Review Article

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Lignin Whitening and Deploying Lignin-based Functional Materials

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Abstract
As petroleum reserves decline to diminish and become more expensive, there is a need to explore and develop renewable and carbon-neutral alternatives. The use of plant biomass instead of nonrenewable carbon resources has got considerable attention due to social requirements. Lignin is an aromatic biopolymer made up of phenylpropane units, which accounts for nearly 30% of organic carbon on Earth. Therefore, lignin is employed as a renewable source of aromatic chemicals and encourages sustainable social and economic development through the realization of a carbon neutrality. This mini-review introduces studies conducted by our research group on lignin utilization, such as water-dispersed lignin nanoparticles and whitened lignin derivatives as constituents of functional polymers. The presented results encourage the broader application of lignin in material sciences.

Keywords: *Plant biomass; UV protection film; Lignin Whitening; Heatproof filler; Insulation film*

INTRODUCTION

Transitioning away from petroleum-based materials is crucial for continuous social development and for actualizing a decarbonized society[1,2]. Natural and renewable alternatives to petroleum-based resources, such as plant biomass[2] and polylactide[3], have been explored for functional materials[2,4-17]. Lignocellulose is the major component of nonedible plant biomass, made up of polysaccharides and lignin. Lignocellulosic polysaccharides, such as cellulose and hemicelluloses, have been utilized as pulp[5], biofuels[7,11,12], and nanofibrous materials[13]. Lignin is an aromatic biopolymer made up of phenylpropane units (derived from lignin precursors) and various common linkages[14]. Lignin has therefore the potential to be a renewable alternative to synthetic aromatic polymers like polyimide. Several studies have investigated the potential uses of lignin as polymeric materials[15], e.g., high performance thermoplastics[8], polyurethane[16], and electronic substrate films[17]. Furthermore, there have been numerous scientific programs around the world, such as Horizon2020[18] in European Union and Biological Lignin Valorization Project[19] in United States, to employ lignin as functional monomers. In this review, approaches for the utilization of lignin on my research group as a functional polymer are introduced.

SESC Lignin: Lignin Derivatives Obtained through Simultaneous Enzymatic Saccharification and Comminution

A novel “physicobiological” process has been proposed for the extraction of polysaccharides and lignin from plant biomass. This process involves wet-type ultrafine bead milling and enzymatic saccharification, realizing the simultaneous enzymatic saccharification and comminution (SESC) of plant biomass to isolate polysaccharides and lignin as sugar solution and lignin water dispersion without contamination by harmful chemicals and byproducts[20-23]. The SESC process allows the extraction of lignin under extremely mild conditions (i.e., 50°C, 4 < pH < 6, and 1 psi) without requiring strong harmful chemicals. Although various types of physical comminution without the aid of chemicals and heat energy have been evaluated to process agricultural wastes such as bagasse with promising results[24], the higher lignin content of woody biomass, especially softwood species, presents challenges since they are more recalcitrant to microbial and enzymatic actions[25]. Unlike previous physical comminution approches, the SESC process can be applied not only for hardwood species but also for softwood species[20,26,27]. The polysaccharides are collected as mono- and oligo-sugars through SESC, which can be transformed into ethanol[26] and methane[27] through fermentation. The lignin derivative obtained through SESC (SESC lignin) is a water-dispersed slurry consisting of particles with diameters in the tens of nanometers range and with similar chemical structure to milled wood lignin[20,28]. Grinding freeze-dried SESC lignin produces fine powder with wood-like color (Fig. 1)[20]. SESC lignin is miscible with other components, such as synthetic polymers[29]. Additionally, SESC lignin exhibits various properties that make it ideal for material usage. For example, it can be used as water-dispersed antioxidant nanoparticles[30], a component of shape memory polymers[31], heat-proofing fillers for organic polymer[29,32,33], and ultraviolet-absorption additives[34-36]. The amount of the remaining polysaccharides in the SESC lignin was 8.42 w/w%[33]. Furthermore, adding a small quantity of SESC lignin (0.1 w/w%) improves the ionic conductivity of polymer electrolytes such as poly(ethylene oxide) and poly(ethylene carbonate). This motivated us to fabricate such SESC-lignin-containing electrolytes for all-solid-state battery applications[37,38].

Fig. 1. Photographs of Japanese cedar wood powders (left), lignin derivatives purified through soda-anthraquinone cooking (middle), and lignin derivatives purified through SESC process (right)

The SESC lignin generates a brown self-standing transparent film[20]. However, this film comprises heterogeneous small pieces that are too brittle for use in manufacturing certain products. A combination of SESC lignin and Li^+ montmorillonite, a clay mineral, enables the production of a uniform self-standing soft film with A4 size[35]. The films prepared from Li^+ montmorillonite (70–90 w/w%) and SESC lignin (10–30 w/w%) showed excellent UV-protecting properties due to the UV-absorbing nature of SESC lignin (Fig. 2). The inorganic nature of clay mineral and the aromatic polymer structure of SESC lignin confer nonflammability upon the films. In addition, these films exhibit a phase-separated structure of montmorillonite and SESC lignin. The porous structure in the SESC lignin-rich phase contributes to their high moisture/gas transmittance performance. These characteristics of the films advocate for the usage of mineral and plant resources as alternatives to petroleum-based materials and as novel high-value industrial materials. Furthermore, the optical properties and gas transmittance could be regulated by changing the film structure through optimization of its components, such as the species of clay minerals. In particular, the film's gas transmittance for helium and oxygen could be regulated in the range of numerous mol m^{-2} s^{-1} Pa^{-1} order; i.e., the oxygen transmittance ratio of the clay–lignin film was a maximum of three orders of magnitude lower than that of poly(ethylene terephthalate) (PET) films (2.0×10^{-17} mol m m^{-2} s^{-1} Pa^{-1})[36].

Functional “White” Lignin Materials Synthesized via Solvent-Controlled Encapsulation (SCE)

The characteristics of SESC lignin impart various functionalities to the lignin-based materials as shown above. However, SESC lignin, similarly to other typical lignin-based products, has browish color due to the presence of chromophores in lignin, such as (1) the carbon-carbon double bonds conjugated with aromatic rings[39)], (2) quinone methides, and (3) quinones[40,41)]. To circumvent this color issue, the SESC lignin and the organic group were linked via urethane bonds. These bonds were formed through a condensation reaction between the hydroxy groups of SESC lignin and organic isocyanate, without the need for catalyst and the emergence for toxic byproducts[42,43)]. To induce effective encapsulation of SESC lignin by non-chromophoric organic groups, two compatible solvents with different solubilities for organic groups were used for the reaction. Specifically, the isocyanate derivatives were mixed with SESC lignin in H_2O/EtOH solvent for modification of SESC lignin. By adjusting the polarity of the solvent, the distribution of chromophores and non-chromophoric organic groups was controlled, leading to solvent-controlled encapsulation (SCE) of chromophores in lignin derivatives. According to the SCE protocol, the reaction of SESC lignin with organic isocyanate for 5 h at 50°C in H_2O/EtOH solvent yielded a white solid in the mixture. The white powder of the modified SESC lignin can be collected by filtration and washing of the solid residue with H_2O/EtOH solvent (Fig. 3)[44)]. The reaction of SESC lignin and organic isocyanate in H_2O under identical reaction conditions to the SCE process yielded a brown powder, indicating that the SCE process is essential for whitening SESC lignin.

Fig. 2. Photograph of typical nonflammable and moisture-permeable UV protection films with approximately A4-paper size prepared from a clay mineral and SESC lignin (Li^+ montmorillonite: SESC lignin = 8: 2 w/w%).

Fig. 3. Typical photographs are neat SESC lignin powder (left), hexyl isocyanate modified SESC lignin (middle), and *m*-xylylene diisocyanate modified SESC lignin (right).

Hereafter, SESC lignin modified organic isocyanate is denoted as X modified SESC lignin; X = organic group in the isocyanate. The modified SESC lignin has dispersibility for various organic solvents such as chloroform (e.g., dodecyl or phenethyl modified SESC lignin) and ethanol (e.g., hexyl, heptyl or 2,6-diisopropylphenyl modified SESC lignin), whereas the neat SESC lignin can only disperse in water[20)]. The modified SESC lignin gave colorless transparent dispersion, whereas the neat SESC lignin water dispersion was brown. The absorption of SESC lignin in the visible light region was eliminated by the modification of organic isocyanate; specifically, a dispersion of modified SESC lignin transmit 80%–90% of visible light. The weight ratio of hexyl isocyanate in the modified SESC lignin was estimated to be 40 wt% by quantitating organic isocyanate in the modified SESC lignin. Therefore, the modified SESC lignin gives white colored powder and colorless transparent dispersion in ethanol, acetone, and chloroform even in the presence of 60 wt% of lignin component; in contrast, composites consisting of several percent SESC lignin have brown color[29,34-36)]. Whitening of SESC lignin nanoparticles could be achieved through a combination of factors: covering with substituents (i.e., suppression of light absorption), blocking of phenolic hydroxyl groups (i.e., diminishing quinoid structure), and assembling into uniform shapes (i.e., light reflection).

The reaction of organic isocyanates with lignin derivatives purified through sulfite cooking (lignin sulfonate) and soda-anthraquinone cooking (soda lignin) produces white powders similar to SESC lignin[44)]. These results indicate that SCE can whiten lignin derivatives other than SESC lignin purified from cedar. Additionally, the white color of modified SESC lignin is retained even after several years of storage. Thus, the modification of organic groups to lignin derivatives via SCE procedure brings permanent whitening of lignin derivatives. In contrast, the reaction of organic isocyanate to lignin derivative purified by kraft cooking (kraft lignin) only reduces its black coloring, i.e., the modified Kraft lignin has a slight brown color, unlike the case for SESC lignin, lignin sulfonate, and soda lignin as described earlier. Lignin sulfonate after alkali treatment (alkali lignin) also exhibited only color reduction through organic isocyanate modification. The solubility of lignin derivatives differs according to their extraction method[15)]. For example, lignin sulfonate and kraft lignin can dissolve in water and organic solvent, respectively. This difference in encapsulation efficiency of lignin derivatives (i.e., chromophores) by non-chromophoric organic groups affects the whitening degree of modified lignin derivatives. Based on this hypothesis, we achieved whitening modified kraft lignin and alkali lignin by adjusting the polarity of dispersed solvents. Specifically, immersing modified kraft lignin in an acetone/H_2O mixture resulted in its scuccessful whitening. Furthermore, whitening of brown-colored hexyl modified SESC lignin was successful by immersing it in EtOH or acetone/H_2O mixture. Thus, the coloring of modified lignin derivatives can be controlled by the SCE of the lignin derivatives (i.e, chromophores) by adjusting the polarity of dispersed solvents[44)].

Effect of Chemical Structure of Isocyanate Derivatives on Physical Properties of Whitened Lignin

To investigate the effect of the substituent structure on lignin whitening via modification of the organic isocyanate through SCE, we synthesized lignin derivatives modified by isocyanates containing alkyl chains with difference carbon numbers (i.e., varying alkyl chain lengths) via SCE and then estimated their colorability. The length of the alkyl chain likely affects lignin whitening via SCE due to differences in the bulkiness of the alkyl chain depending on its length.

SESC lignin was reacted with isocyanates containing alkyl chains with 2–4, 6, 7, 12, and 18 carbon number. Despite of the progress of the reaction between SESC lignin and isocyanates containing alkyl chain, the colorability of the modified SESC lignin completely differed in response to the carbon number of the alkyl chain. As shown in Fig. 4, SESC lignin was whitened by reaction with isocyanates containing the alkyl chain with more than four carbon atoms. Essentially, the lignin derivatives themselves (i.e., without the alkyl chain) assembled uniform nanoparticles in the H_2O/EtOH solvent[45)], and this assembly contributes to light reflection, leading to lignin whitening. This result indicates a necessary of modification of the alkyl chain with large molecular size for lignin whitening via SCE, i.e., the bulkiness of the substituent is an important structural factor for the encapsulation of the lignin's aromatic polymer chains[46)]. Butyl isocyanate modified the SESC lignin, resulting in a considerable amount of isocyanate groups (57 wt%) compared to the hexyl isocyanate-modified SESC lignin (40 wt%). The smaller molecular size of the butyl chain, relative to the hexyl chain, should enable the modification by a larger amount of isocyanate moieties.

We anticipated that applying diisocyanate derivative for lignin whitening via SCE could improve the physical properties (such as thermal stability) of the whitened lignin derivatives because of the removal of free terminal of substitutes and crosslinking of lignin polymer chains. The bond formation between the hydroxy groups of the lignin derivative with organic diisocyanates, such as hexamethylene diisocyanate, which is widely used in various industrial fields[47)], was carried out similar to the mono-isocyanate derivatives in H_2O/EtOH solvent. This reaction induces the whitening of lignin derivatives; specifically, the SCE reaction for the lignin derivatives occurs by reacting diisocyanate derivatives in two polarity-tuned compatible solvents. The replacing the terminal of alkyl chain from the methyl moiety (i.e., mono-isocyanate) to urethane bonds (i.e., di-isocyanate), thus removing free terminal, and restricting the mobility of lignin polymer chain by crosslinking prevent the thermal degradation of the whitened lignin. Additionally, the replacement of the substituent between isocyanate moieties from the alkyl chain (i.e., hexamethylene diisocyanate) to xylene (*m*-xylylene diisocyanate; Fig. 3) enhances the thermal stability of the whitened lignin[46)].

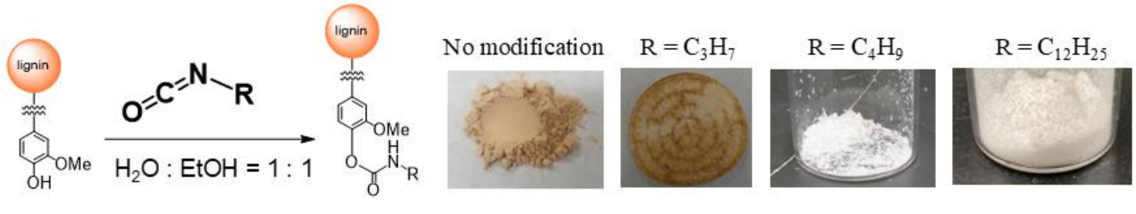

Fig. 4. (Left) Reaction route of whitening lignin derivatives via reaction with organic isocyanates in accordance with SCE. The reaction route of lignin and isocyanate represents an example of a possible general process, not specific, selective reaction, i.e., other hydroxy groups in lignin derivative can also react with the isocyanate group. (Right) Typical photographs are neat SESC lignin powder and SESC lignin reacted with isocyanates containing alkyl chain with 3 (isopropyl group), 4 (butyl group), and 12 (dodecyl group) carbon number.

Functions of “Whitened” Lignin

The whitened lignin nanoparticles possess various functions for material applications. The casting and drying of hexyl-modified SESC lignin ethanol solution result in a transparent coating film with 91% total light transmittance and a haze value of 7.0 (Fig. 5a). Additionally, dodecyl- and hexyl-modified SESC lignins melt upon heating at 110°C and 70°C, respectively, indicating that these whitened lignins can be treated as hot-melt-type polymers.

Previously, the heatproofing of synthetic polymers was reported by feeding a small amount of SESC lignin. This effect is attributed to the combination of preferential pyrolysis and radical scavenging of the lignin structure[29,32,33)]. The whitened SESC lignin nanoparticle enables it to be dispersed in hydrophobic polymers such as poly(ε-caprolactone) (PCL), a bio-originated polyester. Furthermore, feeding 5 w/w% of hexyl- or heptyl-modified SESC lignin to PCL increases its 5% and 50% weight decomposition temperature to approximately 20°C and 60°C, respectively. Therefore, unlike neat SESC lignin, whitened SESC lignin nanoparticles can be used as a heat-proofing filler for bio-originated polyester without causing coloration. These results support the use of whitened SESC lignin nanoparticules as functional additives for synthetic polymers.

The PCL films containing whitened SESC lignin derivatives were obtained by kneading and hot-pressing. The PCL films containing neat lignin derivatives such as SESC lignin and kraft lignin have blown color originating from the lignin derivatives. Contrastingly, the PCL films containing hexyl modified whitened SESC lignin show transparency without coloring (Fig. 5b) because of the white coloring nature and the processability as transparent film of the whitened lignin48).

The addition of SESC lignin increased the Young's modulus and yield stress of PCL films. The yield strain of the PCL films containing SESC lignin was inversely proportional to the content of SESC lignin. Thus, the SESC lignin acts as an anti-plasticizer of PCL due to the rigid aromatic polymer chain s of SESC lignin relative to PCL. The PCL films containing whitened lignin exhibited higher Young's modulus, yield stress, and yield strain than PCL films containing neat SESC lignin The modification of SESC lignin with hexyl groups for whitening would increase its miscibility with PCL due to the hydrophobicity of the whitened lignin relative to neat SESC lignin, which, in turn, enhances the mechanical strength of PCL-SESC lignin composites48).

Because *m*-xylylene diisocyanate modified SESC lignin (XyDNCO) is an aromatic group-rich polymer, it exhibits electrical insulating properties. For example, a XyDNCO-based tablet (Fig. 5c) has a volume resistance of $6.6 \pm 0.26 \times 10^{13}$ Ωcm, which is comparable to that of typical aromatic resins49). Moreover, XyDNCO has small peak at 152 ºC on its differential scanning calorimetry (DSC) curve, which corresponds to its thermal melting behavior, similar to other whitened lignin derivatives described above. Therefore, XyDNCO can be mixed with synthetic polymers, such as PCL, solely by heat kneading. Hot pressing of the kneaded composites (i.e., pellets) containing equal amounts of XyDNCO and PCL endows the resultant films with higher electrical insulation properties (volume resistance: $1.1 \pm 0.0022 \times 10^{14}$ Ωcm) than those of the neat PCL films (volume resistance: $3.0 \pm 0.17 \times 10^{12}$ Ωcm), demonstrating that the addition of XyDNCO increases insulation nature of PCL films and XyDNCO therefore acts as an insulating filler for PCL44). The composite films with equal amounts of XyDNCO and PCL exhibited good mechanical strength with a self-standing nature (tensile fracture stress: 8.4 MPa; tensile fracture strain: 0.5 mm/mm).

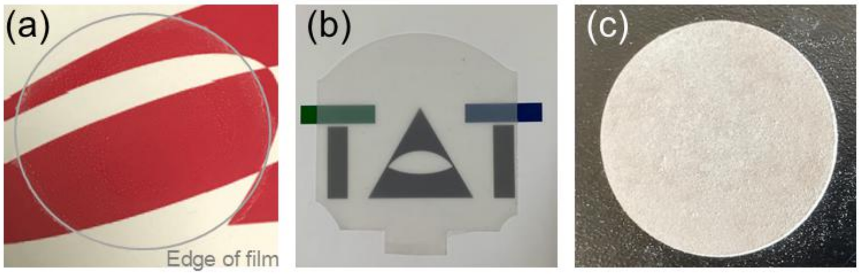

Fig. 5. Photographs of the transparent film consisting of hexyl modified SESC lignin obtained by solvent casting on PET substrate (a), PCL film containing 1 wt. % of hexyl modified SESC lignin (film thickness = ~0.3) (b), and pressed tablet of *m*-xylylene diisocyanate modified SESC lignin (XyDNCO).

CONCLUSIONS

1. The simultaneous enzymatic saccharification and comminution (SESC) process is a novel, mild, and environmentally-friendly process for the treatment of lignocellulosic biomass, enabling its utilization in a wide range of novel applications. The obtained lignin derivative (SESC lignin) can be used as a functional polymer due to its radical scavenging properties and its stiff polyphenolic backbones.

2. A novel technique for permanently whitening lignin derivatives was proposed through their solvent-controlled encapsulation (SCE). This novel process enables lignin derivatives to be applied as functional polymeric materials with high design flexibility, thereby broadening the utilization of lignin to realize the transition from the oil-based refinery to the biomass-based refinery.

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