignin-based composites. *ACS Sustain. Chem. Eng.* **2013**, *1*, 334−340.

(65) Sivasankarapillai, G.; McDonald, A. G. Synthesis and properties of lignin-highly branched poly (ester-amine) polymeric systems. *Biomass Bioenergy* **2011**, *35*, 919−931.

(66) Mahendran, A. R.; Wuzella, G.; Aust, N.; Mueller, U.; Kandelbauer, A. Processing and characterization of natural fibre reinforced composites using lignin phenolic binder. *Polym. Polym. Compos.* **2013**, *21*, 199−205.

(67) Gargulak, J. D.; Lebo, S. E. Commercial Use of Lignin-Based Materials. In *Lignin: Historical, Biological, and Materials Perspectives*; Glasser, W. G., Northey, R. A., Schultz, T. P., Ed.; ACS Symposium Series 742; American Chemical Society: Washington, DC, 1999; pp 304−320.

(68) Baumberger, S.; Dole, P.; Lapierre, C. Using transgenic poplars to elucidate the relationship between the structure and the thermal properties of lignins. *J. Agric. Food Chem.* **2002**, *50*, 2450−2453.

(69) Lora, J. H.; Glasser, W. G. Recent industrial applications of lignin: A sustainable alternative to nonrenewable materials. *J. Polym. Environ.* **2002**, *10*, 39−48.

(70) Botros, S. H.; Eid, M. a. M.; Nageeb, Z. A. Thermal stability and dielectric relaxation of natural rubber/soda lignin and natural rubber/thiolignin composites. *J. Appl. Polym. Sci.* **2006**, *99*, 2504−2511.

(71) Huang, J.; Zhang, L.; Wei, H.; Cao, X. D. Soy protein isolate/kraft lignin composites compatibilized with methylene diphenyl diisocyanate. *J. Appl. Polym. Sci.* **2004**, *93*, 624−629.

(72) Mosier, N. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour. Technol.* **2005**, *96*, 673−686.

(73) Gregorova, A.; Kosikovka, B.; Osvald, A. The study of lignin influence on properties of polypropylene composites. *Wood Res.* **2005**, *50*, 41−48.

(74) Kosikova, B.; Demianova, V.; Kacurakova, M. Sulfur-free lignins as composites of polypropylene films. *J. Appl. Polym. Sci.* **1993**, *47*, 1065−1073.

(75) Yue, X.; Chen, F.; Zhou, X. Synthesis of lignin-g-MMA and the utilization of the copolymer in PVC/wood composites. *J. Macromol. Sci., Part B: Phys.* **2012**, *51*, 242−254.

(76) Baumberger, S.; Lapierre, C.; Monties, B. Utilization of pine kraft lignin in starch composites: Impact of structural heterogeneity. *J. Agric. Food Chem.* **1998**, *46*, 2234−2240.

(77) Kosikova, B.; Kacurakova, M.; Demianova, V. Photooxidation of the composite lignin polypropylene films. *Chem. Pap.* **1993**, *47*, 132−136.

(78) Kadla, J. F.; Kubo, S.; Venditti, R. A.; Gilbert, R. D.; Compere, A. L.; Griffith, W. Lignin-based carbon fibers for composite fiber applications. *Carbon* **2002**, *40*, 2913−2920.

(79) Chaochanchaikul, K.; Jayaraman, K.; Rosarpitak, V.; Sombatsompop, N. Influence of lignin content on photodegradation in wood/HDPE composites under UV weathering. *Bioresources* **2012**, *7*, 38−55.

(80) Li, J.; Li, S.; Wang, H.; Yang, Y.; Guo, G. Preparation of a lignin-based composite and its properties. *Bioresources* **2011**, *6*, 1532−1542.

(81) Liu, F.; Xu, K.; Chen, M.; Cao, D. The roles of polyacrylate in poly(vinyl chloride)−lignin composites. *Polym. Compos.* **2011**, *32*, 1399−1407.

(82) Marklund, E.; Eitzenberger, J.; Varna, J. Nonlinear viscoelastic viscoplastic material model including stiffness degradation for hemp/lignin composites. *Compos. Sci. Technol.* **2008**, *68*, 2156−2162.

(83) Megiatto, J. D.; Silva, C. G.; Rosa, D. S.; Frollini, E. Sisal chemically modified with lignins: Correlation between fibers and phenolic composites properties. *Polym. Degrad. Stab.* **2008**, *93*, 1109−1121.

(84) Park, Y.; Doherty, W. O. S.; Halley, P. J. Developing lignin-based resin coatings and composites. *Ind. Crops Prod.* **2008**, *27*, 163−167.

(85) Nenkova, S. Study of sorption properties of lignin-derivatized fibrous composites for the remediation of oil polluted receiving waters. *Bioresources* **2007**, *2*, 408−418.

(86) Morandim-Giannetti, A. A.; Agnelli, J. A. M.; Lancas, B. Z.; Magnabosco, R.; Casarin, S. A.; Bettini, S. H. P. Lignin as additive in polypropylene/coir composites: Thermal, mechanical and morphological properties. *Carbohydr. Polym.* **2012**, *87*, 2563−2568.

(87) Pupure, L.; Varna, J.; Joffe, R.; Pupurs, A. An analysis of the nonlinear behavior of lignin-based flax composites. *Mech. Compos. Mater.* **2013**, *49*, 139−154.

(88) Stiubianu, G.; Cazacu, M.; Cristea, M.; Vlad, A. Polysiloxane−lignin composites. *J. Appl. Polym. Sci.* **2009**, *113*, 2313−2321.

(89) Pucciariello, R.; Villani, V.; Bonini, C.; D'Auria, M.; Vetere, T. Physical properties of straw lignin-based polymer blends. *Polymer* **2004**, *45*, 4159−4169.

(90) Reza Barzegari, M.; Alemdar, A.; Zhang, Y.; Rodrigue, D. Mechanical and rheological behavior of highly filled polystyrene with lignin. *Polym. Compos.* **2012**, *33*, 353−361.

(91) Barzegari, M. R.; Alemdar, A.; Zhang, Y.; Rodrigue, D. Thermal analysis of highly filled composites of polystyrene with lignin. *Polym. Polym. Compos.* **2013**, *21*, 357−366.

(92) El-Zawawy, W. K.; Ibrahim, M. M.; Belgacem, M. N.; Dufresne, A. Characterization of the effects of lignin and lignin complex particles as filler on a polystyrene film. *Mater. Chem. Phys.* **2011**, *131*, 348−357.

(93) Canetti, M.; Bertini, F. Influence of the lignin on thermal degradation and melting behaviour of poly(ethylene terephthalate) based composites. *e-Polym.* **2009**, 049.

(94) Canetti, M.; Bertini, F. Supermolecular structure and thermal properties of poly(ethylene terephthalate)/lignin composites. *Compos. Sci. Technol.* **2007**, *67*, 3151−3157.

(95) Pouteau, C.; Baumberger, S.; Cathala, B.; Dole, P. Lignin−polymer blends: Evaluation of compatibility by image analysis. *C. R. Biol.* **2004**, *327*, 935−943.

(96) Kadla, J. F.; Kubo, S. Miscibility and hydrogen bonding in blends of poly(ethylene oxide) and kraft lignin. *Macromolecules* **2003**, *36*, 7803−7811.

(97) Yin, Q.; Yang, W.; Sun, C.; Di, M. Preparation and properties of lignin-epoxy resin composite. *Bioresources* **2012**, *7*, 5737−5748.

(98) Doherty, W.; Halley, P.; Edye, L.; Rogers, D.; Cardona, F.; Park, Y.; Woo, T. Studies on polymers and composites from lignin and fiber derived from sugar cane. *Polym. Adv. Technol.* **2007**, *18*, 673−678.

(99) Stanzione, J. F.; Giangiulio, P. A.; Sadler, J. M.; La Scala, J. J.; Wool, R. P. Lignin-based bio-oil mimic as biobased resin for composite applications. *ACS Sustain. Chem. Eng.* **2013**, *1*, 419−426.

(100) Setua, D. K.; Shukla, M. K.; Nigam, V.; Singh, H.; Mathur, G. N. Lignin reinforced rubber composites. *Polym. Compos.* **2000**, *21*, 988−995.

(101) Kosikova, B.; Alexy, P.; Gregorova, A. Use of lignin products derived from wood pulping as environmentally desirable component of composite rubber materials. *Wood Res.* **2003**, *48*, 62−67.

(102) Kosikova, B.; Gregorova, A.; Osvald, A.; Krajcovicova, J. Role of lignin filler in stabilization of natural rubber-based composites. *J. Appl. Polym. Sci.* **2007**, *103*, 1226−1231.

(103) Mathew, T. V.; Kuriakose, S. Molecular transport of aromatic hydrocarbons through lignin-filled natural rubber composites. *Polym. Compos.* **2007**, *28*, 15−22.

(104) Rozman, H. D.; Kumar, R. N.; Adlli, M. R. M.; Abusamah, A.; Ishak, Z. a. M. The effect of lignin and surface activation on the mechanical properties of rubberwood-polypropylene composites. *J. Wood Chem. Technol.* **1998**, *18*, 471−490.

(105) Xiao, S.; Feng, J.; Zhu, J.; Wang, X.; Yi, C.; Su, S. Preparation and characterization of lignin-layered double hydroxide/styrene-butadiene rubber composites. *J. Appl. Polym. Sci.* **2013**, *130*, 1308−1312.

(106) Jiang, C.; He, H.; Jiang, H.; Ma, L.; Jia, D. M. Nano-lignin filled natural rubber composites: Preparation and characterization. *Express Polym. Lett* **2013**, *7*, 480−493.

(107) Khalil, H. P. S. A.; Marliana, M. M.; Alshammari, T. Material properties of epoxy-reinforced biocomposites with lignin from empty fruit bunch as curing agent. *BioResources* **2011**, *6*, 5206−5223.

(108) Réti, C.; Casetta, M.; Duquesne, S.; Bourbigot, S.; Delobel, R. Flammability properties of intumescent PLA including starch and lignin. *Polym. Adv. Technol.* **2008**, *19*, 628−635.

(109) El-Wakil, N. A. Use of lignin strengthened with modified wheat gluten in biodegradable composites. *J. Appl. Polym. Sci.* **2009**, *113*, 793−801.

(110) Ma, H.; Joo, C. W. Investigation of jute-lignin-poly (3-hydroxybutyrate) hybrid biodegradable composites with low water absorption. *Fibers Polym.* **2011**, *12*, 310−315.

(111) Sahoo, S.; Misra, M.; Mohanty, A. K. Enhanced properties of lignin-based biodegradable polymer composites using injection moulding process. *Composites, Part A* **2011**, *42*, 1710−1718.

(112) Sahoo, S.; Misra, M.; Mohanty, A. K. Effect of compatibilizer and fillers on the properties of injection molded lignin-based hybrid green composites. *J. Appl. Polym. Sci.* **2013**, *127*, 4110−4121.

(113) Camargo, F. A.; Innocentini-Mei, L. H.; Lemes, A. P.; Moraes, S. G.; Duran, N. Processing and characterization of composites of poly(3-hydroxybutyrate-co-hydroxyvalerate) and lignin from sugar cane bagasse. *J. Compos. Mater.* **2012**, *46*, 417−425.

(114) Çalgeris, İ.; Çakmakçı, E.; Ogan, A.; Kahraman, M. V.; Kayaman-Apohan, N. Preparation and drug release properties of lignin-starch biodegradable films. *Starch - Stärke* **2012**, *64*, 399−407.

(115) Spiridon, I.; Teaca, C.-A.; Bodirlau, R. Preparation and characterization of adipic acid-modified starch microparticles/plasticized starch composite films reinforced by lignin. *J. Mater. Sci.* **2011**, *46*, 3241−3251.

(116) Del Saz-Orozco, B.; Oliet, M.; Alonso, M. V.; Rojo, E.; Rodríguez, F. Formulation optimization of unreinforced and lignin nanoparticle-reinforced phenolic foams using an analysis of variance approach. *Compos. Sci. Technol.* **2012**, *72*, 667−674.

(117) Luo, X.; Mohanty, A.; Misra, M. Lignin as a reactive reinforcing filler for water-blown rigid biofoam composites from soy oil-based polyurethane. *Ind. Crops Prod.* **2013**, *47*, 13−19.

(118) Hatakeyama, H.; Kato, N.; Nanbo, T.; Hatakeyama, T. Water absorbent polyurethane composites derived from molasses and lignin filled with microcrystalline cellulose. *J. Mater. Sci.* **2012**, *47*, 7254−7261.

(119) Stevens, E. S. Starch-lignin foams. *EXPRESS Polym. Lett.* **2010**, *4*, 311−320.

(120) Casenave, S.; AitKadi, A.; Riedl, B. Mechanical behaviour of highly filled lignin/polyethylene composites made by catalytic grafting. *Can. J. Chem. Eng.* **1996**, *74*, 308−315.

(121) Adcock, T.; Shah, V.; Chen, M. J.; Meister, J. J. Graft copolymers of lignin as hydrophobic agents for plastic (wood-filled) composites. *J. Appl. Polym. Sci.* **2003**, *89*, 1266−1276.

(122) Batog, J.; Kozlowski, R.; Przepiera, A. Lignocellulosic composites bonded by enzymatic oxidation of lignin. *Mol. Cryst. Liq. Cryst.* **2008**, *484*, 401−408.

(123) Bobu, E.; Popa, V.; Beleca, C. Modified lignin in composite structures. *Cellul. Chem. Technol.* **1994**, *28*, 55−64.

(124) Chung, Y.-L.; Olsson, J. V.; Li, R. J.; Frank, C. W.; Waymouth, R. M.; Billington, S. L.; Sattely, E. S. A renewable lignin-lactide copolymer and application in biobased composites. *ACS Sustain. Chem. Eng.* **2013**, *1*, 1231−1238.

(125) Nemoto, T.; Konishi, G.; Tojo, Y.; An, Y. C.; Funaoka, M. Functionalization of lignin: Synthesis of lignophenol-graft-poly(2-ethyl-2-oxazoline) and its application to polymer blends with commodity polymers. *J. Appl. Polym. Sci.* **2012**, *123*, 2636−2642.

(126) Manjarrez Nevárez, L.; Ballinas Casarrubias, L.; Canto, O. S.; Celzard, A.; Fierro, V.; Ibarra Gómez, R.; González Sánchez, G. Biopolymers-based nanocomposites: Membranes from propionated lignin and cellulose for water purification. *Carbohydr. Polym.* **2011**, *86*, 732−741.

(127) Maldhure, A. V.; Ekhe, J. D.; Deenadayalan, E. Mechanical properties of polypropylene blended with esterified and alkylated lignin. *J. Appl. Polym. Sci.* **2012**, *125*, 1701−1712.

(128) Wang, J.; Ya, K.; Korich, A. L.; Li, S.; Ma, S.; Ploehn, H. J.; Iovine, P. M.; Wang, C.; Chu, F.; Tang, C. Combining renewable gum rosin and lignin: Towards hydrophobic polymer composites by controlled polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 3728−3738.

(129) Sailaja, R. R. N.; Deepthi, M. V. Mechanical and thermal properties of compatibilized composites of polyethylene and esterified lignin. *Mater. Des.* **2010**, *31*, 4369−4379.

(130) Teramoto, Y.; Lee, S.-H.; Endo, T. Molecular composite of lignin: Miscibility and complex formation of organosolv lignin and its acetates with synthetic polymers containing vinyl pyrrolidone and/or vinyl acetate units. *J. Appl. Polym. Sci.* **2012**, *125*, 2063−2070.

(131) Yue, X.; Chen, F.; Zhou, X. Improved interfacial bonding of PVC/wood-flour composites by lignin amine modification. *Bioresources* **2011**, *6*, 2022−2034.

(132) Rosu, L.; Cascaval, C. N.; Rosu, D. Effect of UV radiation on some polymeric networks based on vinyl ester resin and modified lignin. *Polym. Test.* **2009**, *28*, 296−300.

(133) Yu, Y.; Fu, S.; Song, P.; Luo, X.; Jin, Y.; Lu, F.; Wu, Q.; Ye, J. Functionalized lignin by grafting phosphorus-nitrogen improves the thermal stability and flame retardancy of polypropylene. *Polym. Degrad. Stab.* **2012**, *97*, 541−546.

(134) Yu, Y.; Song, P.; Jin, C.; Fu, S.; Zhao, L.; Wu, Q.; Ye, J. Catalytic effects of nickel (cobalt or zinc) acetates on thermal and flammability properties of polypropylene-modified lignin composites. *Ind. Eng. Chem. Res.* **2012**, *51*, 12367−12374.

(135) Thielemans, W.; Wool, R. P. Butyrated kraft lignin as compatibilizing agent for natural fiber reinforced thermoset composites. *Composites, Part A* **2004**, *35*, 327−338.

(136) Rozman, H. D.; Tan, K. W.; Kumar, R. N.; Abubakar, A.; Ishak, Z. a. M.; Ismail, H. The effect of lignin as a compatibilizer on the physical properties of coconut fiber-polypropylene composites. *Eur. Polym. J.* **2000**, *36*, 1483−1494.

(137) Rozman, H. D.; Tan, K. W.; Kumar, R. N.; Abubakar, A. The effect of hexamethylene diisocyanate modified ALCELL lignin as a coupling agent on the flexural properties of oil palm empty fruit bunch - polypropylene composites. *Polym. Int.* **2001**, *50*, 561−567.

(138) Rozman, H. D.; Tan, K. W.; Kumar, R. N.; Abubakar, A. Preliminary studies on the use of modified ALCELL lignin as a coupling agent in the biofiber composites. *J. Appl. Polym. Sci.* **2001**, *81*, 1333−1340.

(139) Wood, B. M.; Coles, S. R.; Maggs, S.; Meredith, J.; Kirwan, K. Use of lignin as a compatibiliser in hemp/epoxy composites. *Compos. Sci. Technol.* **2011**, *71*, 1804−1810.

(140) Tay, G. S.; Shannon-Ong, S. H.; Goh, S. W.; Rozman, H. D. Enhancement of tensile and impact properties of thermoplastic lignocellulose composites by incorporation of chemically treated alcell lignin as compatibilizer. *Polym.-Plast. Technol. Eng.* **2011**, *50*, 160−167.

(141) Tay, G. S.; Shannon-Ong, S. H.; Goh, S. W.; Rozman, H. D. Thermoplastic-lignocellulose composites enhanced by chemically treated Alcell lignin as compatibilizer. *J. Thermoplast. Compos. Mater.* **2013**, *26*, 733−746.

(142) Li, Y.; Lin, X.; Zhuo, X.; Luo, X. Poly(vinyl alcohol)/ quaternized lignin composite absorbent: Synthesis, characterization and application for nitrate adsorption. *J. Appl. Polym. Sci.* **2013**, *128*, 2746−2752.

(143) Khalil, H. P. S. A.; Marliana, M. M.; Issam, A. M.; Bakare, I. O. Exploring isolated lignin material from oil palm biomass waste in green composites. *Mater. Des.* **2011**, *32*, 2604−2610.

(144) Thielemans, W.; Can, E.; Morye, S. S.; Wool, R. P. Novel applications of lignin in composite materials. *J. Appl. Polym. Sci.* **2002**, *83*, 323−331.

(145) Toriz, G.; Denes, F.; Young, R. A. Lignin−polypropylene composites. Part 1: Composites from unmodified lignin and polypropylene. *Polym. Compos.* **2002**, *23*, 806−813.

(146) Toriz, G.; Ramos, J.; Young, R. A. Lignin−polypropylene composites. II. Plasma modification of kraft lignin and particulate polypropylene. *J. Appl. Polym. Sci.* **2004**, *91*, 1920−1926.

(147) Milczarek, G.; Nowicki, M. Carbon nanotubes/kraft lignin composite: Characterization and charge storage properties. *Mater. Res. Bull.* **2013**, *48*, 4032−4038.