Review

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Research and application progress of lignin-based composite membrane

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Abstract: In view of the serious environmental pollution, which is the greatest problem the world is facing, and the continuous consumption of raw materials, it is imminent to search for green and sustainable resources. Lignin is an organic polymer that exists widely in nature, and if it can be transformed from traditional low-value waste product with low range of applications to functional materials with high application prospects, it can be of great significance to alleviate environmental pollution and shortage of fossil resources. One of the functional applications of lignin involves its use to fabricate composite with other polymeric materials, which can then be used to prepare membrane materials. This review summarizes the recent research and application progress of combining lignin with polypropylene, polyvinyl alcohol, starch, cellulose, chitosan, and other polymeric materials to prepare composite membranes; and summarizes the future development direction of lignin-based composite membranes. We hope this review may provide a new perspective to the understanding of lignin-based composite membranes and a useful reference for future research.

Keywords: application; biomass; lignin; membrane; polymer.

1 Introduction

Immense environmental pollution and oil crisis encountered recently, has gradually brought the biodegradable materials based on renewable resources to the forefront [1].

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Lignin is not only widely sourced in nature, but also rich in reserves. Nearly 50 million tons of industrial lignin is extracted every year from the pulping and biorefining industries. However, most of lignin is burned as cheap fuel or discharged directly, which not only wastes resources, but also pollutes the environment [2]. Nonetheless, if lignin is transformed into higher-value functional materials, its abundant reserves may solve the problem of rapid depletion of fossil resources.

As a natural biological macromolecule, lignin offers many excellent properties such as high carbon content, strong thermal stability, biodegradability, good antioxidant activity, and good stiffness [3]. These properties have been reflected in a series of biodegradable products such as fuels, agricultural membranes, food packaging, and disposable products [4–6]. Many types of antioxidants, heat stabilizers, light stabilizers, molding stabilizers, adsorbents, dispersants, surfactants, and other functional materials have also been prepared from lignin [7–12]. With the expansion of the research scope, the technological application value of lignin-based functional materials has also been fully explored. Thakur et al. [13, 14] summarized the recent advances involving the use of lignin in the development of green polymer composites and hydrogels. Wong et al. [15] reviewed the extensive research on the lignin-to-product valorization chain; introduced available platform chemicals and polymeric derivatives generated from lignin via existing depolymerization and functionalization technologies; and provided detailed analyses of various strategies for the downstream processing of lignin derived platform chemicals and materials into fuels, valued-added chemicals, and functional polymers. At present, variety of lignin-based products has been developed, which are used in agriculture, forestry, petroleum, metallurgy, dyes, cement and concrete industries, and polymer material industries [7, 8, 12, 16–18]. In particular, the preparation and development of lignin-based composite membranes have attracted significant research attention.

At this stage, most of the membrane materials prepared at global scale use petroleum-based polymers as raw materials, and the prepared membrane exhibits poor environmental absorbability. In order to alleviate the problems of increasingly serious environmental pollution and the

shortage of fossil-based polymers, the prospect of selecting renewable lignin for the preparation of membrane materials is a promising approach. However, related studies on membrane-forming materials show that, in general, long-chain molecules with extremely long-chain branches or regular structures have good membrane-forming properties [19]. Lignin consists of a three-dimensional (3D) complex network structure with poor regularity. Moreover, the mechanical properties after membrane formation are not ideal, thus in the current studies lignin is mostly blended with other materials to form a composite membrane. Owing to the presence of abundant active functional groups in the lignin molecule, it can easily interact with different types of polymers at the interface to achieve better compatibility and obtain a more homogeneous composite membrane material. These membrane materials are not only cost effective, but also versatile, thus they can be widely used in industrial production process [20]. At present, research reports on the preparation of composite membranes by blending lignin with starch, cellulose, polypropylene (PP), polyvinyl alcohol (PVA), chitosan, and

other polymeric materials [20–24], are available. This review analyzes the blending principle of lignin with polymeric materials, evaluates domestic and foreign research progress and development trends in the preparation and application of lignin-based composite membranes, and provides theoretical support for the research on the preparation of functional materials from lignin.

2 Lignin

2.1 The structure of lignin

Lignin molecules mainly contain the following three elements: carbon, hydrogen, and oxygen. Three basic structural units are present in lignin molecules, namely, p-hydroxyphenyl, guaiacyl, and syringyl, as shown in Figure 1. These phenylpropane structural units contain many active functional groups such as hydroxyl, carbonyl, and methoxy groups, which act as the active centers of lignin modification and utilization [25, 26].

The basic structural units of lignin are randomly linked with ether bonds and C–C bonds to form a natural high molecular polymer with a 3D structure. The more classic lignin structure is the structural model of poplar lignin proposed by Boerjan, as presented in Figure 2 [27, 28].

The key to forming a composite material between lignin and polymer is the improvement of the compatibility between the two. The interaction between the components in the blend system is the focus of the research. These interactions include strong dipole–dipole interaction, ion–dipole interaction,

Figure 1: Basic structures of three phenylpropane units of lignin.

Figure 2: Typical structure of milled wood lignin of poplar [27, 28].

charge transfer complexation, Lewis acid–base interaction, etc. [29]. These interactions are closely related to system compatibility. Figure 2 exhibits that lignin has a huge aromatic ring structure and consists of abundant active functional groups such as phenolic hydroxyl, carboxyl, and methoxy groups on the side chain. Therefore, lignin easily forms hydrogen bonds and intermolecular forces with some functional groups of other components. Furthermore, the compatibility between lignin and other polymeric materials should be enhanced to obtain a more homogeneous composite membrane. These composite membranes not only have degradable properties, but also can significantly reduce manufacturing costs. At the same time, characteristics of lignin such as heat resistant and capable of strong absorption of ultraviolet (UV) rays are also retained in the lignin-based composite matrix, thus a low-cost, multi-functional composite material can be successfully obtained.

Analysis indicates that when lignin is combined with polar polymeric materials, intermolecular hydrogen bonds are easily formed and the interface bonding ability is good, thus it can be directly combined [30]. However, owing to the huge aromatic ring structure in the lignin molecule, a strong π – π interaction exists between aromatic rings; and abundant phenolic hydroxyl, carboxyl, methoxy, and other polar groups can form hydrogen bonds. Therefore, the intermolecular forces of lignin are relatively large and the particles agglomerate seriously. Most of the oxygen-containing groups are wrapped inside the agglomerated structure, and active functional groups exposed on the outer surface of the particles are limited; therefore, the particles of lignin are larger and its dispersibility in polar polymeric materials is poor. In order to improve the compatibility between the two, lignin should be pretreated during the processing, and the influence of lignin particle size, relative molecular weight, and group content on compatibility should also be considered. Lignin and nonpolar polymeric materials have weak interface binding ability [31]. This is attributed to the fact that the hydroxyl, carboxyl, and other polar groups on the lignin macromolecule make the entire lignin molecule polar, thus the compatibility with nonpolar polymer materials becomes poor. In general, when lignin is combined with nonpolar polymeric materials, the compatibility between the two can be improved through lignin modification or compatibilization technology [32].

2.2 Types and applications of lignin

In addition to being extracted from plants, lignin can also be obtained during pulping and papermaking processes. Table 1 summarizes the structure and properties of the four types of lignins [13]. Kraft lignin comes from the kraft

pulping process. During the pulping process, sodium hydroxide and sodium sulfide break the bonds between the phenylpropane units of the lignin molecule under high-temperature cooking conditions to reduce the molecular weight. This results in the formation of aliphatic thiol groups, thus kraft lignin has a high sulfur content (1–2 wt%) and is hydrophobic. Compared to other types of lignin, kraft lignin is generally used for low value-added applications [33]. Lignosulfonate is obtained from sulfite pulping. The sulfonic acid group on the lignosulfonate determines its good water solubility. It is soluble in various aqueous solutions with different pH, but insoluble in organic solvents such as ethanol and acetone. The molecular weight of lignosulfonate is relatively low, and it has good compatibility with other polymeric materials. Alkali lignin is obtained from alkaline pulping. Under the conditions of alkaline high-temperature cooking, many active groups of lignin get destroyed, resulting in reduced activity. As a result, it is difficult to use it directly, and its modification is required to improve compatibility with other materials. Compared to alkali lignin and lignosulfonate, organosolv lignin offers many unique advantages, such as a higher proportion of reactive groups and no sulfur-containing impurities. It only involves solubilization; therefore, its high purity is also ideal for direct use.

Blending of polymeric material is one of the main methods for preparing composite membranes. This method can effectively combine several polymeric materials so that the prepared composite membrane has multiple functional characteristics. Figure 3 presents examples of blending lignin with other polymeric materials, and provides the application of each blended material. Figure 3 exhibits that it has applications in food packaging, coating applications, sewage treatment, drug delivery, etc. This is attributed to the fact that compared to the membrane material without lignin, polymeric materials with blended lignin exhibit improved antiaging performance, mechanical strength, thermal stability modification, degradability, and other properties under experimental verification.

3 Lignin and synthetic polymer material composite

3.1 Lignin/polyolefin composite

Incorporating lignin into polyolefins to prepare membrane is a new approach to make full use of waste from pulp and paper industry and reduce the environmental impact of nondegradable waste plastics based on polyolefins.

Table 1: Different types of technical lignins and their properties [13].

Technical lignins	Structure	Product status	Molecular weight ($\times 10^3 \text{ g mol}^{-1}$)	Solubility
Kraft		Industrial	1.5–5 (up to 25)	Alkali, some organic solvents (DMF, pyridine and DMSO)
Lignosulfonate		Industrial	1–50 (up to 150)	Water
Alkali		Industrial	0.8–3 (up to 15)	Alkali
Organosolv		Laboratory/pilot	0.5–5	Wide range of organic solvents

DMF, dimethylformamide; DMSO, dimethyl sulfoxide.

Polyethylene (PE) and PP are common general nonpolar polymeric materials, while lignin is a strong polar material with strong hydrogen bonds. It is difficult to disperse lignin in PE and PP, thus the blending effect between the two is poor and the mechanical properties are reduced. Therefore, it is generally necessary to add a certain amount of compatibilizer to the nonpolar polymer and lignin blend to improve the two-phase compatibility [31]. Figure 4 shows the mechanism diagram of the compatibilizer containing epoxy groups, capable of enhancing the compatibility between lignin with polyolefin [32].

Li et al. [34] used low-density PE (LDPE) and lignin as raw materials, added appropriate plasticizers and coupling agents, and prepared degradable membranes using ordinary screw extrusion blown membrane machines. The study found that when the mass fraction of lignin was less than 20%, the composite membrane showed a certain light transmittance. Further, when the mass fraction of lignin reached 40%, the mechanical properties of the membrane became better, and its tensile strength and elongation at break were 19.6 MPa and 120%, respectively. The structural analysis indicated that the compatibility between lignin

Figure 3: Types of lignin-based composite membranes and their application prospects.

Figure 4: Mechanism of enhanced interface compatibility of lignin/polyolefin compatibilizer [32].

and PE resin is poor, and obvious lignin dispersed phase is observed in the continuous phase of PE resin, which is the main reason that affects the mechanical properties and light transmittance of the membrane. Another research result by Li's research group [35] also showed the existence of intermolecular hydrogen bonding interactions between lignin and the modified material poly(ethylene-co-vinyl acetate) (EVA) obtained by introducing polar acetate groups on PE, and the thermal stability of the blend was improved. With the increase in the lignin content, large agglomerated lignin particles appeared in the blend membrane, obvious defects such as pores appeared in the microscopic morphology, and the mechanical properties of the blend decreased. In order to solve the problem of the degradability of general-purpose plastics, Mikulasova et al. [36] used the lignin-degrading enzyme produced using the white-rot fungus *Xanthospora* to biodegrade the composite lignin-PP membrane containing 4% organic cell lignin. The experimental results showed that the lignin component of the composite membrane was vulnerable to microbial attack, and its structural integrity was partially lost compared to that of the lignin-free PP membrane. At the same time, regarding the oxidation characteristics of lignin biodegradation, it could be considered that lignin acts as a free radical reaction initiator, capable of causing oxidative degradation of PP polymer exposed to outdoor weathering. Almost entire polymer is susceptible to the attack of molecular oxygen through free radical reactions, and the interaction of free radicals generates peroxides and causes oxidation chain reactions. Kosikova et al. [37] prepared a lignin/PP composite membrane and studied the existence and behavior of free radicals in the membrane by electron spin resonance spectroscopy. The experimental results showed that the concentration of free radicals in the composite membrane increased with the increase of the mass fraction of lignin. The interaction between the lignin-free radicals and the free radicals generated by the thermal oxidation of PP led to the termination of the oxygen-induced polymer chain reaction, indicating that the interaction between the paramagnetic sites of PP and lignin had

free-radical properties. Therefore, lignin could be used as a stabilizer in the photooxidation process of PP membrane.

3.2 Lignin/polyvinyl alcohol composite

PVA is a linear polymer containing a large number of hydroxyl groups, and it is a polar substance with more hydroxyl groups on the chain and strong hydrophilicity. Lignin contains a large number of polar functional groups, and a strong hydrogen bond exists between PVA molecules and lignin. Therefore, theoretical analysis indicates that the two have good compatibility, and have the characteristics of preparing composite membrane [38]. Recently, extensive research efforts have been devoted to the research on lignin/polar plastic composite membrane, but these studies mainly report the improvement of its light-heat stability and mechanical properties. For example, Stival et al. [39] used two types of lignin, namely, sulfate lignin (KL) and acetone-soluble sulfate lignin (AKL), mixed them in appropriate proportion with PVA, and the solvent (DMSO) was evaporated to obtain 25% lignin/composite membrane. The studies found that the incorporation of lignin under the irradiation of UV rays led to the increase in the thermal stability of the PVA membrane, and PVA/KL showed more advantages than PVA/AKL in terms of membrane uniformity and light stability. The alkaline lignin and PVA blend membrane prepared by Xu et al. [40] showed not only better light and heat stability, but also barrier properties to oxygen and carbon dioxide. Moreover, with the increase of the alkali lignin mass fraction, both the tensile strength and elongation at break increased. Chen et al. [41] mixed PVA, polyethylene glycol (PEG), and liginosulfonate, and the prepared membrane exhibited good gas separation performance for CO₂, and exceeded the Robeson upper limit. In order to improve the mechanical properties of lignin composite membrane, relevant explorations have also been carried out from the perspective of material compatibility. For instance, Su et al. [42] used alkali lignin

Figure 5: PVA/lignin blend structure. Reproduced from [44] with permission from Taylor & Francis, copyright 2016.

and PVA as raw materials, glutaraldehyde as a cross-linking agent, and glycerin as a plasticizer to prepare alkali lignin/PVA reaction membranes. When the mass ratio of alkali lignin/PVA was 1:5, the content of glutaraldehyde was 1.67%, and that of glycerin was 7.1%, the mechanical properties and thermal stability of the reaction membrane were optimal, and the crystallinity was slightly reduced, indicating that alkali lignin showed good compatibility with PVA. Tao and Luo [43] also conducted similar studies and prepared a lignin/PVA composite membrane with good mechanical strength and water resistance. The surface of the membrane was uniform and smooth, and the calcium liginosulfonate in the membrane showed good compatibility with PVA. Issa et al. [44] prepared PVA/lignin membrane by casting method, and discussed the intermolecular interaction between lignin and hydrophilic polymer PVA. The study showed the existence of strong intermolecular hydrogen bonds formed between PVA and hydroxyl groups, and also specific intermolecular interactions. Figure 5 shows the structure of a blend with intermolecular hydrogen bonds.

3.3 Lignin/polyvinyl chloride composite

Polyvinyl chloride (PVC) is a common polymeric compound with a large number of polar groups, which shows good compatibility with lignin. PVC has good mechanical strength, superior physical and chemical stability, low

cost, and other advantages, thus it has attracted widespread research attention [45, 46]. Lignin has good heat resistance and strong UV-light absorption characteristics; therefore, it can effectively improve the deficiency of PVC materials after being combined with PVC to form a membrane. A polar interaction occurs between the α -hydroxyl group of lignin and the chlorine of PVC or between the carbonyl group of lignin and the α -hydrogen of PVC, which is conducive to the formation of a homogeneous phase [47]. Yong et al. [48] improved the hydrophilicity and antifouling properties of PVC ultrafiltration (UF) membranes by doping lignin into PVC and used it in the treatment of oily wastewater. The synthesis mechanism is shown in Figure 6. The experimental results showed that with the increase in the content of lignin, the porosity, average pore size, and permeability of the modified membrane increased. The hydrophilic groups of lignin were exposed on the upper surface of the membrane to form a stable hydration layer and strengthened the PVC membrane hydrophilicity, cutting off the interaction between dirt and membrane surface. The membrane showed good stability and durability even after treatment of oily wastewater. Mishra et al. [49] prepared a lignin/PVC blend membrane, and Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA) revealed that the lignin and PVC blend showed enhanced UV absorption, but the intermolecular interaction was weak. Therefore, it would have a certain impact on the strength of the material.

Figure 6: Rational mechanism of PVC lignin UF membrane for oily wastewater treatment. Reproduced from [48] with permission from Elsevier, copyright 2016.

4 Lignin and natural polymer materials composite

4.1 Lignin/chitosan composite

Lignin macromolecules contain a large number of carboxyl and hydroxyl functional groups, and the surface of chitosan macromolecules also consists of abundant amino and hydroxyl groups. The two can be combined through Van der Waals' force or hydrogen bonding. Figure 7 shows the compounding mechanism of chitosan and alkali lignin [50]. The dotted line indicates the possibility of the presence of a weak bond between chitosan and alkali lignin [50]. Therefore, a simple blending method or a membrane casting method can be used to combine the two to prepare a membrane material.

Chen et al. [51] prepared a chitosan/lignin composite membrane by solution casting, studied the structure and properties of the membrane, and found the presence of hydrogen bond between chitosan and lignin. When the lignin content was less than 20 wt%, it showed good

dispersibility in the composite membrane. Compared to pure chitosan membrane, composite chitosan exhibited significant improvement in the tensile strength, storage modulus, glass transition temperature, and degradation temperature; however, the elongation rate was slightly reduced. The membrane preparation method was simple and the membrane exhibited good biodegradability. Li et al. [52] prepared a hydroxymethylated lignin-chitosan composite membrane and studied the effects of the blend ratio of lignin and chitosan on the physical properties, acid resistance, and Cu(II) chelating properties of the composite membrane. When the blending ratio was 1:2, the surface of the composite membrane was smooth and flat with uniform thickness. Compared to chitosan membrane, the chelating performance of the composite membrane on Cu(II) was increased by 52.39%, and the chelating amount reached 0.4741 g m^{-2} ; moreover, the acid resistance also improved. Based on this, Li [53] used glutaraldehyde as a crosslinking agent and glycerin as a plasticizer to prepare a hydroxymethylated alkali lignin/chitosan crosslinking reaction membrane. Compared to pure chitosan membrane

Figure 7: Preparation of chitosan-alkali lignin composite [50].

and chitosan-hydroxymethylated alkali lignin composite membrane, for hydroxymethylated alkali lignin/chitosan crosslinking reaction membrane, the acidic application range was $\text{pH} = 0.1\text{--}7$. Although the acid resistance was significantly improved, the chelating performance of Cu(II) decreased significantly. It was believed that the addition of glutaraldehyde reduced the functional groups that could chelate with Cu(II) , resulting in a decrease in chelating performance; moreover, the slow release performance of membrane for urea and the immobilization effect for lactase were not ideal. Kevin et al. [54] used solvent casting method to prepare chitosan-lignin composite membrane in a water/ethanol co-solvent system. The lignin and chitosan in the composite membrane acquired low-energy dipole-dipole interactions. The addition of lignin resulted in slight decrease in the mechanical properties and barrier properties of the composite membrane, but improved the anti-oxidation performance. Moreover, at the same time, it caused chemical reorganization of the membrane surface to make it hydrophobic. Antioxidant properties of chitosan-lignin membranes were assessed by the method based on the scavenging of the $\text{DPPH}\cdot$ radical molecule to evaluate whether lignin has an effect or not on the antioxidant capacity, and the results are shown in Figure 8. The barrier performance and antioxidant activity of the composite membrane could limit the oxygen transfer of packaging materials and the reactivity of free radicals. Therefore, industrial by-products could be converted into packaging materials for food preservation and the application field of waste could be expanded.

4.2 Lignin/cellulose composite

Lignin shows poor compatibility with cellulose. On the one hand, the hydrophilic groups of lignin are mostly wrapped in hydrophobic chains, making it incompatible with hydrophilic carbohydrates such as cellulose. On the other hand, due to the normal pH and no chemical additives, cellulose and lignin have negative charges, which lead to electrostatic repulsion between them [55]. Cellulose is a polyhydroxy compound that can be combined with other materials through hydroxyl hydrogen bonds, leading to the formation of a space-entangled structure; therefore, trying to use hydrogen bonds to connect polymers can effectively combine cellulose and lignin [56]. The use of green solvents (such as ionic liquids) can aid in the formation of lignin and cellulose composite membranes. Moreover, compared to some hazardous organic solvents such as DMSO/water and dioxane/water systems, ionic liquid is very simple, environmentally friendly, and safe as a process membrane solvent, thus it is widely used [57]. Wu et al. [55] dissolved lignin, cellulose, and starch in 1-allyl-3-methylimidazole chloride, and synthesized a composite membrane with good transparency by solution casting. The intermolecular hydrogen bond was stronger, and its thermal stability and air permeability were better than those of regenerated cellulose (RC) membrane, thus the composite membrane showed great application potential in fresh food packaging. Laura et al. [58] used propionic anhydride for esterification of sulfate lignin, organic solution lignin, and hydrolyzed lignin to obtain propionic lignin; and a water-treated nanocomposite membrane was prepared

Figure 8: Radical scavenging activity evaluated by $\text{DPPH}\cdot$ method: (a) chitosan-lignin films containing 0, 10, 20, and 30 wt% lignin and previously equilibrated at 33% RH and 20 °C ($n = 6$), (b) lignin residues released from these films ($n = 3$), (c) chitosan-lignin films containing 20 wt% lignin and previously equilibrated at 33 and 75% RH, at 20 °C ($n = 6$). Lines are eyeguides. Reproduced from [54] with permission from the American Chemical Society, copyright 2016.

from propionic acid lignin and triacetate cellulose by solution casting. Furthermore, the effect of different types of lignin on the performance of the composite membrane was investigated. The high esterification of lignin could reduce the wettability and flux of the composite membrane. Sulfate lignin is the lignin with a lower degree of esterification among the three test materials mentioned above; therefore, the composite membrane prepared with sulfate lignin as the raw material showed the highest flux. In order to further test the membrane performance, it was used to filter groundwater containing high concentrations of fluoride, arsenic, calcium, sodium, and magnesium. The results showed that the membrane rejection rate of anions was 15–35%, and those of monovalent cations and divalent cations were 12–42% and 27–54% respectively. Moreover, the types of ions and organics in groundwater affected the removal of arsenic and fluoride using the membrane. Sadeghifar et al. [59] dissolved azide cellulose in dimethylacetamide/lithium chloride and reacted to it with proline lignin, and prepared a cellulose/lignin membrane by the acetone regeneration method, as shown in Figure 9. The experimental results showed that the prepared membrane showed high UV protection ability, and the cellulose membrane containing 2% lignin had 100% protection effect against UV-B (280–320 nm) and more than 90% against UV-A (320–400 nm). However, the tensile strength decreased. Therefore, how to increase the proportion of lignin under the premise of maintaining the best performance is worth exploring. Owing to the darker color of lignin, the transparency of the membrane was also one of the main indicators investigated.

Parit et al. [60] used NaOH to treat cellulose nanocrystals (CNCs), and added alkaline lignin (AL) and softwood sulfate lignin (SKL) to the CNC suspension to prepare biodegradable

UV protection membrane. The results showed that the addition of NaOH increased the transparency and uniformity of the CNC membrane, and the lignin was modified by acetylation to reduce the chromaticity and improve the visible light transmission of the membrane. CNC/lignin composite membrane is a biodegradable, low-cost coating/membrane material with UV blocking and optical polarization functions, which can be used in sunglasses, car windshields, home windows, contact lenses, and UV-sensitive polymers and other aspects. Colburn et al. [61] combined iron, polyacrylic acid (PAA) or lignosulfonate with cellulose membrane in 1-ethyl-3-methylimidazole acetic acid ionic liquid to obtain a composite membrane. Lignosulfonate was added to the cellulose membrane to increase the negative charge and steric hindrance in order to enhance the antifouling performance of the composite membrane. When lignosulfonate was functionalized on the surface of the commercial NF270 membrane, similar kind of antifouling behavior was also observed. For these two types of lignin-functionalized membranes, after repeated pollution cycles, the water flux recovery was as high as 90%. In contrast, for the unmodified membrane, it was observed that the water flux recovery was as high as 60%, indicating that lignin can reduce the cost of membrane making and can also be used for sewage treatment, thus achieving the purpose of recycling.

4.3 Lignin/starch composite

Starch is a common resource-rich, renewable, hydrophilic natural polymer. Owing to its poor mechanical properties and hygroscopicity, the development of starch-based products is limited [3, 62]. Mixing starch with hydrophobic polymers such as lignin is an effective method to solve the

Figure 9: A transparent cellulosic membrane with less than 2% chemically bonded lignin capable of absorbing and providing protection from UV light. Reproduced from [59] with permission from the American Chemical Society, copyright 2017.

problems including starch moisture sensitivity and critical aging [63]. According to literature, lignin can reduce the hydrophilicity of starch membranes, and can be used as a reinforcing filler to be incorporated into the starch matrix to improve its mechanical properties, thermal properties, and air resistance properties [64]. Baumberger et al. [65] used wheat starch and lagnosulfonate as raw materials for the first time in 1997 to prepare a membrane by thermoforming or casting in the presence of glycerol, and further compared the mechanical properties and hydrophilicity with standard plasticized starch membranes. Test results showed that addition of 10% lagnosulfonate could improve the tensile properties of starch membranes (the final stress was reduced by three times, and the elongation at break increased by two times). However, lignin becomes water-soluble after being modified by sulfonate; therefore, blending it into starch does not improve the water-resistant property of the membrane. Subsequently, Baumberger et al. [66] blended kraft lignin and starch and produced lignin/starch composite membrane by thermoforming extrusion. The study showed that lignin with low molecular weight showed good compatibility with starch. When the lignin filling rate was as high as 30%, although the elongation resistance of the membrane material was reduced, the water resistance was significantly improved. Lepifre et al. [67] blended three types of sulfur-free alkali lignin (one bagasse lignin and two wheat straw lignins) with starch to prepare composite membranes under electron beam irradiation, and their structure and reaction

activity were comparatively analyzed. The results showed that after electron beam irradiation, the structure of alkali lignin changed drastically, and the reaction activity increased, which significantly improved the compatibility between starch and lignin. Calgeris et al. [68] used lignin and corn starch mixed in different ratios to prepare composite membrane and obtained similar research results. In other words, with the increase of lignin content, the mechanical properties and thermal properties of the membrane were improved. Moreover, with the increase in the pH of the solution, the swelling rate of the starch/lignin membrane also increased significantly, as shown in Figure 10. When the starch/lignin membrane was studied for drug release, it showed a rapid release of ciprofloxacin (CPF) within 1 h, and then the drug release rate decreased. According to Korsmeyer–Peppas model fitting, it was found that the drug release mechanism depended on the pH, and the release increased with the decrease in the pH. The above-mentioned studies indicate that starch/lignin biomembranes can be applied in coatings, food packaging, and drug delivery systems. Acosta et al. [69] dissolved lignin in methanol to obtain alcohol-soluble lignin (ASL), and prepared starch/ASL membrane by casting method and evaluated its mechanical properties, thermal stability, water-solubility, color and antioxidant activity, and structure. The study showed that ASL exhibited a plasticizing effect, and its addition led to a significant decrease in the tensile strength and elastic modulus of the membrane, but it resulted in the increase in

Figure 10: Percent swelling ratios of the biomembranes with different lignin contents versus time at (a) pH 2.0, (b) pH 4.0, and (c) pH 6.0. Reproduced from [68] with permission from John Wiley and Sons, copyright 2012.

Figure 11: Preparation of lignin/chitin membrane and its adsorption on Fe(III) and Cu(II) in aqueous solution. Reproduced from [72] with permission from the American Chemical Society, copyright 2018.

the elongation at break of the membrane. Thermal analysis results showed that the addition of ASL endowed the membrane with a higher resistance to thermal degradation and water solubility. Moreover, with the increase of ASL content, the antioxidant activity of starch/ASL membrane on DPPH free radicals increased, and starch-based membrane with antioxidant properties was successfully obtained.

4.4 Lignin/other natural polymer composite

In addition to the above-mentioned natural polymeric materials, several other lignin-based mixed membranes prepared by mixing other natural polymeric materials have also been reported. For instance, Aadil et al. [70] prepared lignin/sodium alginate mixed membranes under different plasticizers by solution casting method. They investigated the influence of three plasticizers, namely, glycerin, epichlorohydrin (EPC), and polyethylene glycol (PEG) on the physical and chemical properties of the mixed membrane. It was found that compared to EPC- and PEG-plasticized membranes, the solubility and swelling rate of glycerin-plasticized membranes were higher; the tensile strength of PEG-plasticized membranes was the highest; and the thermal stability of EPC-plasticized membranes was the highest. FTIR spectroscopic results showed the presence of a hydrogen bond between lignin and sodium alginate in the presence of plasticizer. The addition of lignin resulted in significant improvement in the photoresistive properties of the membrane. The lignin-sodium alginate membrane plasticized with EPC showed better physical and mechanical properties and light barrier properties, and could be used in packaging materials and coating applications. Shankar et al. [71] prepared agar/lignin biodegradable composite membranes by solution casting and studied the effect of lignin concentration on the performance of composite membranes. Compared to pure agar membrane, the composite membrane showed higher mechanical and water vapor barrier properties. At the same time, with the addition

of lignin, the UV light transmittance decreased, and the thermal stability and coke content increased. Owing to the low penetration of UV light, agar/lignin composite membrane could be used as a UV barrier food packaging membrane. Duan et al. [72] prepared a new type of lignin/chitin membrane with a solvent system composed of ionic liquid 1-butyl-3-methylimidazolium acetate and γ -valerolactone. The application of lignin/chitin membrane as an adsorbent for Fe(III) and Cu(II) cation uptake from aqueous solutions was discussed, as shown in Figure 11. The results showed that the maximum adsorption capacity for Fe(III) within 48 h was 84 wt%, the maximum adsorption capacity for Cu(II) was 22 wt%, and the lignin/chitin membranes could be regenerated by desorption of the Fe(III) and Cu(II) ions. Therefore, the lignin/chitin membrane showed a high ability to adsorb metal ions and was found to be a stable and recyclable biosorbent material.

5 Conclusions

The lignin-based composite membrane possesses many outstanding properties, such as excellent degradability, good heat resistance, and strong absorption of ultraviolet rays. These composite membrane materials are mostly used in coatings, food packaging, sewage treatment, slow release of drug, biosorption, etc. However, the literature on the application of lignin-based composite membranes to separation technology is still relatively small. At the same time, some experts and scholars have also conducted research on lignin-based carbon membrane and found that it has greater application prospects in the field of supercapacitors. At present, the preparation of lignin-based composite membranes still faces some challenges such as complex preparation processes, harsh synthesis conditions, and unsatisfactory compatibility among multiple components. These problems lead to its synthesis application confined mostly in the experimental stage. Future research on lignin-based composite membranes is directed as follows: First, a new

decomposition technology should be developed for carrying out easy decomposition of complex molecular structure of lignin into smaller molecules, and through certain measures its molecular structure should be made controllable and easy to compound with other materials. Second, the research should focus on how to overcome the hydrogen bonding between lignin macromolecules, realize the uniform dispersion of lignin macromolecules in the matrix, and improve the compatibility of lignin with other materials. Third, the preparation process should be streamlined, with reduced costs and pollution, so that it can be used industrially. Finally, research on the lignin-based composite membrane with selective separation function should be conducted, in order to break through the biggest limitation of polymer material blending “trade-off” effect, and to allow for its large-scale application in industrial gas separation, aqueous solution separation, separation and purification of chemicals and biochemical products, and other important processes. The continuous research on lignin-based composite materials is of great significance to protect the environment, save resources, and for green and sustainable development.

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