Chapter 8
Material Applications of Lignin

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Abstract Recently, lignin has extensively been investigated for its material applications such as biocomposites, hydrogels, surfactants, and other materials. Owing to its aromatic nature, three-dimensional network structures, and abundance of functional groups, lignin is beneficial for replacing petroleum resources and is compatible with other commercial resins, expanding its applications. However, the applications of lignin-based materials are still at an early stage compared to cellulose-based materials due to the inherent molecular complexity and heterogeneity of lignin with technical challenges in its processing. This chapter introduces recent progress in lignin-based composites and hydrogels among various approaches. To better understand lignin-based materials, the impacts of lignin species, contents, synthesis/fabrication methods, and other co-components on the technical performance and characteristics of the lignin-based composites and hydrogels in recent studies are reviewed. In composite applications, lignin can enhance thermal, chemical, and dimensional stability, as well as biodegradability, UV blocking, antioxidant property, and antimicrobial activity. Similarly, lignin-based hydrogels demonstrate excellent biocompatibility with antibacterial and antioxidant properties. Current challenges and future perspectives of lignin-based materials are also discussed in this chapter.

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8.1 Introduction

Recent resource scarcity and environmental concerns increased the demand for green technology to replace petroleum-based chemicals with renewable and sustainable resources. Biomass is one of the promising resources for diverse industrial applications from traditional construction, papermaking, and direct combustion energy source to biofuels, biochemicals, and renewable materials. Except for direct applications of whole biomass for construction and furniture, papermaking is the most typical biomass application. While cellulose has been highlighted as a promising renewable material for paper, nanocrystals, and nanofibers, lignin has been considered an undesired component in most biomass applications. Lignin is an aromatic macromolecule, mainly composed of syringyl, guaiacyl, and *p*-hydroxyphenyl units with different C–O and C–C bonds like β-O-4, β-β, β-5, α-O-4, and 5-5 linkages. Lignin provides structural strength to the plant fibers and protects polysaccharides in the plant cell walls from microbial attacks in nature. However, lignin is a major recalcitrance factor in biological conversion processes since it limits cellulose access to enzymes and deactivates enzymes (Yoo et al. 2020). Similarly, lignin has been removed from biomass during the pulping process to enhance the quality of paper. For these reasons, a certain amount of lignin is necessary to be removed from biomass to accomplish effective biomass utilization. Through mechanical, thermochemical, and biological treatments like pretreatment and pulping, unwanted fractions such as lignin and other extractives are separated from cellulose. The generated lignin has been considered a waste stream or a byproduct in many traditional biorefinery processes. However, lignin has great potential, due to its aromatic structure, relatively high energy content, and sustainability, for industrial applications. Unfortunately, only 2% or less of the generated lignin is used in limited applications such as wood adhesive, surfactant, and other chemical or material uses, while the rest is directly combusted as an energy source (Bajwa et al. 2019). Therefore, further investigation of lignin and its applications is necessary for effective lignin utilization. Valorization of lignin can contribute to the economic competitiveness as well as carbon neutrality of biomass-derived products including pulp products and cellulosic biofuels.

The importance of lignin has been highlighted in many recent publications. More than 64,000 lignin-related articles have been published during the recent four years (2018–2021) according to Web of Science.[1] These articles include fundamental lignin chemistry and biochemistry, lignin-related plant science, lignin utilization, and others. Among these lignin-related publications, articles on "lignin material" or "lignin-based material" were exported for the network map using the keyword co-occurrence analysis in 1006 scientific publications by the full counting method of VOSViewer (Perianes-Rodriguez et al. 2016). As Fig. 8.1 shows, lignin material applications in various fields such as polyurethane, activated carbon, electrodes, fibers, nanoparticles, nanofibers, and films, as well as composites and hydrogels are mainly covered in this chapter.

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[1] Searching date: December 27, 2021.

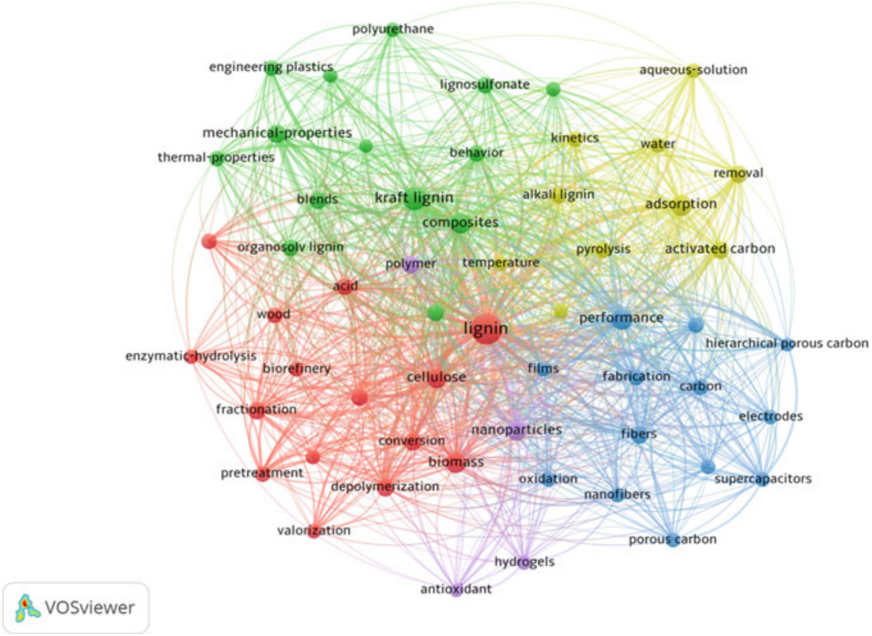

Fig. 8.1 The network map on “lignin material” or “lignin-based material” in the scientific publications from 2018 to 2021

8.2 Lignin-Based Composite Materials

For emerging technologies, the requirements for new materials are increasing with unique properties and multifaceted performance (e.g., lightweightness with high mechanical strength/toughness, flexibility, biodegradability, chemical/thermal resistance). Toward this end, composite materials have been investigated to achieve desirable performances not found in a single material. Typically, the discontinuous constituent is called filler (or reinforcement), and the continuous constituent surrounding the filler is called matrix. The tailored combination of constituent materials enhances their performances and/or imparts new properties with a facile tunability for a wide range of industrial applications. In particular, biocomposites composed of one or more phase(s) derived from a biological origin have been highlighted due to their environmental-friendly characteristics and sustainability.

8.2.1 Fabrication Methods of Lignin-Based Composites

The interaction of lignin with other composite constituents, particle size of lignin, target product shape and size, and other technical and economic factors are considered to determine the proper composite fabrication strategy. The current progress of lignin-based composite fabrication has not yet reached the industrial production level; therefore, among these factors, the interaction of lignin with matrix materials has mostly been discussed at the laboratory scale in previous studies. For maximizing the interfacial areas between materials, homogeneous blending is crucial. However, dispersion of lignin in matrix materials is often challenging because lignin–lignin interaction is stronger than polymer–lignin interaction, resulting in aggregation of lignin molecules. Hence, the dispersion quality of lignin in the polymer matrix depends on the interaction of lignin with the polymer matrices. For instance, Szabó et al. (2017) studied the interaction of lignosulfonate with polypropylene (PP), polystyrene (PS), polycarbonate (PC), and glycol-modified poly(ethylene terephthalate) (PETG) matrix. The authors reported that π electron interactions between lignin and PS, PC, and PETG resulted in better compatibility compared to the reference polymer (i.e., PP) blended by dispersion forces. Also, the authors discussed that the formation of hydrogen bonds between functional groups of PC and PETG with lignosulfonate makes the interactions stronger than the one with PS, which has only aromatic rings without functional groups (Szabó et al. 2017). In this chapter, the fabrication strategy for lignin-based composites is introduced by the dispersion methods: (1) solvent casting, (2) melt-mixing, and (3) extrusion methods (Table 8.1). The applications of lignin-based composites are also discussed with their advantages and disadvantages.

8.2.1.1 Solvent Casting

For the fabrication of lignin-based composite materials, lignin and matrix material(s) are dissolved in a solvent and transferred to substrates or a predefined three-dimensional (3D) mold (Ye et al. 2019). Filler is dispersed in a solvent along with polymer and has a large interparticle distance. The solvent is allowed to evaporate, which increases the solute concentration and thereby increases the viscosity of the composite solution. The increased viscosity reduces the diffusion of the fillers and eventually makes them immobilized in polymer matrices. For the solvent casting method, finding a common good solvent for both lignin and matrix materials is a prerequisite based on the solubilities of lignin and matrix materials. For instance, dimethylsulfoxide (DMSO) was used for the solvent casting of sulfonated poly(ether ketone) (SPEEK) and lignin (Ye et al. 2019), and dimethylformamide (DMF) was applied for that of Nafion and lignin (Ye et al. 2021). Alkali lignin was dissolved in water along with agar for the composite formation (Shankar et al. 2015). Some lignins were chemically modified prior to the dissolution in common solvents to increase

Table 8.1 Summary of fabrication methods and applications of lignin-based composites

	Lignin source	Lignin content	Matrix material	Method	Application	References
Solvent casting	Lignin (source unknown)	0–25 wt%	Sulfonated poly(ether ether ketone) SPEEK	Dissolve SPEEK and lignin in DMSO	Vanadium redox flow battery	Ye et al. (2019)
	Lignin (source unknown)	0–10 wt%	Nafion	Dissolve Nafion and lignin in DMF	Vanadium redox flow battery	Ye et al. (2021)
	Kraft lignin and acetylated kraft lignin	0–10 wt%	Poly(lactic acid)	Dissolve PLA and lignin in chloroform	Biodegradable composite materials	Kim et al. (2017)
	Alkali lignin	20 wt%	Chitosan	Mix chitosan-dispersed lactic acid solution and lignin-dispersed ethanol, and homogenize them for composite film-forming	Food packaging	Crouvisier-Urion et al. (2017)
	Alkali lignin (lignin copolymerized with β-butyrolactone and ε-caprolactone)	0 and 5 wt%	Poly(3-hydroxybutyrate)	Dissolve lignin and poly(3-hydroxybutyrate) in 1,1,1,3,3,3-hexafluoro-2-propanol and process by electrospinning	Biomedical applications	Kai et al. (2018)

(continued)

Table 8.1 (continued)

	Lignin source	Lignin content	Matrix material	Method	Application	References
	Steam pretreatment followed by DES, soda-anthraquinone, hydrotrope, organosolv lignin	0 and 5 wt%	Microcrystalline cellulose	Dissolve lignin and MCC in ionic liquid (DMAc/ LiCl solvent)	Advance packaging materials such as active drugs storage, long-time food storage, and biodegradable packaging	Guo et al. (2019)
	Organosolv lignin	0–50 wt%	Kraft birch pulp	Dissolve lignin and pulp in ionic liquid (1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH] [OAc]))	Low-cost carbon fibers	Le et al. (2021)
	Alkali lignin	0–10 wt%	Agar	Dissolve lignin, agar, and glycerol in distilled water	Food packaging	Shankar et al. (2015)
Melt-mixing	Organosolv hardwood lignin	0–40 wt%	Acrylonitrile-butadiene-rubber 41 & acrylonitrile–butadiene–styrene	Mix lignin and matrix material using Brabender Plasti-Corder Torque Rheometer	3D printing	Nguyen et al. (2018b)
	SW kraft and HW organosolv lignin	0–60 wt%	Nitrile-butadiene rubber, nylon 12, and carbon fibers	Mix lignin and matrix material at elevated temperature using Brabender Plasti-Corder Torque Rheometer	3D printing	Nguyen et al. (2018a)
	Hardwood kraft lignin	0–15 wt%	Poly(lactic acid)	Mix lignin and PLA in a high-speed mixer (MH50-H, DRAIS mixer)	Biodegradable food packaging	da Silva et al. (2019)
	Softwood kraft lignin	0–15 wt%	Poly(butylene succinate)	Mix lignin and PBS by Brabender plastograph internal mixing machine	Biomedical applications	Domínguez-Robles et al. (2020)

(continued)

Table 8.1 (continued)

	Lignin source	Lignin content	Matrix material	Method	Application	References
Extrusion	Softwood kraft lignin	0–3 wt%	Poly(lactic acid)	Extrude lignin and PLA by single screw extruder	Wound dressing	Domínguez-Robles et al. (2019)
	Hydrothermal lignin from eucalyptus	0–60 wt%	Poly(butylene adipate-co-terephthalate)	Extrude lignin and PBAT by twin screw extruder; maleic anhydride-graft-PBAT used as a compatibilizer	Packaging materials, and hygiene products	Xiong et al. (2020)
	Sodium lignosulfate	10 wt%	Polypropylene	Extrude lignin and PP by twin screw extruder; PP-grafted MAH used as a compatibilizer; Isophorone diisocyanate for covalent bonding	Biocomposites	Gil et al. (2019)
	High-temperature mechanical pretreatment followed by enzymatic hydrolysis of lignin	0–50 wt%	Polyhydroxybutyrate	Extrude lignin and PHB by twin screw extruder	3D printing	Vaidya et al. (2019)

their compatibility with the matrix materials. For instance, Kim et al. (2017) acetylated kraft lignin to improve its compatibility with poly(lactic acid) (PLA) and reduce the lignin aggregation by decreasing its hydrogen bond strength (Kim et al. 2017). In addition, Guo et al. (2019) used ionic liquids (i.e., N,N-dimethylacetamide/LiCl solvent) to dissolve both cellulose and lignin for the formation of the composite film (Guo et al. 2019). After the solvent casting, the resultant mixture was kept at ambient temperature to form a film, and then the film was washed with distilled water and dried.

Solvent casting method can also be applied with the mixture of two different solvents with homogenization treatment (Crouvisier-Urion et al. 2017). Crouvisier-Urion et al. (2017) individually dispersed chitosan in 1% (w/w) lactic acid aqueous solution and dispersed lignin in ethanol, and then formed the solution by mixing two solutions for solvent casting. For better dispersion of lignin, the blended solution was further homogenized. Light scattering and two-photon microscopy showed that the homogenization process reduced the particle size of lignin from 5 to 0.6 μm and enhanced the distribution of lignin in the chitosan matrix. The authors also discussed that the reduced lignin particle size via homogenization made the composite film more hydrophobic by exposing more hydrophobic groups like C–C groups of the subunits of lignin at the surface of the film.

The advantage of solvent casting is the superior mixing performance of lignin in the polymer matrix as the starting materials are solubilized at a molecular level prior to the fabrication of the composites. Relatively high lignin loading is applicable in the solvent casting method because of the better dispersion of lignin in the matrix materials. While solvents can enhance the blending of lignin and matrix materials, only limited solvents have good solubility for both lignin and matrix materials. Moreover, many of these solvents have a certain level of toxicity and require additional processing steps for solvent removal, which cause additional operation and equipment costs for the handling of the waste chemicals; therefore, minimal solvent use is desired.

8.2.1.2 Melt-Mixing

Lignin composite materials can also be fabricated by batch-type melt-mixing using an internal mixing machine (Jaafar et al. 2019). In this process, both the matrix material and the filler (i.e., lignin) are added to a mixing chamber of the internal mixing machine. Melting of the matrix material takes place due to the applied heat and friction between mixing components and the equipment rotor. A high-speed mixer (3000 rpm) was used for the fabrication of PLA-lignin composite with 0, 5, 10, and 15 wt% of hardwood kraft lignin loading (da Silva et al. 2019). Homogeneous composite was obtained after 1 min of mixing and molded into a film using a hot press. Nguyen et al. (2018a) fabricated nylon–lignin composite using a Brabender Plasti-Corder Torque Rheometer fitted with a mixing chamber and high-shear twin roller blades for melt-mixing of nylon and lignin (Nguyen et al. 2018a). Nylon 12 was premelted at 190 °C at 90 rpm for 5 min, then mixed with organosolv hardwood (HW) lignin (40–60 wt%) for 15 min to form the composites. Domínguez-Robles et al. (2020) also fabricated poly(butylene succinate)–lignin composite using a Brabender plastograph internal mixing machine. Softwood kraft lignin was melt-mixed with poly(butylene succinate) in the mixing chamber at 150 °C at 80 rpm for 10 min for the composite production (Domínguez-Robles et al. 2020).

Compared to the solvent casting method, melt-mixing does not require processing solvents for fabricating composite materials. However, the challenges of the melt-mixing method are its large energy consumption, high equipment cost, and potential thermal degradation of lignin and/or polymer matrix. Melt-mixing is performed in a batch process; hence, quality variation can occur with each batch, and the mass production of the composite materials is difficult.

8.2.1.3 Extrusion

The other lignin-based composite fabrication method is extrusion which utilizes elevated temperature and shear forces. As the temperature of the extruder increases, solid polymer pellets become polymer melt and form a continuous matrix, and lignin works as a reinforcement constituent. Polymer matrix coats the surface of lignin particles to form the composite. The temperatures of the extruder heating zones are adjusted according to the fluidity of the matrix material (Balasubramanian 2016). Domínguez-Robles et al. (2019) fabricated PLA–lignin composite using a single screw extruder (Domínguez-Robles et al. 2019). PLA pellets were mixed with softwood kraft lignin and castor oil and then extruded at 170–190 °C with an extruder speed of 5 rpm. Xiong et al. (2020) fabricated poly(butylene adipate-co-terephthalate) (PBAT)-lignin composite using a twin screw extruder (Xiong et al. 2020). Kraft lignin was obtained from eucalyptus and methylated with dimethyl carbonate to reduce the lignin aggregation. Maleic anhydride (MAH)-grafted PBAT was used as a compatibilizer. The temperature profile from the feed port to the discharging hole of the extruder was: 130, 135, 142, 138, and 130 °C, with the feed port screw speed at 30 rpm and extruded twin screw at 50 rpm. The process of extrusion was repeated three times, and then the composite was dried at 60 °C for 12 h. Vaidya et al. (2019) fabricated polyhydroxybutyrate (PHB) composite filaments using biorefinery lignin, formed by mechanical pulping and enzymatic hydrolysis (Vaidya et al. 2019). A twin screw with a 40:1 length to diameter ratio (L/D) was used for extrusion at 300 rpm. Lignin was dry-blended with PHB powder at 10, 20, and 50 wt%. A reverse extruder barrel temperature profile, which has a hotter rear zone than the final downstream temperature zone, was used to avoid any potential thermal degradation of the polymer. The temperature profile of this study was: feeder to zone 3: 170 °C, zone 5 to zone 9: 160 °C, and zone 10 and die: 145 °C. The composite filament was cooled at room temperature and used for 3D printing applications with enhanced layer adhesion.

Extrusion has similar advantages (e.g., solvent-free processing) and disadvantages (e.g., high energy consumption, high equipment cost, potential thermal degradation of lignin or polymer matrix) as melt-mixing methods possess. However, extrusion is a continuous process that can fabricate composite materials with consistent quality. Also, 3D printer filaments and masterbatch pellets can be fabricated by the extrusion process.

8.2.2 Impacts of Lignin on the Properties of Lignin-Based Composites and Their Applications

The content and characteristics of lignin affect the composite properties. Ye et al. (2019, 2021) reported that the chemical stability of the composite increased with the lignin content. The authors fabricated the lignin-based composites by dissolving SPEEK and lignin in DMSO (Ye et al. 2019) and Nafion and lignin in DMF (Ye et al. 2021), and the resulted composites showed better chemical stabilities under acidic and oxidizing conditions. These composites were used for vanadium redox flow batteries as hydroxyl groups of lignin provided a transportation path for protons and suppressed vanadium ion permeability through the composite film (Ye et al. 2019, 2021). However, the impact of lignin on the hydrophobicity of the lignin-based composites varied. Vaidya et al. (2019) reported that the increase in biorefinery lignin content improved the hydrophobicity of the PHB-lignin composites (Vaidya et al. 2019). On the contrary, Shanker et al. (2015) reported a decrease in the hydrophobicity of the composite by blending alkaline lignin in the agar composite (Shankar et al. 2015). The authors discussed that the alkaline lignin was more hydrophilic than agar, resulting in the lower water contact angle (i.e., higher hydrophilicity) of the agar–lignin composite than that of the neat agar film. The effect of incorporation of lignin on the hydrophobicity of lignin-based composites depends upon several factors, including relative hydrophobicity of lignin compared to the polymer matrix and exposure of hydrophobic C–C groups on the composite film surface. Incorporating PLA matrix with kraft lignin increased the water vapor permeability (WVP) of the composite, while the incorporation with acetylated kraft lignin reduced the WVP because of the increased hydrophobicity of lignin by acetylation (Kim et al. 2017). The increase of lignin content in agar–lignin composite decreased WVP of the composite because the strong intermolecular interaction between agar and lignin led to good compatibility of these constituents and increased the tortuous path for water molecules (Shankar et al. 2015). The dimensional stability of the composite was also improved by increasing lignin content due to the intermolecular hydrogen bonding of lignin with polymer matrix, rigid benzyl structure of lignin (Ye et al. 2021), and less swelling nature of lignin (Shankar et al. 2015).

The impacts of lignin on the mechanical strength of the lignin-based composite materials were also investigated in previous studies. Ye et al. (2019) reported that the increase of lignin content (up to 15%) showed a positive impact on the mechanical strength of the SPEEK–lignin composite (Ye et al. 2019), while the addition of lignin reduced the tensile strength of the PLA–lignin composite (Kim et al. 2017).

Shanker et al. (2015) also reported that the tensile strength of the composite was improved by up to the inclusion of 3 wt% lignin in agar-lignin composite; however, the tensile strength decreased when the lignin content was increased further. The authors discussed that the lack of uniform dispersion and agglomeration of lignin beyond a certain lignin content reduced the tensile strength (Shankar et al. 2015). The mechanical strength of the composite material was also affected by the compatibility of lignin in the polymer matrix (Xiong et al. 2020). The compatibility can be increased by either chemical modification of lignin (e.g., methylation) or using a compatibilizer. For example, during the fabrication of PBAT–lignin composite, methylated lignin had less lignin aggregation due to the reduced intermolecular hydrogen bonding between hydroxyl groups of lignin molecules. This reduced lignin aggregation enhanced the compatibility of lignin in the composite. Compatibilizer in the polymer matrix also reduced lignin aggregation by increasing interfacial attraction between lignin and polymer matrix. Both methylation of lignin and the addition of a compatibilizer enhanced the tensile strength of the composite film compared to that of PBAT-unmodified lignin composite. The compatibility of lignin in the polymer composite can be further increased by employing primary chemical bonding between lignin and other constituent materials as compared to secondary intermolecular forces such as hydrogen bonding or π-π interactions. Gil et al. (2019) synthesized PP–lignin composite reinforced with glass fiber (GF) via reactive extrusion. Sodium lignosulfonate lignin is utilized with 10 wt% loading in the composites, and PP-grafted maleic anhydride (PP-g-MAH) is used as a compatibilizer. For primary bonding, isophorone diisocyanate (IPDI) was introduced in-situ during the extrusion process for the urethane reaction with hydroxyl groups of lignin and GF. An increase of the IPDI content to 7.5 wt% improved the tensile strength of PP–lignin composites from 28 MPa of 0 wt% IPDI counterpart to 35 MPa by the urethane formation. Above 10 wt% of IPDI content, the crosslinking reaction occurred between IPDI and urethane via allophanate reaction, which further increased the tensile strength to 46 MPa at 20 wt% IPDI content (Gil et al. 2019).

During FDM (fused deposition modeling) 3D printing, the high melt viscosity of polymers often causes clogging at the printing nozzle and reduces the deposition throughput. This problem can be solved by fabricating the composite with a shear-thinning profile. Nguyen et al. (2018a) fabricated the nylon–lignin composite, which showed a shear thinning behavior. At 230 °C and a shear rate of 100 rad/s, nylon 12 showed a high melt viscosity of 1050 Pa · s, while the composite containing 40, 50, and 60 wt% lignin showed a significantly lower melt viscosity of 150, 91, and 32 Pa · s, respectively (Nguyen et al. 2018a). The shear-thinning behavior of the composite was attributed to the formation of spherical lignin particles in the composite, which behaved like a lubricant phase and mobilized the nylon molecules. Vaidya et al. (2019) fabricated a lignin-based composite with biorefinery lignin in the PHB matrix (Vaidya et al. 2019). Melt rheology analysis showed that the melt viscosity of this composite was lower than that of pure PHB. The reduction in shear viscosity (shear thinning profile) enhanced the layer adhesion during 3D printing. However, due to the other impurities such as cellulose and hemicellulose, which have much lower thermal degradation temperatures than lignin and PHB, this biorefinery lignin-based composite material has limited application temperature.

The addition of lignin in the polymer matrix can improve the UV barrier and antioxidant properties of the composites, making them suitable for applications in food packaging. Domínguez-Robles et al. (2019) showed that increasing the lignin content in PLA–lignin composite enhanced the radical scavenging activity. The concentration of residual 2,2-diphenyl-1-picrylhydrazyl (DPPH) after 5 h reduced from 100% with PLA composite to 40, 35, 30, and 25% with 0.5, 1, 2, and 3 wt% lignin content in PLA–lignin composite, respectively (Domínguez-Robles et al. 2019). Biodegradability of the composite is also important in food packaging applications because the package is usually discarded in the waste. According to the biodegradability of PLA–lignin composite in garden soil over 180 days, neat PLA had a negligible reduction in mass, while PLA–lignin composite with 10 wt% lignin content showed a 5 wt% of mass reduction (da Silva et al. 2019).

As discussed earlier, lignin-based composites have various advantages in future material applications. However, there are still several technical challenges in lignin-based composite applications. The amount of lignin loading in the composite materials is currently limited because high lignin content composite showed a poor mechanical strength due to weak cohesive energy of phase separated lignin particles, operating as defect sites in the polymer composites. Also, the surface of composite materials became rough with an increase in lignin loading due to aggregation of lignin, which can cause abrasiveness in the composite. Lignin feedstock variability on the composite performance should be addressed with a deeper fundamental understanding. Further study is necessary to fully elucidate the unrevealed processing-structure–property-performance relationships in lignin-based composite toward practical use of lignin in future composite materials.

8.3 Lignin-Based Hydrogels

Hydrogels are 3D network structures having high water absorption and retention capacity. In the swollen state, hydrogels can retain water up to thousands of times their own dry weights (Meng et al. 2019b). Hence, hydrogels are useful in various applications such as water absorbents for soil water retention in arid and semi-arid regions, enzyme immobilization, drug delivery, wound dressing, tissue engineering, electrodes, biosensors, and food packaging. Petroleum-based monomers and polymers (e.g., acrylic acid, polyacrylamide) are widely used for hydrogel synthesis. However, these petroleum-based hydrogels are limited in biological degradation, and their decomposition compounds have biological toxicity (Song et al. 2020). Natural-based materials like cellulose and lignin have been explored for hydrogel synthesis due to their biodegradability, eco-friendliness, and sustainability (Teow et al. 2018; Song et al. 2020). For instance, cellulose-based hydrogel crosslinked with epichlorohydrin showed an excellent swelling capacity (4650%) and biodegradability (79.5% weight loss in 10 days) (Teow et al. 2018). Lignin also has great potential in this application due to its inherent characteristics such as antibacterial and radical scavenging activity (e.g., antioxidant) (Li et al. 2019; Zhang et al. 2019b). Lignin-based hydrogels showed antibacterial and antioxidant properties, whereas cellulose-based hydrogels need additional Ag nanoparticles or ZnO nanoparticles for these properties (Yadollahi et al. 2015). In this section, synthesis methods and applications of lignin-based hydrogels will be introduced with recent studies.

8.3.1 Synthesis Methods of Lignin-Based Hydrogels

Depending on the crosslinking nature, the synthesis of lignin-based hydrogels can be categorized into three approaches: (1) physical crosslinking, (2) chemical crosslinking, and (3) hybrid double crosslinking. Hydrogels prepared via physical crosslinking are also known as reversible hydrogels because some of them are thermally and mechanically reversible due to the relatively weak bond strength of the crosslinks (Morales et al. 2020). Chemically crosslinked hydrogels have an excellent mechanical strength; however, their synthesis often involves toxic chemicals, which can cause environmental issues and limit their applications in some fields like biomedical applications. Hybrid double-crosslinked hydrogels adopt the advantages of both chemical and physical crosslinking. Chemical crosslinks distribute the stress throughout the structure, and physical crosslinks dissociate to absorb more energy (Liu et al. 2020a). The hydrogel synthesis strategy can be determined according to the desired properties for the targeted applications. Table 8.2 summarizes lignin-based hydrogel synthesis methods with their potential applications.

8.3.1.1 Physical Crosslinking

Lignin-based hydrogels can be synthesized via several physical interactive forces such as hydrogen bonding, hydrophobic association, interpenetrating polymer networking, and electrostatic attraction (Thakur and Thakur 2015). Lignin can form hydrogel via intermolecular hydrogen bonding because of its abundant hydroxyl and carboxyl groups. Lignin-based hydrogel can also be formed by its π-π interaction with other hydrophobic materials. The hydrogel can be synthesized by partial interlacing of lignin with other polymers at the molecular scale in a polymer matrix through an interpenetrating polymer network (IPN) (Karak 2012). In addition, anionic groups of lignin like hydroxyl, carboxyl, and sulfonate groups can have an electrostatic attraction with other polymers having cationic groups like chitosan for the hydrogel synthesis (Ravishankar et al. 2019).

The mechanical strength of physically crosslinked hydrogels is relatively weak because of their low interactive forces. In general, the physical crosslinking approach for hydrogel formation has been applied through: (i) dissolution of lignin and other polymers such as cellulose, polyvinyl alcohol (PVA), chitosan, etc.; (ii) freeze–thaw cycles of the solution for physical crosslinking; and (iii) washing unreacted polymers

Table 8.2 Summary of lignin-based hydrogel synthesis methods and their applications

Crosslinking	Lignin source	Co-material	Crosslinker	Applications	References
Physical	Alkali lignin	Cellulose fibers	–	Hydrogel beads for immobilizing lipase	Park et al. (2015)
	Alkali lignin	Polyvinyl alcohol	–	Agriculture applications	Morales et al. (2020)
	Alkali lignin	Chitosan	–	Wound healing	Ravishankar et al. (2019)
	Lignocellulose from kraft pulping	–	–	Adsorption of lead and copper	Zhang et al. (2019a)
	Poly(ethylene glycol) methyl ether methacrylate grafted kraft lignin	–	–	Biomedical applications	Kai et al. (2015)
	Sodium lignosulfonate	Polyvinyl alcohol	–	Antibacterial application	Li et al. (2019)
	Sodium lignosulfonate	Sodium alginate, konjaku flour	–	Agriculture applications	Song et al. (2020)
	Sodium lignosulfonate	Chitosan, polyvinyl alcohol	–	Wound dressing	Zhang et al. (2019b)
	Cellulolytic enzyme lignin nanoparticles	Chitosan, polyvinyl alcohol	–	Biomedical applications	Yang et al. (2018)
	Aminated alkali lignin	Cellulose	–	Adsorption of dyes and heavy metal ions	Meng et al. (2019a)
Chemical	Alkali lignin	Microcrystalline cellulose	Epichlorohydrin	Alkali lignin fractionation from ethanol–water solution	Dai et al. (2019)
	Kraft lignin	Poly(ethylene glycol) diglycidyl ether	Poly(ethylene glycol) diglycidyl ether	pH-controlled actuator	Dai et al. (2020)

(continued)

Table 8.2 (continued)

Crosslinking	Lignin source	Co-material	Crosslinker	Applications	References
	Kraft lignin	N-isopropylacrylamide	N,N′-methylenebisacrylamide	Biomedical and environmental applications	Zerpa et al. (2018)
	Hydrothermally extracted lignin	Acrylamide	N,N′-methylenebisacrylamide	Catalyst backbone	Gao et al. (2021)
	Alkali lignin	Agarose	Epichlorohydrin	Personal hygiene products, underwater devices, water reservoirs for dry soils	Sathawong et al. (2018)
	Alkali lignin	Poly(ethylene glycol) diglycidyl ether	Poly(ethylene glycol) diglycidyl ether	Soil water retention	Mazloom et al. (2020)
	Sodium lignosulfonate	–	N,N′-methylenebisacrylamide	Removal of cadmium from the soil	Liu et al. (2020b)
	Alkali lignin	Polyacrylonitrile	Poly(ethylene glycol) diglycidyl ether	Flexible supercapacitor	Park et al. (2019)
Hybrid	Corncob lignin	Poly(ethylene glycol) diglycidyl ether	Poly(ethylene glycol) diglycidyl ether	Electrolyte in a flexible supercapacitor	Liu et al. (2020a)
	Alkali lignin nanoparticles	Polyacrylamide	N,N′-methylenebisacrylamide	Tissue engineering, artificial muscles, underwater antifouling materials	Chen et al. (2019)

to obtain the hydrogel. For example, Zhang et al. (2019b) individually dissolved the PVA in deionized water, chitosan in 2% acetic acid solution, and lignosulfonates in deionized water. These solutions were homogeneously mixed for casting (Zhang et al. 2019b). The casted solution in the mold was frozen at −18 °C for 8 h and thawed at room temperature. The freeze–thaw cycle was performed five times to obtain PVA–chitosan–lignin hydrogel, as described in Fig. 8.2. The hydrogel was formed via ionic bonding between amino groups of chitosan and sulfonic groups of lignin, hydrogen bonding between hydroxyl groups of PVA and chitosan, and hydrogen bonding between lignin and PVA as well as lignin and chitosan (not shown in Fig. 8.2). The increase of lignin content from 0 to 30 wt% improved the tensile strength of the hydrogel from 38.55 to 46.87 Mpa. Different freezing and thawing temperatures, time, and numbers of the cycle were investigated in previous studies (Yang et al. 2018; Morales et al. 2020). Yang et al. (2018) synthesized PVA–chitosan–lignin hydrogel with lignin nanoparticles (LNPs) formed by nanoprecipitation of lignin (Yang et al. 2018). The authors reported that the hydrogel formed with 1 wt% LNP had more uniform micropores and better swelling properties than the one with 0 and 3 wt% LNP. As compared to PVA-chitosan hydrogel, the swelling rate of hydrogel with 3 wt% LNP didn't improve despite more homogeneous pore structures.

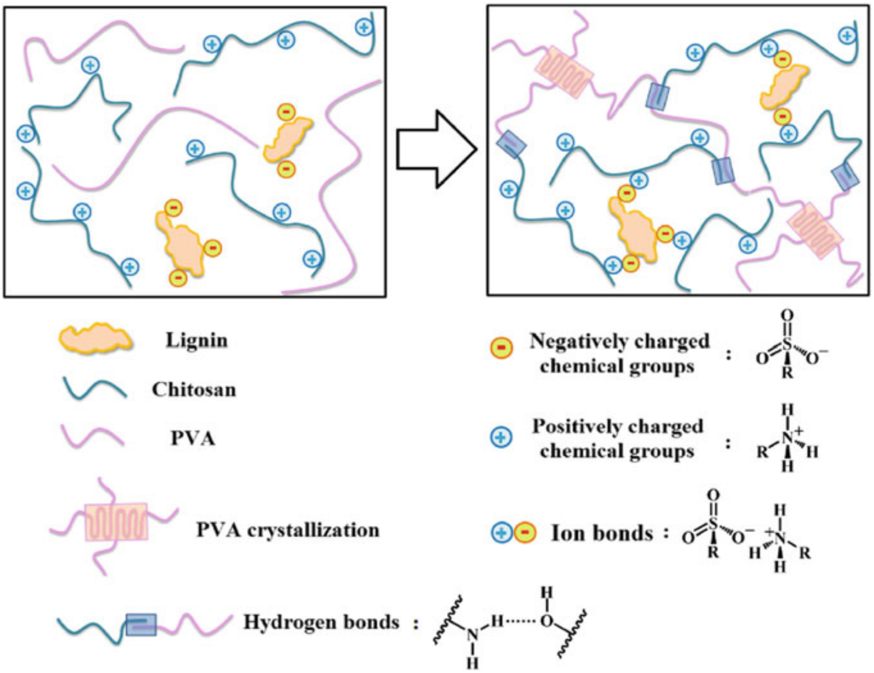

Fig. 8.2 Physical crosslinking mechanism of PVA-chitosan-lignin hydrogel (Reprinted from Mater. Sci. Eng., C 104, 110,002, Zhang, Y., Jiang, M., Zhang, Y., Cao, Q., Wang, X., Han, Y., Sun, G., Li, Y., Zhou, J., Novel lignin–chitosan–PVA composite hydrogel for wound dressing, Copyright (2019), with permission from Elsevier)

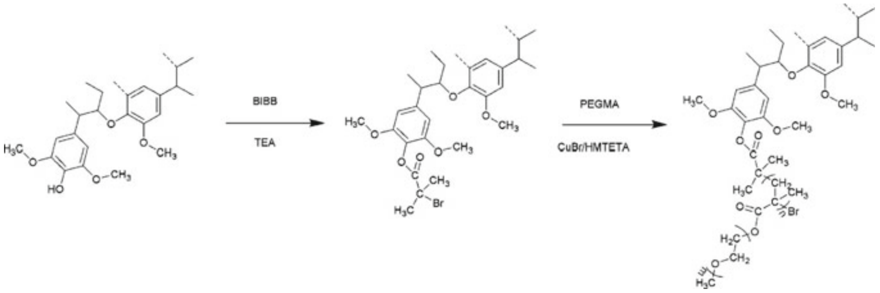

Fig. 8.3 Synthesis of polymer-grafted lignin via atom transfer radical polymerization (ATRP) (Reproduced with permission from Kai et al. (2015), Copyright 2015 American Chemical Society)

Lignin-based hydrogels were also synthesized via physical crosslinking by the inclusion complexation of lignin-based copolymers with α-cyclodextrin (α-CD) (Kai et al. 2015). As shown in Fig. 8.3, lignin-based copolymers were synthesized by atom transfer radical polymerization (ATRP) of kraft lignin with poly(ethylene glycol) methyl ether methacrylate (PEGMA). Firstly, lignin-based organic halide was synthesized, and it worked as a macroinitiator and a polymer backbone for ATRP reaction. In the second step, PEGMA-graft lignin copolymer was synthesized through the ATRP reaction. For the synthesis of hydrogel, PEGMA-lignin copolymer was dissolved in phosphate buffered saline (PBS) and mixed with the α-CD solution in PBS. The mixed solution was kept at room temperature for the formation of hydrogel via physical crosslinking by the inclusion complexation between PEGMA-grafted lignin and α-CD.

8.3.1.2 Chemical Crosslinking

Lignin has plenty of phenolic and aliphatic hydroxyl groups (Rico-García et al. 2020), which enable chemical reactions between lignin and crosslinking agents to synthesize lignin-based hydrogels. Strong covalent bonds in the polymeric networks make it difficult to change the shape of chemically crosslinked hydrogels; therefore, these are often referred to as permanent hydrogels (Thakur and Thakur 2015). Lignin-based hydrogels can be synthesized by chemical crosslinking of lignin with other polymers such as cellulose, PVA, chitosan, poly(ethylene glycol) diglycidyl ether (PEGDGE), polyacrylamide, and polyacrylonitrile with crosslinking agents such as epichlorohydrin, formaldehyde, PEGDGE. Also, unsaturated monomers such as acrylamide and N-isopropylacrylamide can be grafted on the lignin backbone and synthesize hydrogels by radical polymerization of monomers and crosslinkers. Dai et al. (2020) synthesized lignin-based hydrogel with hardwood kraft lignin and PEGDGE as a polymer as well as a crosslinker at 40 °C for 12 h (Dai et al. 2020). The phenolic hydroxyl groups of lignin reacted with epoxy rings of PEGDGE to form the hydrogel by chemical crosslinking. Mazloom et al. (2019, 2020) formed the hydrogel by crosslinking alkali lignin with PEGDGE at different crosslinker concentrations (0.3, 0.4, 0.5, 0.75, and 1.0 mmol/g of lignin) in three types of solvents (deionized water, 1.5 M NaOH, and 3 M NaOH) (Mazloom et al. 2019, 2020). The hydrogel was not formed in deionized water, while it formed in NaOH solutions. Higher swelling capacity (34 g/g-hydrogel) was observed with 1.5 M NaOH compared to 16 g/g-hydrogel with 3 M NaOH. Dai et al. (2019) synthesized lignin-containing cellulose hydrogel with epichlorohydrin (ECH) as a crosslinking agent. Microcrystalline cellulose was dissolved in NaOH/urea solution, and then ECH and alkali lignin were added. Crosslinking reaction was allowed at 60 °C for 12 h to form the hydrogel (Dai et al. 2019). Agarose–lignin hydrogel was also prepared with ECH as a crosslinker. Agarose was dissolved in water at 68 °C and crosslinked with kraft lignin for hydrogel formation (Sathawong et al. 2018). Free radical polymerization by grafting the unsaturated monomers on lignin was also applied for the lignin-based hydrogel synthesis (Meng et al. 2019b). In brief, free radicals can be generated by the thermal decomposition of azobisisobutyronitrile (AIBN) (Fig. 8.4a). Free radical is transferred to lignin to generate a phenoxy radical (Fig. 8.4b). The phenoxy radicals attack the carbon double bond of monomer N-isopropylacrylamide (NIPAAm) and crosslinker N,N′-methylenebisacrylamide (MBAAm) to form the initial propagating chain (Fig. 8.4c). The crosslinked structure of hydrogel is constructed by chain elongation (Fig. 8.4c) (Zerpa et al. 2018). The hydrogel is rinsed with acetone to remove the unreacted monomers. The lignin-based hydrogel had a more porous structure than synthetic hydrogel. Lignin was also modified with functional materials to tailor the hydrogel properties (Gao et al. 2021). Hydrothermally extracted lignin was modified with glycine, which contains amino and carboxyl groups. Glycine–lignin-based hydrogel was synthesized by free radical polymerization with acrylamide as a monomer, MBAAm as a crosslinker, and ammonium persulfate as an initiator.

8.3.1.3 Hybrid Double-Crosslinking

The performances of lignin-based hydrogels can be improved by synthesizing hybrid double-crosslinked hydrogels via a two-step network formation: (1) formation of covalent bonds through chemical crosslinking reaction; and (2) physical crosslinking formed by hydrophobic interactions, ionic interactions, and/or hydrogen bonding (Chen et al. 2019; Liu et al. 2020a). A schematic diagram of the hybrid double crosslinking is shown in Fig. 8.5 (Liu et al. 2020a). Chemical crosslinking reaction of ring-opening polymerization was carried out at 50 °C for 2 h with phenolic groups in lignin and epoxy rings of PEGDGE crosslinker for the formation of single crosslinked (SC) hydrogel. For physical crosslinking, the SC lignin hydrogel was immersed in 1 M H_2SO_4 for 12 h to obtain a double-crosslinked (DC) hydrogel. The protonation of unreacted phenol and carboxyl groups of lignin induced the hydrophobic interactions among lignin chains. The DC hydrogel resulted in 40-fold higher compressive mechanical strength (4.74 MPa) than that of SC hydrogel (0.12 MPa). The covalent crosslinks in the hydrogel efficiently distribute the stress throughout the network and

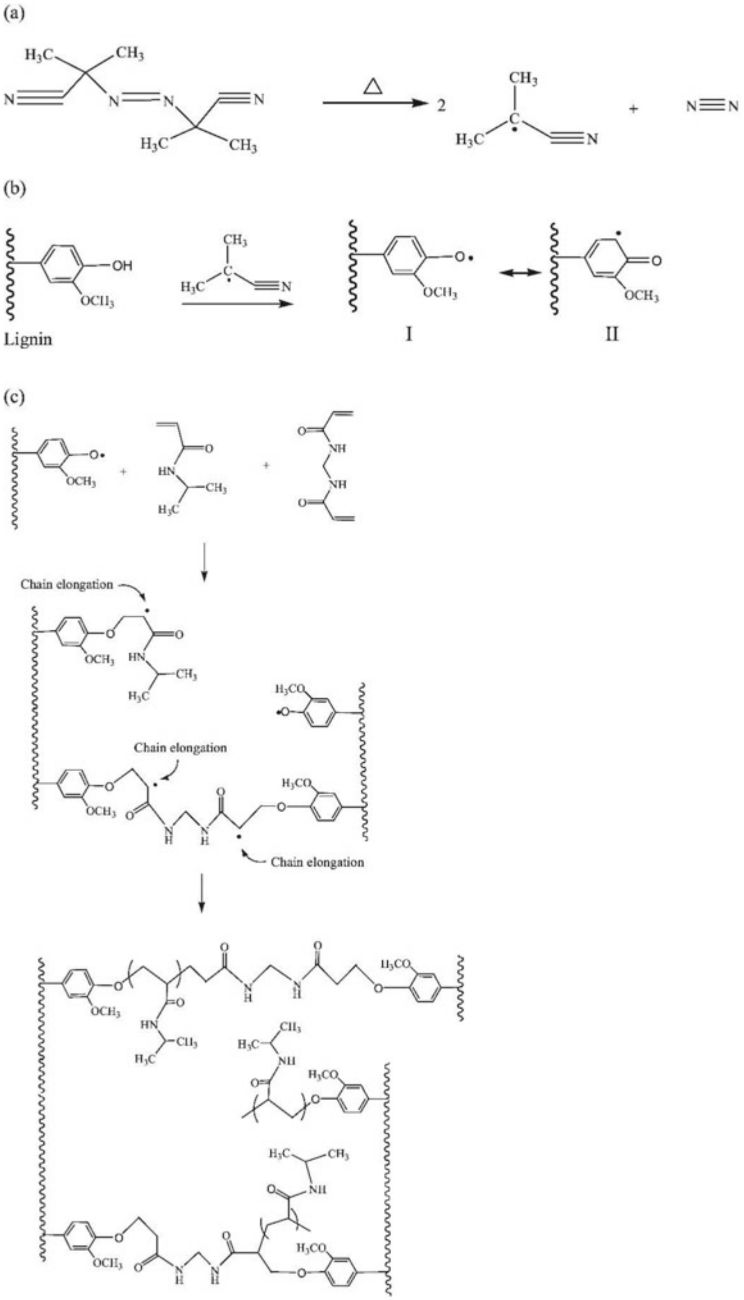

Fig. 8.4 Synthesis of lignin-based hydrogel by free radical polymerization. **a** thermal decomposition of AIBN initiator to generate free radical, **b** formation of phenoxy radicals, and **c** crosslinking reaction (Reproduced with permission from Zerpa et al. (2018), https://pubs.acs.org/doi/10.1021/acsomega.8b01176, Copyright 2018 American Chemical Society)

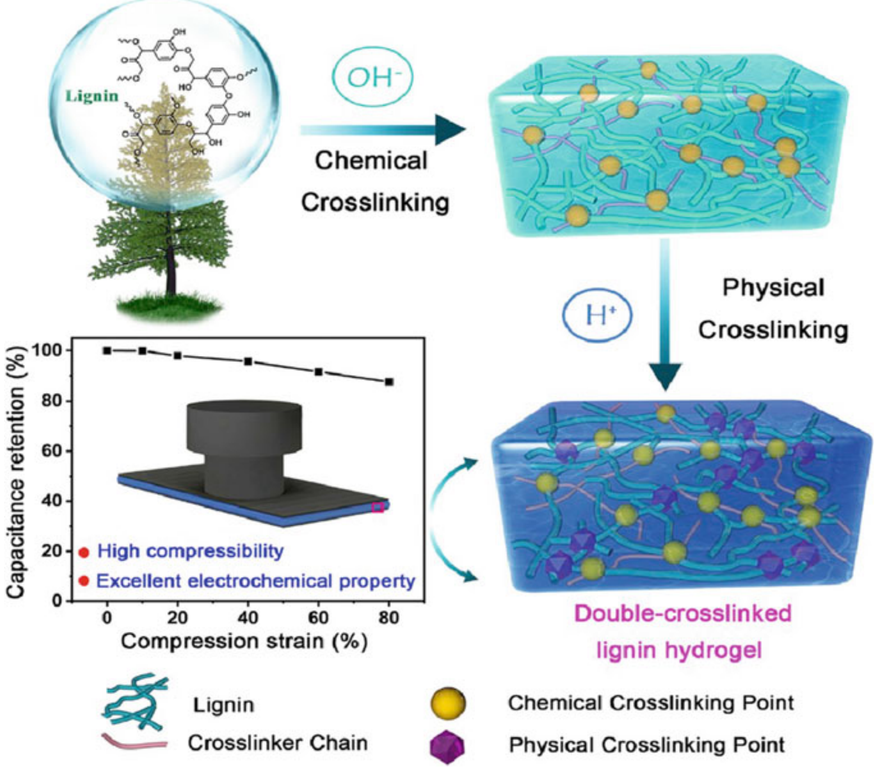

Fig. 8.5 Synthesis of double-crosslinked hydrogel via sequential chemical crosslinking and physical crosslinking (Reprinted from J. Power Sources 449, 227,532, Liu, T., Ren, X., Zhang, J., Liu, J., Ou, R., Guo, C., Yu, X., Wang, Q., Liu, Z., Highly compressible lignin hydrogel electrolytes via double-crosslinked strategy for superior foldable supercapacitors, Copyright (2020), with permission from Elsevier)

maintain the hydrogel shape to ensure recovery to the original state. The reversible physical crosslinks can dissociate to absorb energy and sustain deformations. The DC hydrogel had high ionic conductivity (0.08 S/cm), which was comparable to that of pure H_2SO_4 solution. The DC lignin hydrogel electrolyte-based supercapacitor showed nearly 100% capacitance retention after 500 cycle numbers and 85% capacitance retention at 80% compressive strain.

The single-step hybrid double-crosslinked hydrogel was also performed with lignin nanoparticles (Chen et al. 2019). LNPs with an average particle size of 200 nm were synthesized by ultrasonication. Hydrogen peroxide/ascorbic acid, acrylamide, and MBAAm were used as a redox initiator, a monomer, and a crosslinker, respectively. Hydroxyl free radicals were produced via the reduction of H_2O_2 by ascorbic acid, which had a strong interaction with LNPs and formed phenoxy free radicals on the LNP surface. Free radical polymerization was initiated on the surface of LNPs by the phenoxy free radicals and propagated. Then, MBBAm crosslinked the polyacrylamide (PAM) chains by connecting the neighboring LNPs. Some PAM chains were covalently bonded, and others were intertwined with LNPs via hydrogen bonding. PAM-LNP hydrogel showed higher toughness, elasticity, and stretchability as compared to PAM hydrogel. The inclusion of LNP into PAM hydrogel increased the fracture stress from 0.04 to 7.87 MPa, the toughness from 0.68 to 45.26 kJ/m^3, and the elongation at break from 190 to 750%. No serious deformation or strength degradation was observed after 100 loading–unloading cycles at 80% strain.

8.3.2 Applications of Lignin-Based Hydrogels

Lignin-based hydrogels have a wide range of applications such as soil water retention, adsorbent, flexible supercapacitor, food packaging, wound dressing, drug delivery, and tissue engineering because of their biodegradability, biocompatibility, antibacterial property, antioxidant activity, higher mechanical strength, and chemical and thermal stability.

8.3.2.1 Adsorption Applications

Lignin-based hydrogels showed a highly porous structure and negatively charged phenolic and aliphatic hydroxyl groups, making the lignin-based hydrogels ideal adsorbents. They were applied for the adsorption of both organic (Wang et al. 2017; Dai et al. 2019) and inorganic materials (Zhang et al. 2019a). Large varieties of dyes are used in textile dyeing, leather tanning, printing, and food packaging. These dyes are carcinogenic and mutagenic and need to be removed from wastewater before discharging into the environment. The lignin-based hydrogel was applied to adsorb methylene blue dye, a cationic dye, at pH 1–11 (Wang et al. 2017). The adsorption capacity of lignin-based hydrogel increased as the solution pH increased and leveled off when the pH reached 7 and higher. Protons at low pH competed with dye for adsorption sites, which resulted in poor dye removal. In contrast, high solution pH increased the negatively charged hydroxyl groups, which increased the dye adsorption by higher electrostatic attraction. The adsorption capacity of methylene blue dye on lignin-based hydrogel was up to 9.65 g/g of the hydrogel.

The chemically crosslinked cellulose–lignin hydrogel was also used for the fractionation of alkali lignin (Dai et al. 2019). The hydrogel was immersed in an alkali lignin solution, which had a weight average molecular weight (M_w) of 1054 g/mol with a polydispersity index (PDI) of 1.43. Lower molecular weight lignin (M_w of 499 g/mol) with PDI of 1.13 was adsorbed on the hydrogel, while the unadsorbed lignin showed M_w of 1220 g/mol with PDI of 1.21 in the filtered solution. This lignin-based hydrogel fractionated more uniform lignin fractions with narrow molecular weight distribution. The fractionation of lignin with the lignin-based hydrogel was attributed to smaller pore size and noncovalent π–π interactions between aromatic rings of alkali lignin and the lignin present in the hydrogel. Heteronuclear single quantum coherence (HSQC) nuclear magnetic resonance (NMR) and ^{31}P NMR results showed that the adsorbed and filtered lignin had very similar lignin composition and hydroxyl group contents.

Lignocellulosic (LC) hydrogels were used for the adsorption of copper and lead ions (Zhang et al. 2019a). Biomass with different lignin contents (6.5, 11.6, and 18.4 wt%) was obtained from poplar wood chips by the kraft pulping process using different alkali concentrations of cooking liquor. Lignin-free biomass was also obtained by bleaching the kraft pulp. These biomass solids were dissolved in N-methylmorpholine-N-oxide, and the hydrogels were obtained by solvent exchange with ethanol followed by water. As the lignin content increased up to 11.6 wt%, the adsorption of heavy metal ions (Cu^{2+} and Pb^{2+}) on lignin was improved, while the adsorption decreased when the lignin content was 18.4 wt%. The highest adsorption by the hydrogels with 11.6 wt% lignin content was attributed to the porous network of the hydrogel, which exposed more phenolic groups of lignin and hydroxyl groups of carbohydrates for the complexation with metal ions. However, further increase of lignin content in the hydrogel reduced the uniformity of pore structure due to the aggregation of lignin particles and led to the destruction of the network structure resulting in the decrease of active sites for heavy metals adsorption.

8.3.2.2 Biomedical Applications

Biocompatibility, antibacterial property, antioxidant activity, and low cytotoxicity of lignin (Kai et al. 2018; Domínguez-Robles et al. 2019; Zhang et al. 2019b; da Silva et al. 2019) make lignin-based hydrogels a potential material in biomedical applications such as wound dressing, drug delivery, and antimicrobial coatings. Physical hydrogels and hydrogels crosslinked by non-toxic crosslinkers have been investigated for biomedical applications (Larrañeta et al. 2018; Ravishankar et al. 2019; Zhang et al. 2019b). Hydrophobic drug loading was improved by the inclusion of hydrophobic materials in the hydrogel structure (Larrañeta et al. 2018). The lignin-based hydrogel was loaded with curcumin, a polyphenolic compound, for drug delivery applications. Higher loading of curcumin was available with higher lignin content in the hydrogel as both the lignin and curcumin contain aromatic rings.

Lignin-based hydrogels were also explored for wound dressing. The ideal requirements for a wound dressing material are a physical barrier with higher mechanical strength, antibacterial activity to avoid infections, high absorption capacity to clean up the metabolites, moisture-holding capacity, free radical scavenging, and antioxidant properties (Zhang et al. 2019b). Lignin-based hydrogels fulfill these requirements for wound dressing. For instance, PVA–chitosan–lignin hydrogel was prepared, which improved the mechanical strength from 38.55 to 46.87 MPa, protein adsorption capacity from 5 to 45 mg/g, and wound closure from 80% to nearly 100%, when lignin content increased from 0 to 30 wt% (Zhang et al. 2019b). Although the antibacterial activity of lignin has been demonstrated in previous studies (Larrañeta et al. 2018), Zhang et al. (2019b) reported that the antibacterial activity of the PVA–chitosan–lignin hydrogel was mainly due to cationic groups of chitosan. The authors reported that the increase of lignin content in the hydrogel reduced the antibacterial activity due to partial neutralization of cationic groups from chitosan with anionic groups of lignin. Chitosan–lignin hydrogel synthesized by physical crosslinking (electrostatic attraction) was also investigated for its wound dressing application (Ravishankar et al. 2019). Cytotoxicity of this hydrogel was evaluated in vitro and in vivo against mesenchymal stem cells and zebrafish, respectively. Hydrogels synthesized with alkali lignin were non-toxic, while those with sodium lignosulphonate were highly toxic. Cell viability was 114 ± 0.2% with alkali lignin, 99 ± 2% with chitosan, 99 ± 3% with chitosan–alkali lignin, while it was relatively low with sodium lignosulphonate (~60%).

8.3.2.3 Agricultural Applications

Hydrogels are used in arid and semi-arid regions for soil water retention and controlled release of fertilizers in the soil. However, synthetic materials-based hydrogels can cause soil pollution due to their limited biodegradability and/or biological toxicity of the degraded products. Lignin-based hydrogel, synthesized by crosslinking of lignosulfonate (L), konjaku flour (KJ), and sodium alginate (SA), was used for controlling the release of water and nutrients for tobacco plants (Song et al. 2020). The pore size of soil affects the saturated hydraulic conductivity of the soil. The addition of SA-KJ-L (sodium alginate-konjaku flour-lignosulfonate) hydrogel in the soil reduced the water loss during the infiltration process by blocking the soil pores and increasing friction between soil particles, hydrogel, and water. Saturated hydraulic conductivity of soil was reduced from 0.020 cm/min in no-hydrogel soil to 0.008 cm/min in 0.375% hydrogel soil, 0.003 cm/min in 0.650% hydrogel soil, and 0.002 cm/min in 0.975% hydrogel soil. The maximum water holding capacity (MWHC) of soil without hydrogel was 52.66% (i.e., 52.66 g of water in 100 g of dry soil). The MWHC increased to 61.63% with the addition of 0.975% lignin-based hydrogel. Nitrogen (N), phosphorus (P), and potassium (K) are the three main macronutrients in the fertilizers used for plant growth (Song et al. 2020). These nutrients entered the SA–KJ–L hydrogel molecular structure along with water which reduced the leaching and infiltration of nutrients in the soil. The addition of 0.975% hydrogel reduced the leaching of nitrate nitrogen, ammonium nitrogen, total phosphorus, and plant available potassium by 38.83%, 32.35%, 28.22%, and 26.89%, respectively, compared to the soil without hydrogel. Proline and reducing sugar are protective substances against tobacco stress, and their contents are used to identify the degree of drought in crops. The increase of proline content indicates the higher drought stress. Proline contents in plants treated with 0.375, 0.650, and 0.975% of SA–KJ–L hydrogel were lower (~0.40 μg/g, ~0.35 μg/g, and ~0.30 μg/g, respectively) than that of the untreated plants (0.88 μg/g).

Hydrogel crosslinked with alkali lignin and PEGDGE was applied to alleviate drought stress in maize and compared with the hydrogel synthesized with sodium polyacrylate (Mazloom et al. 2020). Maize plants were taller in soil amended with both hydrogels. In general, the P content in maize shoots declines with water shortage. In this study, the lignin-based hydrogel amended soil showed higher P contents (1.48–1.56%) in maize shoots than the content with no-hydrogel condition (0.44%). These were comparable to the P contents with the synthetic hydrogel amended soil (1.45–1.50%). Proline content in the maize grown in soil amended with lignin-based hydrogels was lower (0.6 and 1.4 μmol/g) than the contents with synthetic hydrogels (1.6 and 4.2 μmol/g) and no-hydrogel condition (4.8 μmol/g). The drought stress can also be identified by electrolyte leakage which occurs mainly due to cell membrane damage under drought-induced oxidative stress. The electrolyte leakage reduced from 71% in no-hydrogel condition to 62% with sodium polyacrylate hydrogel as well as lignin-based hydrogel treated soils due to alleviation in drought stress. Sodium polyacrylate hydrogel had a detrimental impact on soil chemistry due to the dissolution of sodium. The soil pH increased with sodium polyacrylate hydrogel, which interferes with the nutrient uptake by plants, while the pH was not increased with the lignin-based hydrogel because methoxyl, carbonyl, carboxyl, and hydroxyl functional groups of lignin contributed to soil buffering.

8.3.2.4 Other Applications

Lignin has a unique pH-stimuli-responding property currently used for the dissolution and precipitation of lignin at different pH (Dai et al. 2020). At low pH, hydroxyl and carboxyl groups of lignin remain protonated; hence reduction in repulsive forces decreases the swelling of lignin-based hydrogels. Conversely, the increase of pH deprotonates these groups and induces swelling due to electrostatic repulsion (Meng et al. 2019b). The hydrogel was synthesized by chemically crosslinking lignin with PEGDGE, and its pH-stimuli responsiveness was tested (Dai et al. 2020). The hydrogel filament was bent when immersed in an acidic solution, while the filament recovered its original shape in an alkaline solution. Mechanical switches and actuators can be synthesized by using the pH-responsive behavior of lignin-based hydrogels.

Although the above applications have been investigated, lignin-based hydrogels have not yet been successfully produced at industrial scales. Extraction of lignin at a certain molecular weight with narrow polydispersity is challenging. Most lignins are biocompatible and non-toxic, but some sulfur-containing technical lignins are not. For example, sodium lignosulfonate showed high cytotoxicity, which may not be proper for biomedical applications (Ravishankar et al. 2019). As mentioned earlier, physically crosslinked hydrogels have relatively low mechanical strength, while many chemically crosslinked hydrogels are still formed with toxic chemicals. Further study is required to form a lignin-based hydrogel with superior or at least comparable performances to synthetic hydrogels without toxic chemical uses.

8.4 Conclusion and Future Perspectives

Current lignin-based materials still have many technical limitations in their performances and processing methods. Lignin alone cannot meet the mechanical strength and/or flexibility; therefore, it is applied with other co-materials as a composite to overcome these challenges. Since two or more materials will be chemically and/or physically blended to form the materials, feedstock compatibility is a crucial factor. To improve the performances of lignin-based materials, refining or modification of lignin prior to the synthesis or processing of materials would be beneficial. Feedstock variability is another challenge in lignin utilization. Compared to cellulose, the properties and composition of lignin have relatively large variations depending on biomass species, growing environments, and processing methods (e.g., pulping and pretreatment) and conditions. Since the performance of lignin-based materials can be influenced by lignin, the understanding of lignin characteristics via proper analyses is essential. Machine learning can be applied with a sufficient experimental database to identify the best methodology based on the lignin source as well as the target performance of the products. Also, environmental aspects of lignin-based materials need to be considered further. One of the key features of lignin-based materials is carbon negativity; however, most studies simply discussed the alternation of petroleum resources with lignin. For developing true eco-friendly future materials, it is necessary to design carbon negative lignin-based materials on a cradle-to-grave life cycle basis.

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