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Recent approaches and future trends for lignin-based materials

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ABSTRACT

Known as the main source of aromatic compounds in nature, lignin possesses heterogeneous composition which has high potential to be used in many industrial purposes. Lignin has been used as retardants of fire, thermal stabilizer, hydrophobicity agent, carbon fiber, aerogels and antioxidants. This review summarizes several uses of lignin-based components and their potential applications. We focused on the industrial uses of lignin in order to diminish the dependence of petroleum-based materials.

KEYWORDS

Applications; biomaterial; biopolymer; lignin; properties

1. Introduction

Lignin is a highly heterogeneous aromatic biopolymer based on three phenolic monomers crosslinked to form a 3D network structure [1, 2]. Produced in large scale mainly from paper mill industries, commercial use of lignin over various potential application as feedstock for biorefinery, carbon nanostructure, feedstock for resins, composites, aerogels, antioxidants, etc [3, 4].

The notable properties of lignin, including high availability, low cost, ecologically friendliness, biodegradable properties, reinforcing for composites, and biological effect succeeds its exploration as the ideal candidate for an extensive variety of applications. As a result, substantial effort are now being made to successfully use lignin as one of the components in polymer matrices for high performance composite, cosmetics, food and other industrial applications [5].

In general, lignin-based materials have become a friendly alternative as substituents for petroleum-based materials. Lignin-based polymeric materials are highly cross-linked network structures which can be used as thermoplastic materials owing suitable properties such as moldability, elasticity, durability, strength, and toughness [6]. Addition of lignin to polypropylene (PP) blends improved flexural strength and maintained toughness when compared with neat PP [7]. Lignin reverse micelles (LRM) prepared from alkali lignin showed good UV-absorbing properties, once LRM blocked the phenolic hydroxyl structures and protected high density polyethylene (HDPE) from UV radiation [8]. Lignin can improve mechanical and thermal extra protection of film made with poly (vinyl alcohol) (PVA), mainly due to cross-linking reaction that occurred between the components [9]. Bioplastic composites have the advantage of having biological degradable properties and preserving of fossil based-raw

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compounds. Nowadays, PLA and PHB (polylactic acid and poly 3-hydroxybutyrate, respectively) has become one the most used biopolymer incorporated with lignin [10]. Inclusion of lignin to PLA has increased the impact strength, thermal stability and hydrophobicity of PLA, as well as protecting it against weathering [11, 12]. Chemical or biological modification of lignin opens new possibilities to use hole lignin-derived fractions. Enzymatic-modified lignin can be used for preparing phenol formaldehyde resin to replace petroleum-based phenolic resin [8].

Carbon fibers can be made from lignin which has properties similar to the same material made from polyacrylonitrile, with the advantage of being a low-cost product [13, 14]. However, some characteristics related to the morphology of the macromolecule should be overcome in order to increase the yield of lignin-based carbon fibers. In general, lignin-based carbon nanotubes have shown high thermal stability and super-hydrophobicity properties [15]. Aerogels are another example of nanostructure network made from lignin are aerogels. Nanoporous ultralight aerogels have different diameter size possessing unique properties such as high specific surface area and mechanical strength, low density with desirable porosity, thermal stability and electric conductivity. Those materials can be applied as thermal insulator, adsorbent, catalyst, chemical sensors and drug delivery [16, 17, 18, 19, 20].

Microspheres prepared from lignin possess the advantage of being renewable materials with the special ability to retain and control the release of chemicals, such as agricultural additives, drugs and cosmetics [21]. Micro or nanoscale lignin-based materials can be used to retain antioxidants to be applied to protect biomaterials, food or plastics from oxidative processes. Lignin-based antioxidants have been studied by increasing compatibility between lignin and the polymer matrix as well as protection against thermo oxidation [22]. Lignin incorporation on composites improved flexural strength and increased temperature of degradation of composites [7].

The antioxidants-based lignin are highly dependent on size. Thus, low molecular weight lignin-fractions composed by phenolic compounds have radical scavenging activity for several purposes. The size can vary from simple molecules to highly polymerized compounds known as polyphenols [23]. In addition, several biological beneficial effects have been owned to lignin-derived antioxidants such as anticancer, anti-inflammatory, antibacterial, antiviral, cardioprotective, therapeutical use on diabetes, osteoporosis, DNA protecting etc [24, 25].

This review summarizes notable properties of lignin, including high availability, low cost and reinforcing ability to made environmentally friendly materials. Low molecular weight lignin fractions own properties that can be used as antioxidant. Antimicrobial and biological applications have been studied in medicine against several diseases. Substantial efforts are now being made to successfully use lignin as one of the components in polymer matrices for high performance material applications into the biorefinery concept [5].

2. Lignin-based composites

2.1. Thermoplastic composites

Lignin-based polymeric materials are highly cross-linked networks structures created mostly by the multi functionality of the lignin precursors [5]. Thermoplastic materials based on lignin derivatives have attracted attention for their improved processability and recyclability when compared to with the thermosetting polymer networks [26]. The methods developed by the researchers have resulted in a product with advantageous properties including moldability,

Table 1. Studies of lignin on thermoplastics composites.

Polymer Matrix	Source of Lignin	Lignin modification	Remarkable properties	Refs.
PP	Hardwood Kraft	Esterification by anhydride	Flexural strength and thermal stability	[7]
PP	Softwood Kraft	Esterification by anhydride	Stiffness and tensile strength	[27]
PP	Sugarcane bagasse	Alkylation and arylation modification in different solvents	High accurate modeling for mechanical properties by various volume fraction of lignin	[28]
PP	Wheat straw alkali	Chemical grafting with P, N and Cu elements	Fire-retardant	[29]
PE	Alkali	Reverse micelle formation	UV-blocking	[8]
PE	Softwood Kraft	Functionalized SEBS	Flexural strength, modulus and toughness	[30]
PE	Softwood Kraft	Free-radical grafting	Tensile strength	[31]
PE	Softwood Kraft	Methylation and fractionation of lignin	Melt Stability and strength	[32]
PS	Kraft	Graft copolymerization of styrene by ATRP	Toughness	[33]
PS	Softwood Kraft	Esterification by anhydride	Flexural and impact strength and thermal stability	[34]
PA	Soda straw	Used as a filler	Ductility	[35]
PVA	Industrial alkali	Used as a filler	Tensile strength and thermal stability	[9]

Refs. = References. PP = polypropylene. PE = polyethylene. PS = polystyrene. PA = polyamide. PVA = Poly (vinyl alcohol). ATRP = atom transfer radical polymerization. SEBS = styrene ethylene and butylene copolymer.

elasticity, ductility, strength, durability, and toughness [6]. Some studies on lignin-based thermoplastics that have been performed recently are displayed in Table 1.

2.1.1. Polypropylene (PP)

In a study conducted by Bozsódi et al. (2016) [27], PP/lignin blends were prepared in a wide composition range (0–70%) from two lignosulfonates of different compositions by homogenization in an internal mixer and compression molding. According to their results, even though coupling enhances the strength of the blends, the deformability was small at high lignin contents affecting practical application.

Scanning electron microscope (SEM) images of PP/lignin blends structure can be seen in Figure 1. Fig. 1(a) exhibits clearly the debonding of particles of all sizes and the fracture of

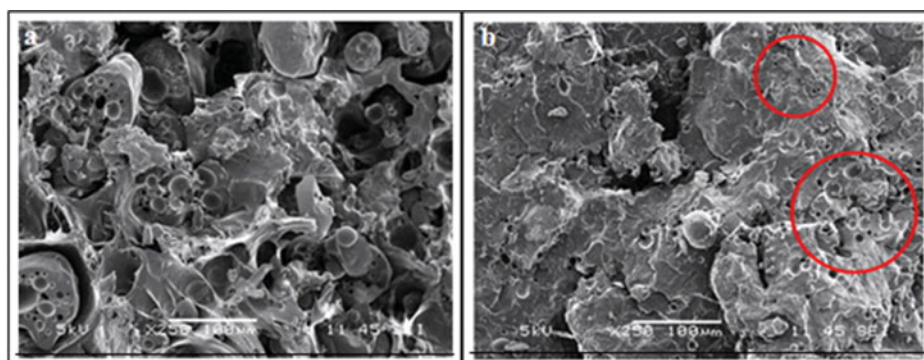


Figure 1. SEM structures of deformation and failure mechanism of PP/lignin blends containing 20% lignin. a) No coupling; debonding, shear yielding and particle fracture; b) MAPP; limited debonding, and particle fracture [7]. © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholder.

large particles. A homogeneous image is observed by the micrograph obtained from the blend containing MAPP as coupling agent (Fig. 1(b)). Debonding properties are revealed in the micrographs, less shear deformation and less well distinct interfaces are observed (Fig. 1(a)). Similarly, Dias et al. (2016) [7] studied the PP and hardwood lignin blend with MAPP. According to them, the addition of lignin within the PP matrix imparts better flexural strength and maintains toughness when compared with neat PP. Therefore, some properties of lignin-based polypropylene composites, in general, are lignin-concentration dependent, as well as the addition of coupling agent to ensure better interaction between lignin and matrix.

Maldhure and Ekhe (2015) [36] have studied the effect of chemical modification of lignin on the thermal, structural, and mechanical properties of polypropylene/modified lignin. The results showed increase in thermal stability of blends with increasing modified lignin content into PP matrix. Furthermore, intermolecular interactions between blend components were evaluated by applying mathematical models to experimental mechanical property data. They obtained good agreement between the predictions by using mathematical models based on experimental data, revealing the accuracy of these models for predicting the mechanical properties of PP/modified lignin blends.

Some investigators have added lignin as fire-retardant agent. Liu et al. (2016) [29] created a novel and green method for flame retarding polymeric materials, in order to overcome the poor thermal stability and flame retardancy properties of wood-plastic composites (WPC). Functionalized lignin was successfully produced by grafting phosphorus-nitrogen with a metal element. According to their results, the incorporation of functionalized lignin into WPC improved the thermal stability of the PP/WPC and the flame retardancy properties, whereas the char residue increased by 30% and smoke production was reduced at the same percentage.

2.1.2. Polyethylene (PE)

Hu et al. (2015) [30] developed a novel biocomposite based on Kraft lignin (KL). They investigated the study of the performance of free-radical grafting as a compatibilization method applied to the composites containing KL and esterified lignin. Maleated lignin (ML) was first obtained via esterification by maleic anhydride. KL and ML were combined with high density polyethylene (HDPE) up to 60% wt and dicumyl peroxide was used as a free-radical generator. As results, the adhesion between KL and HDPE was clearly enhanced by free-radical grafting. Compared with KL, porous ML showed better adhesion to the HDPE. In addition, thermal analysis results revealed that free-radical grafting enhances the thermal stability of ML-based composites. As well its density was increased after free-radical grafting due to the cavity collapse.

In another study carried out by Hu et al. (2015) [31], a novel method by modification of Kraft lignin after polystyrene-co-ethylene-co-butylene-co-styrene (SEBS) as unreactive compatibilizers was developed to enhance the compatibility with HDPE. SEBS was functionalized via nitration followed by amination to obtain nitrated (SEBS-NO₂) and aminated (SEBS-NH₂) SEBS. In their study, an efficient unreactive compatibilizer of the blends was miscible with polyethylene after functionalization and capable of interacting with Kraft lignin through hydrogen bonding to decrease interfacial energy. The results obtained by the functionalization of lignin support to elucidate the compatibilizing mechanisms between Kraft lignin and HDPE for composites produced with unreactive compatibilizers.

The effects at a macroscopic level of original and modified Kraft lignin was discussed by Sadeghifar et al (2016) [32], focusing on melt stability of polyethylene (PE) in blends with fractionated and unfractionated softwood kraft lignin. Thermally stable melts and significant

reductions in torque may be obtained through methylation of phenolic hydroxyl groups in softwood kraft lignin. Subsequently, melt viscosities were observed after methylated acetylated softwood kraft lignin (ASKL) and PE blending, offering plasticization effects.

Qiao et al. (2015) [8] reported a novel class of lignin reverse micelles (LRM) and their application as UV blocking additive for thermoplastics. Lignin reverse micelles (LRM) were prepared from alkali lignin (AL) in cyclohexane-dioxane mixture. The hydrophobicity of LRM increased substantially, which is particularly important for lignin-polymer blends miscibility. Once LRM blocked the phenolic hydroxyl structure of AL, the HDPE-LRM samples showed an excellent UV-absorbing performance. The phenolic hydroxyl groups blocked in the LRM structure protected HDPE from UV radiation by effect of free radical scavengers. Moreover, there were improvements in mechanical performance such as Young's modulus and elongation at break.

Buono et al. (2016) [37] developed and compared bio-based materials by the different functionalized lignin. Soda lignin was modified with tert-butyldimethylsilyl groups by the reaction with tert-butyldimethylsilyl chloride. High hydrophobic behavior of the silylated lignin was observed by the water contact angle measurements. According to the authors, the enhanced thermal stability, hydrophobicity and solubility of the silylated lignin was found to be an interesting approach to incorporating it into hydrophobic polymer matrices.

2.1.3. Polystyrene (PS)

Hilburg et al. (2014) [33] manufactured a nanocomposite based on polystyrene grafted from kraft lignin with nanoparticle size using atom transfer radical polymerization (ATRP). Mechanical testing exhibited a decreased tensile modulus, but improved toughness of all nanocomposites compared to homopolymers. Moreover, nanocomposites had toughness values greater than 10-times compared to the corresponding kraft-lignin/polymer blend system. In this context, according to the authors, the combination of mechanical properties along with the fine control of the composite microstructure should render polymer-grafted lignin composites a platform for developing advanced materials based on renewable resources. Schorr et al. (2015) [34] used unmodified and maleated Kraft lignins as fillers in recycled polystyrene (RPS) made with different ratios by means of melt blending. Interestingly, the morphological study revealed better compatibility with RPS for unmodified Kraft lignins than maleated Kraft lignins except for the composite in which maleated lignins surface treatment was used.

2.1.4. Polyamide (PA)

Environmentally friendly bio-filled composites of various proportions of polyamide 6 (PA6) and technical lignin have been prepared using a twin-screw extruder by Sallem-Idrissi (2016) [35]. Young modulus and yield stress have been found to be near to the pure PA6. Moreover, the addition of lignin seems to lead to an improvement of the ductility of the composite, due to the plasticization effect of lignin and to the strong hydrogen-bonding interactions formed between hydroxyl groups of lignin and amine groups of the PA6 [35]. To support these results, the infra-red analysis of lignin-based composite presented a decrease of relative intensities of the PA6 bands at 960 and 930 cm^{-1} (CO-NH in plane vibration), 690 cm^{-1} [out of plane bending of N-H] likely indicating the presence of chain folding and phase modifications in PA6. Therefore, new hydrogen-bonding interactions formed between hydroxyl groups of lignin and amine groups of the PA6 can be attributed to the reactive intermolecular interaction between the two components.

2.1.5. Poly (vinyl alcohol) (PVA)

An innovative investigation has been carried out by Su et al. (2016) [9] by means of preparation of bio-based films of Poly (vinyl alcohol) with alkali lignin and PVA as the matrix materials, glutaraldehyde as the cross-linker, and glycerin as plasticizer. The authors reported that mechanical and thermal properties of the film were better than that of pure PVA film. SEM and FT-IR analysis confirmed that a cross-linking reaction occurred between alkali lignin and PVA.

2.1.6. Lignin in bioplastic composites

According to Sain and Faruk (2015) [10], biopolymers provide an answer to maintaining sustainable development of an economically and environmentally attractive technology. Biological degradable properties, preservation of fossil-based raw compounds and growing environmental concerns have been attracting attention for development of materials from biopolymers. The polylactic acid (PLA) and poly(3-hydroxybutyrate) (PHB) are the most used biopolymers and studies have been conducted to incorporate lignin resin within these polymers.

Spiridon et al. (2015) [11] prepared bio-plastics by melt compounding of two types of lignin obtained from softwood (LB) and hardwood (LO) and PLA. They found an increase in the impact strength and thermal stability of PLA by adding lignin to the PLA matrix. Furthermore, the accelerated weathering had no significant effect on the elastic properties of PLA lignin composites. However, their tensile and impact strength slowly decreased. Additionally, the free surface energy increased after weathering for all materials, especially for PLA and PLA/LB composite, while the thermal properties were less affected after UV exposure for the composite containing softwood lignin. In accordance with the obtained results, lignin-based composites provide an enormous opportunity to design environmentally friendly materials that present higher values compared to the pure PLA.

Likewise, Gordobil et al. (2015) [12] investigated the incorporation of Kraft and acetylated Kraft lignin as filler to produce composites with poly(lactic acid) (PLA) in different concentrations by the extrusion method. Overall, lignin content increased the thermal stability and hydrophobicity of PLA, with the addition of both types of lignin. At low concentrations of both lignins, the tensile strength did not severely deteriorate.

In another approach, Poly(lactide) PLA-lignin composites were manufactured by blending lignin-g-rubber-g-poly(D-lactide) copolymer particles and commercial poly(L-lactide) (PLLA) in chloroform (Sun et al., 2015) [38]. In this study, the resulting renewable and biodegradable composites exhibited a six-fold increase of elongation at break and enhancement in their tensile strength and Young's modulus. Approaches such as light scattering, small angle X-ray scattering (SAXS) and scanning electron microscope (SEM) analysis proposed that a good lignin dispersion and filler/matrix highly interact due to the stereo complexation which is the effective mechanism behind the excellent mechanical performance of these composites. Spiridon et al. (2015) [11] also reported that PLA/lignin nanocomposites have UV light barrier properties, which together with their excellent mechanical performance ensure great potential in packaging applications for these nanocomposites.

Luo et al. (2016) and Kovalcik et al. (2015) [39, 40] studied the blend of lignin and PHB. Green biopolymer blends based on the bacterial polyester poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and softwood Kraft lignin were successfully prepared by Luo et al. (2016). The authors initially used free radical grafting during melt extrusion to improve the interfacial adhesion. Glass transition temperature, melt strength and thermal stability of the biopolymer blend confirmed the better molecular interaction by grafting process.

Kovalcik et al. (2015) [40] combined microbial poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBHV) bio-polyester and Kraft lignin to design new advanced composite materials for packaging applications. The lignin-based composite of microbial PHBHV with methanol fractionated Kraft lignin was prepared by melt processing method. The authors observed that the applied Kraft lignin is highly compatible with microbial PHBHV, and the low thermo-oxidation stability and gas barrier were increased for the lignin-containing materials.

2.2. Lignin in thermosets composites

Several polymer composite systems have been prepared using epoxy as the matrix and lignin as reinforcement (Thakur et al., 2014) [5]. Ferdosian et al. (2016) and Asada et al (2015) [41, 42] synthesized bio-based epoxy resin to replace petroleum-based epoxy resins. Bajwa et al. (2016) [43] studied the application of wheat straw and corn stover based lignin derived from ethanol production for thermosets bio-based composites manufacturing. According to their investigation, both lignins investigated improve some properties such as impact strength, and thermal stability maintaining the modulus and strength features, and it can be used as fillers to improve certain properties of epoxy matrix. Moreover, they emphasized that particle size and weight fraction affected the mechanical properties of composites.

Qiao et al. (2015) [8] used enzymatic hydrolysis lignin (EHL) to partially replace phenol for preparing phenol formaldehyde (PF) resin. According to the authors, up to 50 wt% phenol in PF resin could be replaced by lignin without deteriorating the adhesive strength. Sun et al. (2015) [44] performed complementary studies on the covalent incorporation of depolymerized lignin epoxide into amine-cured epoxy matrix. The resulting lignin-epoxy composites showed improved mechanical properties compared to the neat epoxy. This method presents a promising way to convert lignin to an alternative epoxy monomer and effective additive in epoxy composites.

Stücker et al. 2016 [45] optimized through a steam refining process to extract lignins from non-debarked poplar wood from short growth plantations by enzymatic hydrolysis (EHL) and alkaline extraction (AEL) for the utilization in lignin-phenol-formaldehyde resins (LPF). The physicochemical properties of lignin-phenol-formaldehyde resins produced with these lignins were evaluated, and glue bond performance was tested by the Automated Bonding Evaluation System (ABES). The mechanical properties of these panels showed high dry and wet internal bond strength of LPF bonded particleboards. The internal bond properties of all particle boards fulfill the requirements of P6 commercial particle boards.

The methanol-soluble lignins were used as raw material for the synthesis of bio-based epoxy resins by Asada et al. (2015), in epichlorohydrin and tetramethylammonium chloride (TMAC) under alkaline conditions. According to them, high yields of biomass-derived epoxy resins up to 68% were found, in agreement with the yield from petroleum-based epoxy resin as Bisphenol A. In their study, the thermal stability of cured biomass-derived components was higher than epoxy resins. Furthermore, the cured lignin epoxy resins satisfy the heat-stability property in the field of electronics and make it a potential substitute for fossil resource-derived bisphenol A.

3. Lignin-based carbon fibers

The use of lignin as a renewable resource to produce less-expensive carbon fibers has been taken into great consideration in recent years [5]. The level of interest in lignin-based carbon fibers can be seen in some recent government and industrial programs.

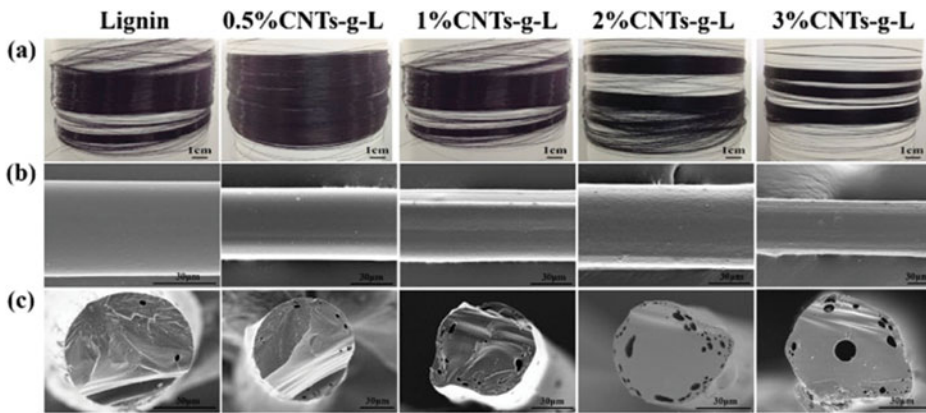


Figure 2. Continuously spooled lignin/CNTs-g-L fibers and their carbonized fibers. Lignin/CNTs-g-L fibers spooled on cylinders (a); surface morphology (b) and cross-sectional morphology (c) of lignin/CNTs-g-L-based carbon fibers [50]. © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rights holder.

The properties of carbon fiber enable their application in a broad variety of products. Carbon fiber has inherent superior specific mechanical, electrical and thermal properties. Among the precursors for the production of carbon fibers, polyacrylonitrile (PAN) is the predominant material, due to the excellent mechanical properties of PAN-based carbon fibers [13, 14]. However, the high cost of PAN precursors, which makes up 43% of the carbon fiber manufacturing cost, limits its utilization in automotive parts [14].

Faced with this situation, lignin has become a potential precursor that may fulfill many of the requirements for carbon fiber [46]. Kubo and Kadla (2005) [49] produced carbon fibers from a blend of hardwood lignin and poly (ethylene terephthalate) (PET) in the ratio of 75:25; the resultant showed modulus of 94 GPa and tensile strength of about 703 MPa.

Some industries have been dedicated to the commercialization concept of intensifying capacity, lowering costs, and growing new markets. As example, Zoltek, a company manufacturer of industrial-grade carbon fiber has used lignin-based carbon fiber as a viable commercial product [48]. This manufacturer has collaborated with Weyerhaeuser to produce carbon fibers by partial substitution of polyacrylonitrile with lignin by using the wet spinning method. The Zoltek and Weyerhaeuser team achieved in producing pilot scale carbon fibers containing up to 45 wt.% lignin. However, the porosity of the spun fibers increased substantially above 15 wt.% addition, which resulted in micron sized voids that were elongated along the fiber axis. The carbon fiber yield was very low due to morphology problems, indicating need for further optimization for maximum lignin content. However, using a lignin loading of 35 wt%, they report carbon fiber strengths of 1.68 GPa and moduli of 201 GPa, which essentially meets DOE (The U.S. Department of Energy) automotive targets [49]. Furthermore, Zoltek determined that the morphology problem is related to the molecular weight distribution difference between the pilot scale and industrial scale lignin-based carbon fiber. Therefore, imparting divergence performances in solution spinning rheology and fiber coagulation (Figure 2).

Attempts to increase the mechanical properties of lignin-based carbon fibers, Wang et al. (2016) [50] prepared carbon nanotubes grafted with lignin (CNTs-g-L) synthesized by grafting lignin molecular chains onto the surface of CNTs to improve the interfacial adhesion between CNTs and lignin chains. The authors synthesized carbonized fibers by the incorporation of CNTs-g-L, enhancing the melt spinnability of lignin, able to perform a continuously

spooled Lignin/CNTs-g-L melt spun fibers. Moreover, the interaction between CNTs-g-L and lignin phases improved the thermal stability and tensile strength of the fibers. The formation of voids was observed and, according to them, it can be controlled by optimizing the stabilization and carbonization processes, and additional work is ongoing to synthesize a suitable compatibilizer that can mitigate void formation.

Lignin-based carbon fibers (CFs) embedded with carbon nanotubes (CNTs) were synthesized through electrospinning lignin/polyacrylonitrile solutions with high thermal stability and super-hydrophobicity properties [15]. In another report, Liu et al. (2016) [29] has been suggested that the incorporation of lignin could potentially increase polyacrylonitrile stabilization efficiency, and improved tensile modulus, tensile strength, and toughness, as compared to the PAN fiber processed. They added that the incorporation of softwood lignin was revealed to reduce the activation energies and increase reaction rates of cyclization, oxidation and crosslinking of gel spun polyacrylonitrile/lignin blend fiber. Zhang and Ogale (2016) [51] studied the processibility of a softwood lignin and its conversion into a meltable precursor. This particularly study found a significant effect of precursor composition and processing conditions on microstructure and properties of resulting precursor and carbon fibers. Oroumei et al. (2015) [52] and Youe et al. (2016) [53] manufactured carbon nanofiber produced from electrospin lignin-g-polyacrylonitrile copolymer. Youe et al. (2016) [53] successfully achieved the graft copolymerization of acrylonitrile (AN) onto methanol-soluble kraft lignin (ML) by electrospinning a solution containing copolymer in N,N-dimethylformamide. Oroumei et al. (2015) [52] stated that organosolv lignin powder is suitable for conversion to carbon fibers. They revealed that lignin-based composite fibers exhibited higher decomposition temperatures and larger carbon yield compared to neat PAN fibers. This specific study showed that, although organosolv lignin, has low-cost precursor of carbon fiber, it possesses low molecular weight compared to PAN, which it becomes viable to implement in carbon fiber production. Ding et al. (2016) [54] investigated organosolv lignin before and after butyration and PAN, as plasticizing additive. In their study, the esterification of lignin with butyric anhydride decreased the viscosity of lignin/PAN blend spinning solutions. They manipulated the molecular structure of lignin following by thermo-stabilization and carbonization treatment. In their study, the authors found a new method for the controlling the interfiber bonding of lignin-based carbon nanofiber mats. The results indicated that interfiber bonding in electrospun CF mats, induced by the high thermal mobility of butyrate lignin, enhanced their mechanical properties even higher than PAN-based carbon fiber.

4. Lignin-reinforced rubber

Natural rubber (NR) is an important industrial raw material used extensively in many applications. NR displays remarkable properties and reinforcing fillers are often added in this matrix to improve the modulus, hardness, wear resistance and reduce the material cost [55]. Recently, numerous academic papers related to preparations of rubber/lignin composites have been published. Phakkeeree et al. (2016) and Bahl et al. (2014) [56, 57] showed the role of filler networks for the excellent reinforcement of rubber in which lignin acted similarly to inorganic fillers. In another study, Tran et al. (2016) [58] developed 50% renewable thermoplastic elastomers called acrylonitrile-butadiene-lignin (ABL) as alternative to ABS by replacing styrene with nanoscale lignin (Figure 3).

Lignin was dispersed in a network of sheets throughout the rubber matrix. SAXS was used to characterize the network of lignin clusters within the rubber matrix on this green renewable polymer which is ten times tougher than ABS. According to the researchers, the smallest lignin particle size in rubber matrix improved the tensile property of epoxidized

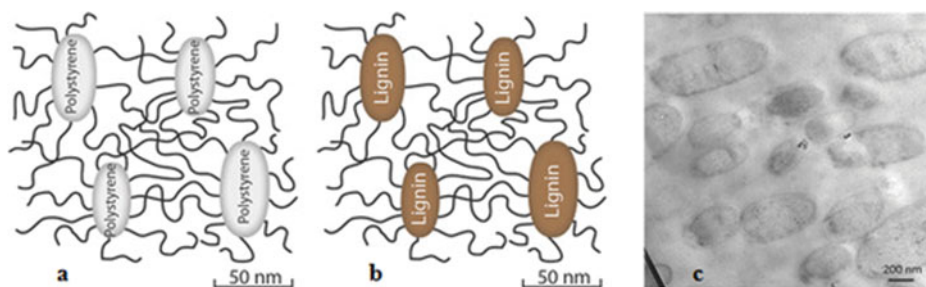


Figure 3. a) Schematic of styrene-butadiene-styrene block copolymer morphology. b) Hypothetical lignin multiphase polymer in soft matrix. c) Transmission electron microscopy image of NBR-33/Kraft softwood lignin blend (50/50) [58]. © John Wiley and Sons. Reproduced by permission of John Wiley and Sons. Permission to reuse must be obtained from the rightsholder.

natural rubber matrix. In addition, the interaction between fractionated lignin and NR had a very large effect on both the morphology and mechanical properties [58].

Yu et al. (2016) [59] stated that using silica and lignin as a hybrid filler could combine both advantages of the two fillers. Partial replacement of silica by lignin in the blends slightly decreased the mechanical properties of composites. However, the inclusion of lignin can improve the processability, anti-aging resistance and anti-flex cracking of composites. Interestingly, the vulcanize containing 1:1.5 of lignin/silica in hybrid filler exhibited optimal mechanical properties. According to the authors, this specific composition possesses the high wet grip property and low rolling resistance, which makes the composite promising for the green tire products. A hot reactive mixing has been confirmed by Bova et al. (2016) [60] to be an effective method for increasing the compatibility of lignin/carbon black fillers and nitrile containing butadiene rubber. The addition of carbon black acting as rubber reinforcement, polyethylene oxide as adhesion promoter and hydrogen bond acceptor, and boric acid and dicumyl peroxide as crosslinkers, produces a range of materials with high elongation when used with hardwood lignin, and high tensile strength near that of engineering materials. Bova et al. (2016) [60] pointed out that these results opens new opportunities for using lignin not simply as a filler, but as an independent polymeric phase in polymer blends, and expands upon the opportunities available for the future commercial valorization of lignin into greener durable products.

5. Lignin-based foaming materials

The use of polyols obtained from renewable sources combined with the reuse of industrial residues such as lignin is potentially approaching as a valid substitute for petroleum-based polymers [61]. Recently, discussions regarding lignin as substitute for polyols in polyurethane foams, phenols in phenolic foams, and as reinforcing agent have been investigated. In an interesting approach, Santos et al. (2016) [62] used polyurethane foam embedded with lignin as filler for the removal of crude oil from contaminated water. Zhang et al. (2015) [63] employed two types of modification of lignin to improve the compatibility of lignin fillers and polyurethane matrix. Lignin modified with octadecyl isocyanate revealed to be more compatible with the polyurethane matrix than lignin modified with butyric anhydride. High lignin content (up to 30 wt.%) increased Young's modulus and tensile strength, and increased their thermal degradation at high temperatures. Carriço et al. (2016) [64] synthesized a green polyurethane foam with good properties using a mixture of residual raw materials (glycerol and lignin) and castor oil as bio-based polyols. The foams with higher lignin contents confirmed a decrease in thermal stability and an increase in the density, as shown in Figure 4,

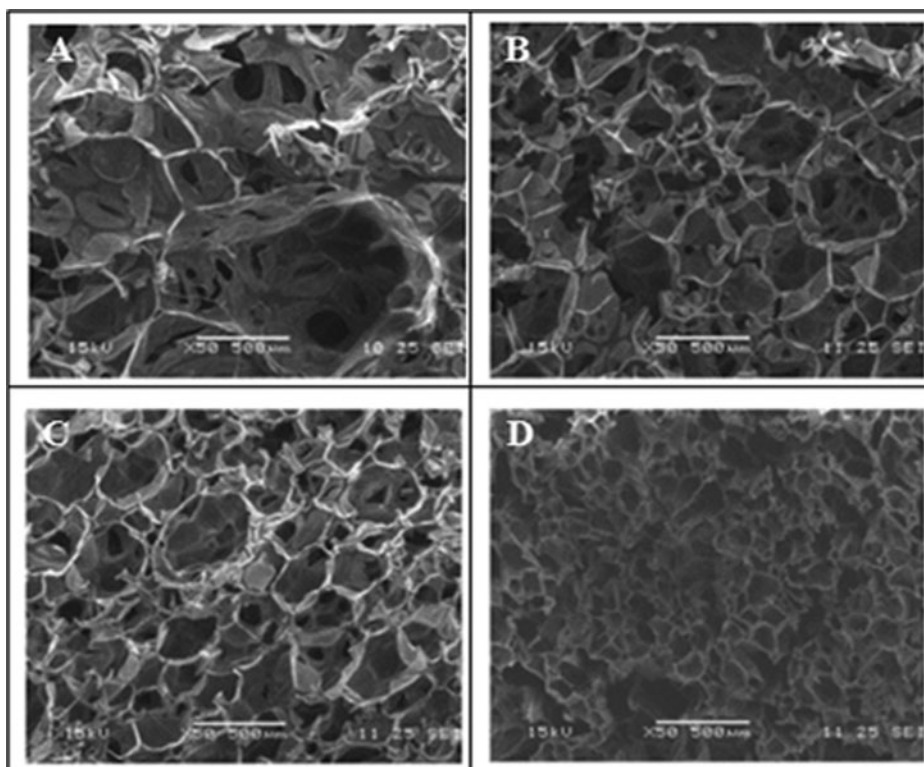


Figure 4. SEM micrograph of bio-based foams varying lignin content: (A) 10%, (B) 17.5%, (C) 20% and (D) 40% [64]. © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholder.

and compressive strength. Lignin-based foams synthesized with 17.5% lignin exhibited better dimensional, thermal properties and the best cell homogeneity.

Tavares et al. 2016 [61] also synthesized polyurethanes based on kraft lignin and castor oil. The results indicate that lignin increases the glass transition temperature, and consequently the crosslinking density and the ultimate stress. Cateto et al. (2015) [65] produced rigid polyurethane (RPU) foam using lignin-based polyols obtained by oxypropylation of four distinct lignins (Alcell, Indulin AT, Curan 27-11P, and Sarkanda). Although the 100% of lignin-based polyols foams obtained were brittle and heterogenous, the foam with ratio of 20% of lignin led to similar properties to the reference foam. Mahmood et al. (2015) [66] demonstrated that the hydrolysis lignin can be liquefied and applied as a promising alternative source to produce low molecular weight product which can be a suitable precursor for polyols/polyurethanes. They liquefied (HL) to a low average molecular weight intermediate by using water–ethanol mixture. According to their results, bio-based rigid polyurethane (BRPU) foams displayed higher compression modulus and strengths to a reference foam prepared from commercial sucrose polyols. The BRPU foams were thermally stable up to 200 °C and the thermal conductivity was low, making them candidates for insulation and construction materials.

6. Lignin-based aerogels

Lignin is a biopolymer based on three phenolic monomers crosslinked to form a 3D network structure. Thus, some authors have used the lignin molecules to partially replace phenolic resins, such as resorcinol-formaldehyde, employed in the synthesis of aerogels [18, 67, 68].

Lignin-based aerogels belong to a special class of materials which has been gaining prominence in the area of research for the use of lignocellulosics [17, 18, 67, 69,70]. Aerogel is a general term for solid nanoporous materials with organic or inorganic origin that exhibit a conserved three-dimensional polymeric network. This nanostructured network is produced by sol-gel process wherein the liquid solvent contained within the pores of the gel is replaced by a gas through hypercritical drying which prevents the collapse of the gas with the gel solid network [17, 20, 71]. The resulting material is a nanoporous ultralight aerogels whose pores can have different diameters sizes: micropores (<2 nm), mesopores (between 2–50 nm) and macropores (>50 nm) [17, 72]. Thus, the aerogels present unique properties such as transparency, high specific surface area and porosity, low density, flexibility, high mechanical strength, good thermal stability and low thermal and electric conductivity [17, 19, 20, 68]. From these features, organic aerogels have potential applications including thermal insulator, adsorbent, filter materials, catalyst, chemical sensors and drug delivery materials [16, 18, 20].

Chen et al. (2011) [67] produced a lignin-resorcinol-formaldehyde (LRF) aerogel under supercritical ethanol drying conditions (250 °C; 10 MPa) and compared to resorcinol-formaldehyde (RF) aerogel. Although lignin is a low-cost natural raw material, it is less reactive to formaldehyde than the resorcinol. Results showed that the high concentration of lignin (100–90%) prevented the sol-gel reaction of LR and formaldehyde. Like this, the surface area and volume of micropore of the LRF was lower than RF, but the density became larger.

On the same line, Grisechko et al. (2013) [17] studied the lignin-phenol-formaldehyde (LPF) aerogels. However, their studies showed that aerogels can be obtained using more lignin and less formaldehyde. Besides, although phenol is less reactive than resorcinol, it is much cheaper.

Phenol is considered a small molecule being able to form micropores and lignin is a macromolecule that generates mainly mesopores when crosslinked with formaldehyde. Thus when phenol and lignin concentrations is increased, the density of crosslinks decreases and more mesopores are observed. Grisechko and co-workers replaced synthetic phenol for tannin, a phenolic natural compound found in several plants [73]. The tannin-lignin-formaldehyde aerogel has been showed an important level of natural component which may be applied in the biomedical area.

LRF, RF and LPF aerogels are fragile structures. Thereby, Xu et al. (2015) [68] used in their studies bacterial cellulose (BC) in order to toughen the LRF aerogel. By using a simple methodology the authors first impregnated BC gel with LRF gel by sonication to form the BC–LRF hydrogel. This hydrogel was converted to aerogel by CO₂ supercritical drying. The BC–LRF aerogel obtained was carbonized using an horizontal tube furnace (Atomate). The BC–LRF Carbon aerogels form a unique blackberry-like nanostructure that consist core-shell structured carbon nanofibers and large mesopore concentration that facilitate ion transportation and adsorption. These characteristics allow several applications, including oil/water separation, supercapacitors and sensors.

Wang et al. (2016) [70] developed lignin aerogels of nanocellulose which acts as an adhesion agent. They tested aerogels containing lignin content from 0 to 95% of material. The aerogels were prepared using 1-butyl-3-methylimidazolium chloride (BMIMCl) that simultaneously dissolves cellulose and lignin. After water addition, wet gel was produced and subsequently lyophilized to preserve the porous network formed. Lignin filled the larger pores and decreased the porosity of aerogels, promoting a potential improvement in the mechanical and thermal insulation performance of these materials. The aerogel containing 90% lignin presented an uniform structure. However, the addition of 95% lignin increased abruptly the density, leading to rupture the nanocellulose network.

Recent studies showed the use of aerogels in biomedical application as drug delivery, scaffolds for tissue engineering and regenerative medicine (TERM) [19, 69]. Quraishi et al. (2015) [69] developed alginate-lignin aerogels toward TERM applications. In vitro tests showed that aerogels are bioactive, non-cytotoxicity and feature good cell adhesion on surface of the scaffolds.

7. Antioxidant properties

Nowadays, one of most promising use of lignin compounds is due to their antioxidant capacity. Thus, a concise characterization is the first step to know the real antioxidant capacity of natural compounds, once the heterogeneity of lignin negatively influences its applicability (Arshanitsa et al., 2013) [74]. Antioxidants compounds are chemicals that inhibit the oxidation process by acting over free radicals. Those chemicals are species containing one or more unpaired electrons highly reactive which trigger chain reaction mechanisms causing damages in biological or non-biological systems [75, 76]. The oxidation reaction typically follows three main steps including: initiation (free radicals are being produced), propagation (free radicals are created through a chain reaction involving a series of molecules), and termination (when two free radicals interact each other to end the reaction). Antioxidants functionality is related to the effectiveness of activation energy, rate constants, oxidation-reduction potential and antioxidant solubility. In general, potent antioxidants interrupt the free radical chain reaction [75].

Most of the free radicals found in vivo are reactive oxygen species (ROS) or reactive nitrogen species (RNS). The ROS are oxygen-centered free radicals, including the superoxide radical anion ($\text{O}_2^{\bullet-}$), hydroxyl ($\bullet\text{OH}$), alkoxy ($\text{RO}\bullet$), $\text{ROO}\bullet$, and hydroperoxyl ($\text{HOO}\bullet$) radicals. The RNS are nitrogen-based radicals, including peroxyxynitrite ($\text{ONOO}\bullet$), nitrite oxide ($\text{NO}\bullet$), and nitrogen dioxide ($\text{NO}_2\bullet$) [76, 77]. After generation, OH species react immediately to any molecule in its vicinity with little selectivity toward the various possible sites of attack, even causing important oxidative damage to DNA [78]. Among the oxygen-centered radicals, OH is the most electrophilic and reactive, with a half-life of $\sim 10^{-9}$ s (Pryor, 1988). It can react through a wide variety of mechanisms and chemical compounds. The reactions take place at, or close to, diffusion-controlled rates constants of about $\geq 10^9$ M/s [79, 80].

A large number of antioxidant is known and their classification depends on the number of phenols subunit and their mode of action. Phenolic acids are simple phenols containing only a phenol functionality whereas polyphenols contain two (e.g. flavonoids and stilbenes) or more phenol subunits (e.g. tannins). Phenolic acids hold one carboxylic acid function and two carbon frameworks, giving rise to the hydroxycinnamic (e.g. caffeic, *p*-coumaric, ferulic, and sinapic acid, with a three-carbon side chain C6-C3) and hydroxybenzoic structures (gallic, *p*-hydroxybenzoic, protocatechuic, vanillic and syringic, which in common have the C6-C1 structure) [76, 81]. Hydroxycinnamic acid exhibit higher antioxidant activity due to the $\text{CH}=\text{CH}-\text{COOH}$ group, H-donating capacity and radical stabilization than the $-\text{COOH}$ group present in hydroxybenzoic acids [81, 23]. In general, phenolic compounds with functional groups containing oxygen ($-\text{OH}$, $-\text{CO}$, COOH) in the side chain are less inhibitory, whereas the most inhibitory phenolic fragments are those containing a double bound in α , β positions of the side chain, and a methyl group in the γ position [82].

Antioxidants are classified into two types according to their mechanism of action. The Type I mechanism or chain breaking act as chemicals species able to prevent oxidation by acting as free-radical scavengers. It may occur by hydrogen-atom transfer (HAT), proton-coupled electron transfer (PCET), radical adduct formation (RAF), single electron transfer (SET),

sequential proton-less electron transfer (SPLET), sequential electron proton transfer (SEPT), and sequential proton-loss hydrogen-atom transfer (SPLHAT) [84]. The Type II or preventive mechanism, retard the oxidation process by indirect pathways, including metal chelation, decomposition of hydroperoxides to nonradical species, repairing of primary antioxidants by hydrogen or electron donation, deactivation of singlet oxygen or sequestration of triplet oxygen, and absorption of UV radiation [76, 84]. Besides types of mechanism, the geometrical and electronic features determine the antioxidant activity of polyphenols. When an antioxidant (A) interacts with a very reactive radical ($R\bullet$) it becomes a radical itself ($A\bullet$), giving rise to harmless species (RH). The newly formed radical is less reactive and more stable. Thus, the obtained radical $A\bullet$ is highly stable and therefore unreactive. In the most proposed working mechanisms, a hydrogen, an electron, or their mixing is involved. The reaction mechanism by which the primary and secondary antioxidants can act depend on their intrinsic abilities [76].

7.1. Fragmentation of lignin

Lignin is a heterogeneous polar polymer. Even under extremely alkaline conditions, the polymer retains memory of the original macromolecular structure [85]. This may limit their reactivity with the radicals responsible for the oxidation, thus reducing the protecting effect when compared to synthetic antioxidants. Besides, its high polydispersity and high molecular weight limit lignin's applications without previously promote fractionation [22]. When acting as antioxidant, lignin-derived units have the ability to break the oxidation propagation reaction through hydrogen donation, which occurs primarily due to the presence of phenolic hydroxyl groups [75]. Lignin is composed by methoxyl functional groups and a propanoic chain; this configuration has many properties desirable for value-added products [86]. The presence of some functional groups in lignin can exert strong antioxidant activity, being hydroxycinnamic acids the most important antioxidant [87]. Fragmentation of lignin is extremely important step to access those compounds, due to its heterogeneous composition.

Plant phenolic compounds can be divided into four groups: phenolic acids (gallic, caffeic), phenolic diterpenes, flavonoids (quercetin), and volatile oils. Each group acts differently under the free radical [75]. A wide range of lignin-based compounds can be obtained by physical, chemical and biological processes with the specific purpose to fragment the macromolecule. For all cases, extraction methods and solubility affects the phenolic contents, or by reducing power [88] or acting minor effect over the phenolic hydroxyl functional groups, that has straight relationship with antioxidant capacity. Some chemicals can modify specific functional groups. Arshanitsa et al. (2013) [74] observed lignin fractions extracted by single or mixed solvents showed antioxidant activities and methoxyl group differences were more prominent mainly in fractions obtained by mixing dichloromethane and methanol. Impurities as polysaccharides may affect the efficiency of lignin fraction by changing the polarity; polysaccharides are considered more polar than lignin and by diluting the reactive phenolic compounds [22]. Thus, fractionation processes with organic solvents can overcome this bottleneck resulting in chemicals of different structures [74, 89]. Autohydrolysis of liquor from corn residues can provide low molecular weight molecules with better radical scavenging capacity [90]. The essential structure of the natural phenolic antioxidants makes them able to extend the conjugation upon the radicalization process [91]. The size can vary from simple phenolic molecules to highly polymerized compounds, referred as polyphenols. Most occurring phenolic compounds are linked to polysaccharides, as lignin and hemicelluloses [81].

Highest phenolic OH content corresponds to the lowest antioxidant activity. Compared to bran lignin, kraft lignin has the lowest total OH content. Both have low solubility which can be caused by varying the average of molecular weight and high total hydroxyl content, respectively. Solubility is largely affected by the molecular weight (MW) than does polarity. Lignin fractions with low MW and low total content (aliphatic + phenolic) tend to improve the compatibility (blend morphology) and consequently the antioxidant activity. The polydispersity of lignin seems to be a rather negative factor, once high MW chains limiting the solubility of active low molecular species [22]. Undesirable components that decrease antioxidant activity can occur during lignin fractionation. Aliphatic compounds can be originated from waxes and parafins intrinsic to wheat straw. Fractionation of BIOLIGNINtm with organic solvents with different polarity is a prospective tool for obtaining homogeneous lignin products with antioxidant activity [74].

7.2. Antioxidant activity for composites

Lignin can be incorporated into composites to take advantage of its structure and to stabilize the material against photo and thermo oxidation. The phenol content has an important role in antioxidant activity, which is the case of the compatibility between the additive (lignin) and the polymer matrix, while aliphatic and phenolic hydroxyls are supposed to decrease the compatibility with the polypropylene matrix [22]. Incorporation of lignin in polypropylene matrix can improve characteristics such as flexural strength and increase temperature of degradation of the composite. Both parameters showed suitable properties when lignin content has increased. On other side, addition of lignin has poor effect on melting behavior, impact and tensile modulus of the same composite [7]. Poor dispersion of lignin in many composites is attributed to its propensity to self-aggregate. To overcome this negative characteristic, application of lignin at nanoscale has been considered [92]. Lignin-based micro particles or microspheres have been recently studied due to their capacity to retain chemicals. Agricultural additives, drugs, cosmetics, and a range of chemicals can be controlled released when supported by microspheres [21, 93, 94, 95]. That structure synthesize lignin acetate, and some parameters like shear rate, mixing time, concentration of surfactant and the type of organic solvent strongly influence the morphology and size of the microspheres [21].

The presence of sterically hindered phenolic hydroxyl groups in the lignin macromolecules opens the possibility of its application as antioxidant for composites e.g. polyurethanes (PU) [74]. However, technical lignin has weak solubility in organic solvents, which restricts their application in PU systems, thus fractionation is one of the pathways for obtaining more uniform completely soluble products for PU production. Arshanitsa et al. (2013) [74] promoted the solubilization of wheat straw lignin by using dichloromethane and methane yielding 18%. In this case, fractionation had minor influence in the content of phenolic hydroxyl groups. By the opposite, methoxyl group differences were more prominent mainly with fractions obtained by mixing the organic solvents. For this fraction, lignin fractions showed more condensation and high content of phenolic hydroxyl group (included condensed phenolic units, i.e., byphenil- and diphenyl- methane lignin substructures) was observed. Revealed by TGA analysis, the presence of lignin fractions on PU films promoted antioxidant effect which stabilized PU against oxidation.

Replacement of phenol by lignin in the production of phenol-formaldehyde resins has been extensively studied once they have similar structure. However, several obstacles should be overcome. Introduction of lignin at large scale decreased the thermal stability of the resin, leading to a lowered decomposition temperature. Thus, Wang et al. (2009) [96] proposed to

replace the ratio of phenol with lignin less than 50%, although this ratio can be increased by purifying the lignin feedstock from white pine sawdust before the resin synthesis. Eco-friendly alternative to synthetic rubbers can be achieved by using lignin. Styrene-butadiene rubbers are the most frequent adhesive used in the carpet backing system. As an alternative, adhesive-based lignin was produced by pre-activation step to oxidize lignin by a laccase-enhancer system followed by a phenolation step. In this case, natural phenolic compounds were copolymerized with lignin in order to increase its content of quinone structures reactive towards tool [97].

Lignin has antioxidant capacity over a range of UV concentration showing stability after exposition to UVA light. The absorbance of irradiated lignin by UV light appeared similar, showing that the solution-containing lignin remained stable over 60 days [2].

7.3. Radical scavenging and chelating activities for biological purposes

Phenolic compounds are essential for the human diet due to their antioxidant properties. The size can vary from simple phenolic molecules to highly polymerized compounds which are referred as “polyphenols” [81]. Radical scavenging activity is driven by the stability of the radical formed, increasing if additional conjugation with substituents take place simple molecules to polyphenols. However, if this extension of conjugation took place due to carbonyl groups in the propanoic side chain, then the radical scavenging activities decrease significantly. The presence in the propanoic chain of a double bond conjugated with the aromatic ring decreases the scavenging activity of isoeugenol in comparison with guaiacol and propyl guaiacol. At the same time, the presence of a double bond between C_β and C_γ atoms in the side chain of eugenol increased the radical scavenging ability [98].

Oxidative stress, induced by the generation of ROS (O_2^- , OH, H_2O_2 , ROOH, O_3 , 1O_2) are considered the major causative factors of many healthy problems, including diabetes and cardiovascular diseases [77]. Singlet state oxygen (1O_2) can be generated in response to temperature change, reduction of activation energy (presence of transition metals), exposure to UV light, and physical damage to tissues. Those types of free radicals can cause biological damage to macromolecule and membrane constituents. Ionizing radiations cause severe damage to issue owing to OH about 60–70% of damage [75, 99].

Numerous beneficial effects have been owned to antioxidants such as anticancer, anti-inflammatory, antibacterial, antiviral, cardioprotective, neuroprotective, therapeutical use on diabetes, osteoporosis, arthritis, cataracts, anti-HIV, DNA protecting, anticarcinogenic, anti-tumor effects etc [24, 100, 101, 102]. The benefits are related to the ability of antioxidants inhibit oxidative stress (OS) and the associated molecular damage [76]. Antioxidants also present chelating ability against a series of metal ions like Fe(III) and Cu(II) by preventing or inhibit ROS by limiting OH production [76] Green-based suncream offers stability to heat and oxidation in contrast with chemical synthesized chemicals [87].

The addition of antioxidants is required to preserve flavor and color and to avoid vitamin destruction. Fatty foods without antioxidants can become spoilt, with rancid odor and flavor [103]. Lignin can be applied for stabilization for food and feed due to its antioxidant, as well antifungal and antiparasitic properties. Some evidences in dogs has proved that when lignin was used as feed, it can be metabolized by the animal by detecting benzoic acid in their urine [82].

Wheat straw lignin fractions obtained from ozone and soaking aqueous ammonia pretreatment has potential to be used as feedstock for guaiacol and 4-vinylguaiacol as antioxidants. The antioxidant activity was due to the presence of monomers derived from hydroxycinnamic

acids and guaiacyl units [86]. Lignosulfonate is less effective to inhibit lipid peroxidation. Lignosulfonate lignin (with highest Mn) and bagasse (lowest Mn) presented the lowest and greatest antioxidant activity, respectively.

Hydrothermal treatment of vanillin in oxidative conditions may provide a wide array of hydrophilic intermediates, reactive enough to form hydro soluble oligomers. At moderated oxygen pressure, the main products generated are hydrophilic oligomers rich in free and bonded carboxylic groups. CO₂ may be evolved by decarboxylation of vanillic acid opening the aromatic ring, thus the nature of the catalyst significantly affects the nature of the products formed.

Ferric reducing antioxidant power (FRAP) compounds can be obtained by fractioning lignin with acetone. Acetone-extracted lignin fractions showed the highest FRAP value that might be due to the hydroxyl groups together to conjugated double bond. In this case, the antioxidant capacity is based on the mechanism of electron donating activity. Acacia lignin fractions exhibited higher hydrogen peroxide scavenging activity compared to gallic and tannic acids, that can be due to the presence of C=O of carboxyl or ketone groups that appears at 1700 cm⁻¹ in FTIR spectrum [88].

8. Challenges and prospects for the future

This review summarizes recent studies of structures, preparation and application of lignin in high-performance materials. The notable properties of lignin, including high availability, low cost, ecologically friendliness as well as antioxidant, antimicrobial, biodegradable properties and reinforcing ability succeeds in exploiting as an ideal candidate for an extensive variety of applications. Substantial efforts are now being made to successfully use lignin as one of the components in polymer matrices for high performance composite applications [5]. The progress of efficient biorefineries that integrate production of bio-based products can reduce costs and allow bio-based products to compete more effectively with petroleum-based products on price. In contrast to most synthetic polymers, lignin has complex structure, which makes its characterization and processing the main factors limiting for wide-scale use in biorefineries [104].

Systematic studies are still needed considering the complexity of the structure of lignin. Fundamental understandings of lignin molecular architecture, stability, dispersion and the ability to control its morphology, will certainly lead to advancement in synthesizing lignin-based functional materials. Furthermore, it is crucial to characterize the supramolecular structure of lignin in different media to investigate its value-added applications. Molar mass is an important parameter controlling lignin reactivity and rheological performance. In addition, the chemical modification of lignin as an interesting possibility for high value applications. Polymerization systems and reactions should be designed at an industrial scale to allow for ease modification and processing of polymeric materials toward commercially targets. In this context, recent studies have been developed toward the production of lignin-based materials with controlled architecture to the nanoscale. New developments will succeed the synthesis of polymeric materials qualified for competing with commercial polymeric materials and development sustainable practices.

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