Lignin as an Additive for Advanced Composites

Yusuf Polat, Elena Stojanovska, Tolera A. Negawo, Elmas Doner and Ali Kilic

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

Keywords Lignin · Biocomposites · Additive · Compatibilizer · Filler

1 Introduction

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

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

2 Lignin in Polymer Composites

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

2.1 Lignin as a Stabilizer in the Polymer Composites

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

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

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

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

2.2 Lignin as a Reinforcer in Polymer Composites

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

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

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

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

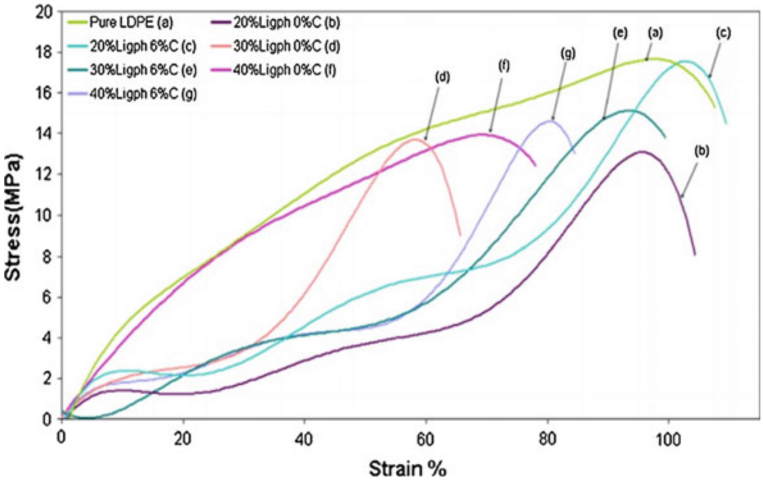

Fig. 1 The stress/strain curves of LDPE/ligph (phthalated lignin) blends (with permission from Elsevier Inc) (Sailaja and Deepthi 2010)

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

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

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

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

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

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

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

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

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

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

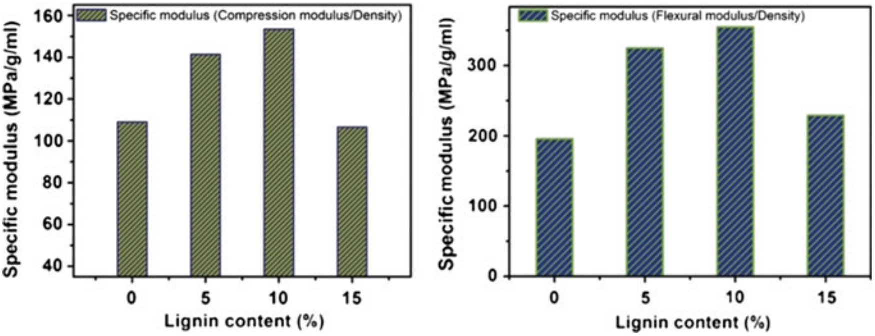

Fig. 2 Specific compressive modulus (ratio of compressive modulus to density) (left) and specific flexural modulus (ratio of flexural modulus to density) (right) of neat biofoam and biofoam composites (with permissions from Elsevier Inc.) (Luo et al. 2013)

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

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

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

F51 is a trade name of an epoxy resin

2.3 Lignin as a Filler in Polymer Composites

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

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

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

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

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

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

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

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

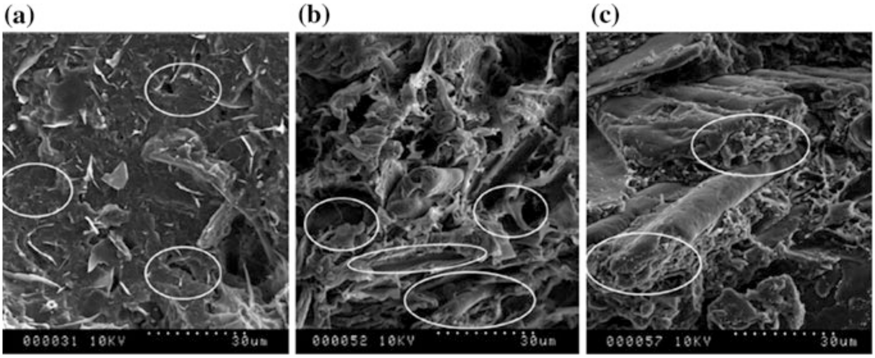

Fig. 3 SEM micrograph of composites at 30 lm scale and 10 kV operating voltage. **a** Lignin composite. **b** Switchgrass composite. **c** Hybrid composite (with permissions from Wiley Inc.) (Sahoo et al. 2013)

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

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

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

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

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

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

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

2.4 *Lignin as a Compatibilizer in Polymer Composites*

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

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

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

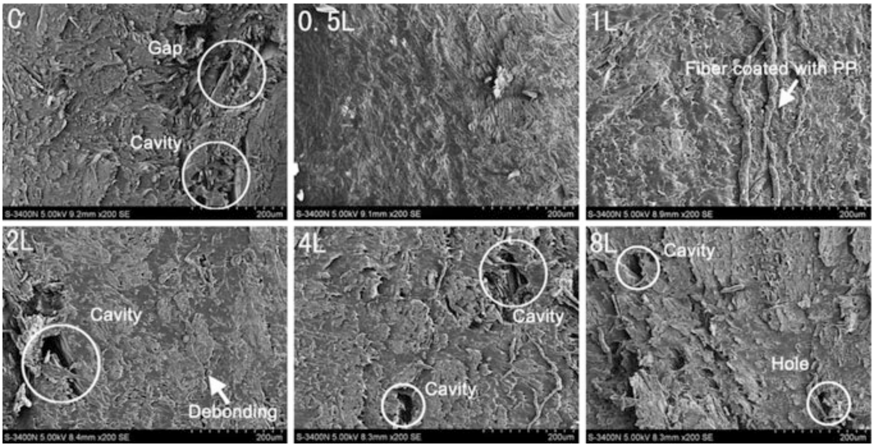

Fig. 4 SEM images of wood flour/PP composites without and with 0.5; 1; 2; 4 and 8 wt. % lignin prepared by extrusion and compression molding (with permission from Wiley Inc.) (Luo et al. 2015)

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

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

3 Applications of Lignin Based Composites

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

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

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

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

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

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

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

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

4 Conclusions and Future Prospective

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

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