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## ARTICLE

# Functional “permanently whitened” lignin synthesized via solvent-controlled encapsulation

Kazuhiro Shikinaka\*<sup>a</sup> and Yuichiro Otsuka<sup>b</sup>

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Here, we present a practical method for whitening lignin derivatives, which is solvent-controlled encapsulation (SCE) to rearrange the chromosphere at the solvent/lignin interface. Water, ethanol, and/or acetone are mixed to adjust the polarity of the solvent, resulting in lignin nanoparticles with hydrophobic chromophores within the core. Whitening lignin derivatives are produced when the hydroxy group is simultaneously modified by a non-chromophoric organic group. The SCE method is used in various organic isocyanates with different substituents and lignin derivatives. The whitened lignin nanoparticle acts as transmittance coating-film, glass/quartz adhesive, and heatproofing additive for poly( $\epsilon$ -caprolactam). Our results first demonstrate that lignin can be used as whitened polymers with high design flexibility and material functionality. A broad-range usage of lignin via its whitening is encouraged to realize conversion from oil-based refinery to biomass-based refinery.

## 1 Introduction

Abandoning petroleum-based materials science is critical to achieve a low-carbon society.<sup>1</sup> Plant polymers, polysaccharides, and lignin are promising alternatives to petroleum.<sup>2</sup> Lignin is an aromatic biopolymer consisting of phenylpropanoid building blocks that accounts for nearly 30% of organic carbon on Earth.<sup>3</sup> The use of lignin as a renewable source of aromatic chemicals encourages sustainable social and economic development via a realization of a low carbon society.<sup>2</sup> Recently, there have been several approaches to using lignin as valuable materials, *such as* functional additives and polymeric resin.<sup>4-7</sup>

However, despite its potential as a functional material, most lignin derivatives extracted from plants (over 90%) have been used not as valuable materials but as fuels as heat sources on factory.<sup>8</sup> One critical issue in the use of lignin derivatives for materials is their brown or black coloring, which makes serious negative effects in many application fields such as polymeric additives and resin, *e.g.*, composites consisting of several percent lignin derivatives have a deep black color.<sup>4-12</sup> The coloring of wood is also brought by lignin, which is a minor component in wood relative to polysaccharides. The removal of lignin coloring will enable it to be used in a broader industrial field, *i.e.*, various design possibilities on lignin-based products will be dramatically expanded via their whitening.

The following chromophores have been proposed for ordinary lignin derivatives: (1) the carbon-carbon double bonds conjugated

with aromatic rings,<sup>13</sup> (2) quinone methides, and (3) quinones.<sup>14,15</sup> The (1) is a primarily inherent structure in aromatic rings of lignin. By contrast, (2) and (3) are generated during the treatment of lignin with acid, base, and steam (*e.g.*, its extraction process from plants). These chromophores induce the coloring of lignin derivatives.<sup>16</sup> Thus, H<sub>2</sub>O<sub>2</sub> treatment and UV irradiation cause the aromatic ring in lignin macromolecules to decompose, reducing their coloring.<sup>17-19</sup> Additionally, the coloring of lignin derivatives was suppressed to light yellow by prevention aromatics from assembling in the lignin structure<sup>13</sup> and by reducing the phenolic hydroxy groups.<sup>20</sup> Previous research has also argued that encapsulating chromophores in lignin reduces the coloring of acetylated lignin derivatives.<sup>21</sup> In these reports, reducing light absorption of lignin derivative by light reflection via its surface smoothing<sup>13</sup> or making it uniform sphere shape<sup>21</sup> also suppressed coloring of lignin derivatives. Furthermore,



**Fig. 1** Reaction route of whitening lignin derivatives via reaction with organic isocyanates in accordance with SCE. Typical photographs are (left) neat SESC lignin powder and (right) hexyl modified SESC lignin described as “whitened” lignin. 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.

<sup>a</sup> Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology, Nigatake, 4-2-1, Miyagino-ku, Sendai 983-8551, Japan. E-mail: kaz.shikinaka@aist.go.jp

<sup>b</sup> Forestry and Forest Products Research Institute, Matsunosato, 1, Tsukuba 305-8687, Japan.

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it has been reported that adding a sulfobutyl ether group to Kraft lignin reduces its color.<sup>22</sup> According to these reports, removal and/or rearrangement of the chromophores of lignin derivatives and suppression of light absorption are valid to remove their coloring. However, these previous approaches brought on only temporally color reduction of lignin derivatives (i.e., the color of lignin derivatives becomes dark color followed by storing for several months<sup>20</sup>). Additionally, "whitening" of lignin derivatives has been never attained.<sup>13,20-22</sup>

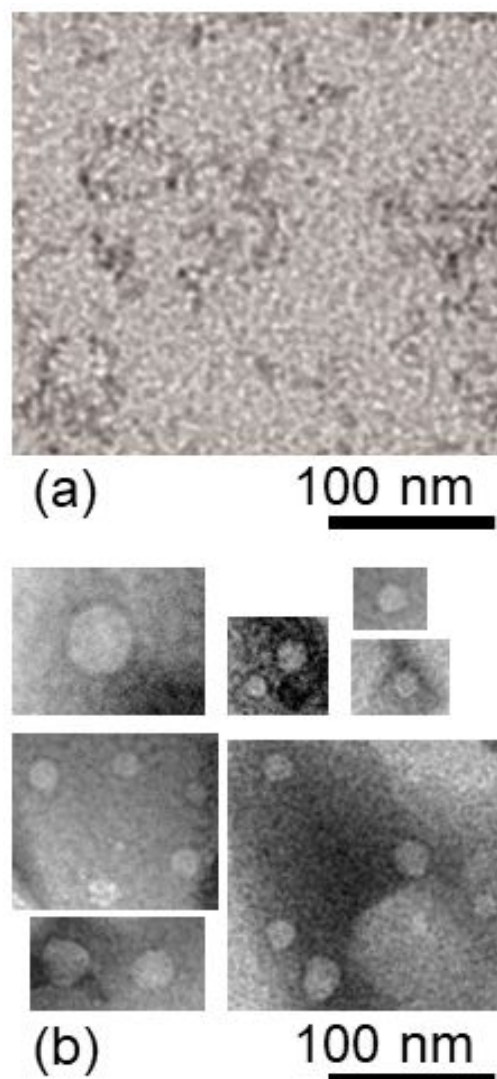
In this study, we designed a method for permanently whitening of lignin derivatives by encapsulating the chromophores of lignin derivatives with organic groups (Fig. 1). Our results first demonstrate that lignin can be used as whitened materials with high design flexibility and material functionality. A broad-range usage of lignin via its permanently whitening is encouraged to realize conversion from oil-based refinery to biomass-based refinery.

## 2 Results and Discussion

### 2.1 Lignin "Whitening" via Solvent-Controlled Encapsulation

First, we describe the whitening of a water-dispersed lignin derivative obtained through simultaneous enzymatic saccharification and comminution (SESC) of plant.<sup>23-30</sup> SESC process is wet-type ultrafine bead milling with enzymatic saccharification for plants to isolate polysaccharides and lignin as sugar solution and lignin water dispersion from plants without contamination by toxic reagents and byproducts.<sup>23,24</sup> In principle, the SESC could enable the extraction of lignin under extremely mild conditions (i.e., 50 °C, 4 ≤ pH ≤ 6, and 1 psi) without requiring strong toxic chemicals. The polysaccharides are collected as mono/oligo sugars through the SESC of plants and can be transformed to methane<sup>25</sup> and ethanol<sup>29</sup> via fermentation. The lignin derivative obtained by SESC (later denoted as SESC lignin) is water-dispersible particle with diameters of several tens of nanometers that have the high purity and non-deteriorated characteristic as lignin because of mild reaction condition on the SESC process.<sup>23</sup> These characteristics give the SESC lignin various functionality as variable materials.<sup>26-28</sup> However, the SESC lignin has light brown color due to the presence of chromophores in lignin as described in Introduction.

Here, the SESC lignin and the organic group were linked via urethane bonds, which are formed via a condensation reaction between the hydroxy group of SESC lignin and organic isocyanate without the need for catalyst and emergence for toxic byproducts.<sup>31,32</sup> SESC lignin is an amorphous nanoparticle (Fig. 2A). Two compatible solvents with different solubility to organic groups were used for the reaction to induce effective encapsulation of SESC lignin by non-chromophoric organic groups, i.e., the isocyanate derivatives were mixed with SESC lignin in H<sub>2</sub>O/EtOH solvent for modification of SESC lignin (Fig. 1). Under the mixing solvent system, organic isocyanate modified SESC lignin formed a nanoparticle with a uniform sphere shape (Fig. 2B) where hydrophobic chromophores



**Fig. 2** Negative stained transmission electron microscopic images of (a) neat SESC lignin and (b) hexyl-modified "whitened" SESC lignin.

should be located within the core. By adjusting the polarity of the solvent, the distribution of chromophores and non-chromophoric organic groups was determined, resulting in solvent-controlled encapsulation (SCE) of chromophores in lignin derivatives. According to SCE protocol, the reaction of SESC lignin with organic isocyanate for 5 h at 50 °C in H<sub>2</sub>O/EtOH solvent yielded a white solid in the mixture. A white powder (i.e., modified SESC lignin) can be collected by filtration and washing of the solid residue with H<sub>2</sub>O/EtOH solvent (Fig. 1). The reaction of SESC lignin and organic isocyanate in H<sub>2</sub>O under the same conditions as the SCE produced a brown powder, indicating that the SCE process is essential for whitening SESC lignin.

In the FT-IR spectrum of the modified SESC lignin (Fig. S1), the peaks from N-H stretching vibration (approx. 3325 cm<sup>-1</sup>) were recognized that indicate urethane bonds and alkyl chains, respectively. The peaks originating from alkyl chains, aromatics, and cyclic ethers were also confirmed. Contrastingly, there was no peak from N=C=O vibration (2280–

**Table 1**  $L^*a^*b^*$  (CIELAB) color space of modified lignin derivatives and raw materials.

sample	$L^*$	$a^*$	$b^*$
2,6-Diisopropylphenyl modified SESC lignin	89.72	0.02	0.96
Heptyl modified SESC lignin (washed by EtOH + H <sub>2</sub> O)	88.33	0.41	4.61
Hexyl modified SESC lignin (washed by EtOH + H <sub>2</sub> O)	85.41	-0.17	1.42
Phenethyl modified SESC lignin	83.81	0.40	8.29
Dodecyl modified SESC lignin	82.46	0.63	4.22
Hexyl modified SESC lignin purified from birch†	81.73	1.61	10.78
Benzyl modified SESC lignin	77.97	2.33	13.05
Hexyl modified SESC lignin (washed by H <sub>2</sub> O)	61.35	5.26	18.24
Heptyl modified SESC lignin (washed by H <sub>2</sub> O)	60.15	2.86	11.58
1,4-butanediol modified SESC lignin‡	70.39	4.11	12.23
SESC lignin	66.84	8.38	19.04
2,6-Diisopropylphenyl modified lignin sulfonate	88.68	-0.30	1.00
Dodecyl modified lignin sulfonate	88.59	-0.16	1.78
Phenethyl modified lignin sulfonate	88.03	0.04	4.66
Hexyl modified lignin sulfonate	85.23	-0.44	6.11
Lignin sulfonate	55.09	10.80	28.45
Dodecyl modified soda lignin	81.49	2.09	8.63
Soda lignin	28.40	3.69	3.62
Dodecyl modified Kraft lignin	74.19	3.37	4.22
Kraft lignin	45.87	8.51	18.90
Dodecyl modified alkali treated lignin sulfonate	73.83	3.02	12.49
Alkali treated lignin sulfonate	19.12	2.10	1.86

† The modified SESC lignin except for "Hexyl modified SESC lignin purified from birch" were synthesized from SESC lignin purified from cedar.

‡ A modification of 1,4-butanediol to SESC lignin at alkali medium (*i.e.*, sulfonation reaction) following the previous literature.<sup>22</sup>

2230 cm<sup>-1</sup>) and OH stretching vibration (approx. 3400 cm<sup>-1</sup>), indicating that isocyanate and hydroxy groups react during the SCE process. From an estimation by Boehm titration,<sup>33,34</sup> the hydroxy groups in SESC lignin decreases after SCE reaction

(Table S1). A modification of phenolic hydroxy groups contributes to the decoloration of lignin derivatives by suppressing phenolic hydroxy groups to a quinoid structure, resulting in a darker color of lignin derivatives.<sup>20</sup> The presence of aromatic rings of lignin and alkyl group of isocyanate is indicated by a broad signal from aromatic (6.2 ppm) and alkyl protons (1.3 ppm, triplet) on the <sup>1</sup>H-NMR spectrum from the solution of the modified SESC lignin (Fig. S2). The broad nature of peaks in the NMR spectrum characterizes a nanoparticle of modified SESC lignin (Fig. 2B). The solution of the modified SESC lignin also showed UV-absorbance around 270–280 nm that originates from aromatic groups in lignin (Fig. S3). Thus, the results of FT-IR, NMR, and UV spectra indicate urethane bonds, organic groups of isocyanate, and lignin's structural units.

The regularity peak pattern in MS of modified SESC lignin (Fig. S4a) is similar to that of neat SESC lignin (Fig. S4b) based on a mass spectrum pattern obtained by laser ionization time-of-flight mass spectroscopy via matrix-assisted laser desorption/ionization (MALDI-TOF/MS). Especially, in the MS of modified SESC lignin, continuous regular peaks were observed at a range of mass-to-charge ratio ( $m/z$ ) from 1000 to 10000 in a linear detection mode (Fig. S4a). The MS of modified SESC lignin at the reflector detection mode showed evenly spaced patterns that originated from ionized fragments such as aromatic derivatives and ether bonds (Fig. S5). The results from MALDI-TOF/MS indicate that modified SESC lignin includes the lignin's macromolecules linked with organic groups via urethane bonding. 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.<sup>23</sup> The modified SESC lignin gave colorless transparent dispersion (Fig. S6), whereas the neat SESC lignin water dispersion was brown. The size distribution of modified SESC lignin in organic solvent was several tens of nanometers, which was slightly higher than the size distribution of neat SESC lignin.

The absorption of visible light of SESC lignin was eliminated by the modification of organic isocyanate, *i.e.*, a dispersion of modified SESC lignin passes 80%–90% of visible light (Fig. S7). A weight ratio of hexyl isocyanate in the modified SESC lignin is 40 wt% was estimated by quantitating organic isocyanate in the modified SESC lignin, *i.e.*, modified SESC lignin gives white colored powder and colorless transparent dispersion even in the presence of 60 wt% of lignin component (the composites consisting of several percent SESC lignin have brown color<sup>26–28,30</sup>). Covering with substituents (*i.e.*, suppression of light absorption), blocking of phenolic hydroxy groups (*i.e.*, diminishing quinoid structure), and assembling to uniform

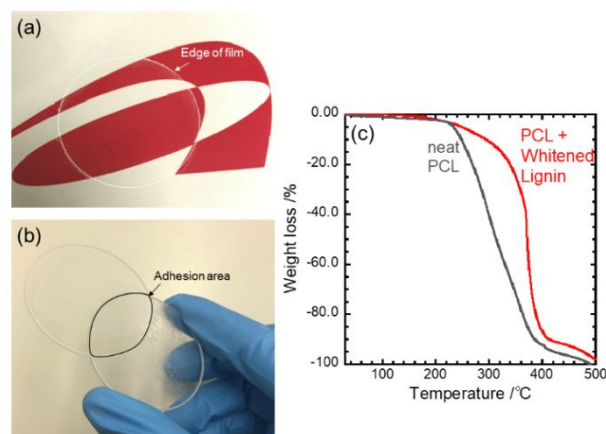
shape (*i.e.*, light reflection) would induce whitening SESC lignin nanoparticles (Fig. S8).

The whitening degree of modified SESC lignin powder differs depending on the species of modified organic groups and solvent for washing (Table 1 and Fig. S9). The whitening degree of hexyl or heptyl modified SESC lignin decreased significantly when the washing solvent was changed from EtOH/H<sub>2</sub>O mixture to pure H<sub>2</sub>O (Fig. S10). The lower solubility of hexyl and heptyl groups in H<sub>2</sub>O than in EtOH inhibits the encapsulation of lignin by organic groups, *i.e.*, the lignin components (the chromophores) in the hexyl/heptyl modified SESC lignin are exposed on the surface of modified SESC lignin (Fig. S11).

As shown in Table 1, the SESC lignin can be whitened by the SCE (*e.g.*, cedar or birch; Table 1), regardless of its origin. Additionally, the reaction of organic isocyanates with lignin derivatives purified through sulfite cooking (later denoted as lignin sulfonate) and soda-anthraquinone cooking (later denoted as soda lignin) produces white powders similar to SESC lignin (Table 1 and Fig. S12). 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 kept followed by storing for several years (Fig. S13), *i.e.*, modification of organic groups to lignin derivatives via SCE procedure brings permanent whitening of lignin derivatives.

Contrastingly, the reaction of organic isocyanate to lignin derivative purified by Kraft cooking (later denoted as 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/soda lignin (Fig. S14 and Table 1). Additionally, lignin sulfonate after alkali treatment (later denoted as alkali lignin) exhibited only color reduction through organic isocyanate modification (Table 1). The solubility of lignin derivatives differs according to their extraction method,<sup>4</sup> *e.g.*, lignin sulfonate and Kraft lignin can dissolve in water or 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/alkali lignin by adjusting the polarity of dispersed solvents, *i.e.*, immersing modified Kraft lignin in an acetone/H<sub>2</sub>O mixture made it whiten (Fig. S15). Furthermore, the brown-colored hexyl modified SESC lignin was whitened by immersing it in EtOH or acetone/H<sub>2</sub>O mixture (Fig. S16). 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.

Lignin derivatives form nanoparticles in H<sub>2</sub>O/EtOH solvent.<sup>35</sup> Here, modified lignin derivatives also formed nanoparticle in chloroform (peak top on a histogram of dodecyl modified lignin sulfate/soda lignin/Kraft lignin are 10.3/17.3/29.8 nm, respectively). This phenomenon supports effective encapsulation of various lignin derivatives by organic groups (*i.e.*, suppression of light absorption) and uniform



**Fig. 3** Photographs of the transparent film consisting of hexyl modified SESC lignin obtained by solvent casting. (b) Photograph of quartz plates adhered by dodecyl modified SESC lignin. (c) The result of thermo-gravimetric analysis of a mixture of poly( $\epsilon$ -caprolactone) (PCL;  $M_n = 10,000$ ) and heptyl modified SESC lignin. (PCL: lignin = 95:5 w/w%)

shape-modified lignin nanoparticles (*i.e.*, light reflection) that induce whitening modified lignin derivatives.

## 2.2 Function of "Whitened" Lignin

The whitened lignin nanoparticle has various functions for its material use. The casting and drying of hexyl-modified SESC lignin ethanol solution result in a transparent coating film with 91% and 7.0 total light transmittance and a haze value (Fig. 3A). Furthermore, dodecyl or hexyl modified SESC lignin melts by heating at 110°C or 70°C (Fig. S17a) because their endothermic behavior is recognized by the differential scanning calorimetry curve (Fig. S17b). Dodecyl modified SESC lignin forms transparent film (Fig. S18) by hot melting and subsequent cooling between glass plates, which is the first case of the preparation of hot-melt-type non-colored materials from lignin derivatives. A transparent film is produced when dodecyl-modified Kraft lignin is melted at 110°C and then cooled. This phenomenon indicates that the modification of organic groups confers meltability not only on SESC lignin but also on Kraft lignin. Because of the meltability of whitened lignin nanoparticle, lignin derivatives can be used as hot melt-type polymer materials.

The plates adhere when the whitened SESC lignin is melted and then cooled to sandwiched between two glass or quartz plates, *e.g.*, the adhered two quartz plates never peeled off by their weight at r.t. (Fig. 3B). Furthermore, the re-heating of adhered to plates causes their peeling by re-melting of modified SESC lignin. Some reaction between hydroxy groups on glass/quartz surface and heterocycle structure with oxygen atoms in SESC lignin might relate this adhesion behavior. These results suggest that whitened SESC lignin nanoparticle could be used as a removable hotmelt-type adhesive as shown in other lignin-originated derivatives.<sup>36,37</sup>

Previously, heatproofing of the synthetic polymer was reported by feeding a small amount of SESC lignin, which is brought by the combination of preferential pyrolysis and radical scavenging of lignin structure.<sup>27,38,39</sup> The whitened SESC lignin

nanoparticle enables it to be dispersed in hydrophobic polymers such as poly( $\epsilon$ -caprolactone), a bio-originated polyester. Furthermore, feeding 5 w/w% of hexyl or heptyl-modified SESC lignin to poly( $\epsilon$ -caprolactone) increases its 5 and 50% weight decomposition temperature to approximately 20 and 60°C (Fig. 3C and S19). Therefore, unlike neat SESC lignin,<sup>26-28</sup> whitened SESC lignin nanoparticle can be used as a heatproofing filler for bio-originated polyester without coloring (Fig. S20). These results support the use of whitened SESC lignin nanoparticle as functional additives for synthetic polymers.

### 3 Conclusions

Here, we developed SCE, a novel method for whitening lignin derivatives. SCE is a simple process, *i.e.*, commercially available isocyanate derivatives reacted with lignin derivatives in polarity-tuned mixed solvents. The whitened lignin nanoparticles can be molded to transparent film via solvent-casting or hot melting. Furthermore, the whitened lignin nanoparticles act as a colorless adhesive for glass/quartz and a heatproofing filler for bio-originated polyester. Additionally, SCE between isocyanate derivatives and sawdust or cedar saccharification residue yields the whitened lignin, *i.e.*, SCE enables us to directly extract and use the whitened lignin from non-purified lignin-contained materials; we will describe details elsewhere. Whitened lignin nanoparticles enable the use of unprecedented industrial fields with high design possibilities. The production of whitened lignin nanoparticle would not only encourage the use of plant components as high-value industrial materials but would also reduce the environmental load of extracting limited petroleum-based resources. For this purpose, we will study the optimization of the synthetic route of whitened lignin nanoparticle to achieve a more effective production. Finally, the substitution of petroleum-based resources with natural resources is expected to establish a novel field of "Agricultural Industry".

## 4 Experimental

### 4.1 Materials

Kraft lignin (Sigma-Aldrich, USA), lignin sulfonate (TCI, Japan), alkali-treated lignin sulfonate (TCI), isocyanate derivatives, 1,4-butanediol, (Tokyo Chemical Industry Co., Ltd., Japan), poly( $\epsilon$ -caprolactone) (Sigma-Aldrich), and methanol, ethanol, acetone, and chloroform (Sp. Gr., Wako Chemicals, Japan) were used as purchased. The SESC lignin was extracted from Japanese cedar as platelet-like nanoparticles<sup>27</sup> of approximately 40 nm diameter according to our previous literature.<sup>23</sup> Soda lignin was extracted from Japanese cedar via cooking with soda and anthraquinone.<sup>40</sup> Ultrapure water, purified in a Milli-Q® Advantage A10® system (Millipore™, Eschborn, Germany), was used throughout the study.

### 4.2 Whitening lignin derivatives

0.2-g of lignin derivatives were dissolved in a mixture of an equal amount of water and ethanol or pure water. 2-mL isocyanate derivative (hexyl, heptyl, dodecyl, benzyl, phenethyl, or 2,6-diisopropyl phenyl isocyanate) was dropped into the lignin dispersion. The mixture was filtered and washed

with a mixture of equal amounts of EtOH and H<sub>2</sub>O or pure water. The collected samples were dried *in vacuo* for 3 h after stirring at 50°C for 5 h to yield 2,6-diisopropylphenyl modified SESC lignin (white colored powder, 0.154 g), heptyl modified SESC lignin washed by EtOH + H<sub>2</sub>O solvent (white colored powder, 0.0136 g), hexyl modified SESC lignin washed by EtOH + H<sub>2</sub>O (white colored powder, 0.568 g), phenethyl modified SESC lignin (white colored powder, 0.592 g), dodecyl modified SESC lignin (white colored powder, 0.307 g), hexyl modified SESC lignin purified from birch (white colored powder, 0.565 g), benzyl modified SESC lignin (light pale colored powder, 0.213 g), 2,6-diisopropylphenyl modified lignin sulfonate (white colored powder, 0.0331 g), dodecyl modified lignin sulfonate (white colored powder, 0.808 g), phenethyl modified lignin sulfonate (white colored powder, 0.448 g), hexyl modified lignin sulfonate (white colored powder, 0.2717 g), dodecyl modified soda lignin (white colored powder, 0.546 g), dodecyl modified Kraft lignin (brown colored powder, 0.563 g), and dodecyl modified alkali treated lignin sulfonate (brown colored powder, 0.7418 g).

1,4-butanediol reacted with SESC lignin in 0.01 M NaOH water solution at 80°C for 3 h following the previous literature.<sup>22</sup> The product was collected by filtration and then dried, yielding the modified SESC lignin as small amount powders attached on filter paper.

### 4.3 Transmission electron microscopy (TEM)

TEM observation was performed using an FEI TECNAI-G20 electron microscope at 200 kV acceleration voltage. A 10  $\mu$ L of 0.35 w/v% sample dispersion was dropped on carbon-coated grids (Nisshin EM Co., Tokyo), which were rendered hydrophilically by glow discharge in reduced pressure. After 1.5 min, 10  $\mu$ L of 2 w/v% phosphotungstic acid aqueous solution (pH = 6–7) was added to the sample on the grids for negative staining of samples. After 30 sec of staining, the solution on the grids was removed, and then the grids were air-dried.

### 4.4 Estimation of composition of modified lignin

The composition of modified lignin was estimated by quantitating the organic isocyanate of the modified lignin based on the following methods. 10–11-mg hexyl modified SESC lignin was mixed with methanol and then the mixture was heated at approximately 230°C and 7 MPa for 70 min to decompose urethane bonding.<sup>41</sup> An alkyl methylcarbamate generated from a urethane bonded alkyl chain in the modified SESC lignin was collected as the filtrate by filtration of the heated mixture. The amount of collected alkyl methylcarbamate (equal to the amount of alkyl isocyanate) was measured by gas chromatography-mass spectrometry (GC-MS). GC-MS measurements were performed using an HP-5MS column (Agilent Technologies, Inc., USA), which was coupled to a QP2010 gas chromatograph-mass spectrometer system (Shimadzu, Co., Japan). The sample was heated in the column by introducing a standard or collected alkyl methylcarbamate into the GC-MS. The column temperature was initially held at 40°C for 3 min and then programmed to increase to 300°C at a rate of 20°C min<sup>-1</sup>. The mass spectra



were recorded under an electron impact ionization energy of 70 eV. The MS detector scanned from 15 to 240  $m/z$  at a rate of five scans per second. A methanol solution of alkyl methylcarbamate synthesized from alkyl isocyanate and methanol (74.5–745  $\mu\text{g mL}^{-1}$ ) was measured as a standard to create a calibration curve. Based on the peak area of alkyl methylcarbamate indicated by the chromatograph, the concentration of alkyl methyl carbamate was calculated using an approximate expression from the calibration curve. The data were averaged at least twice.

#### 4.5 Estimation of color space

$L^*a^*b^*$  (CIELAB) color space of modified lignin derivatives and raw materials was measured by color difference meter with reflector mode (CR-5, Konica Minolta Japan Inc.).  $L^*$ ,  $a^*$ , and  $b^*$  represent the lightness of the color, the position between red and green, and the position between yellow and blue, respectively.  $L^* = 0$  yields black and  $L^* = 100$  indicates diffuse white. Negative and positive values of  $a^*$  indicate green and red coloring, respectively. Negative and positive values of  $b^*$  indicate blue and yellow coloring, respectively.

#### 4.6 Preparation of transparent lignin films

Solvent casting; 2 w/w% of hexyl modified SESC lignin dissolved in ethanol was cast on the PET sheet and then dried, yielding film product. Hot melting; 0.2-g of dodecyl modified SESC lignin powder was put on a Teflon film and then heated at 110°C for melting.

#### 4.7 Measurement of optical properties

The total light transmittance (*i.e.*, change of percentage on amount of light until passing the samples) and haze value (*i.e.*, turbidity of the samples) were measured by a haze meter (NDH5000, Nippon Denshoku Ind. Co., Ltd., Japan).

#### 4.8 Adhesion test of hot melted dodecyl modified SESC lignin

For the adhesion test of dodecyl modified SESC lignin, a powder of modified SESC lignin was sandwiched between two quartz plates. Then, the sample was heated by hotplate at 110°C for 1 min. By cooling the sample at r.t., the quartz plates adhered by re-solidified modified SESC lignin were obtained.

#### 4.9 Preparation of composite consisting of poly( $\epsilon$ -caprolactone) and whitened lignin

About 2-g of poly( $\epsilon$ -caprolactone) consisting of 5 w/w% of modified SESC lignin were mixed and kneaded at 130 °C with a 100-rpm rotational speed for 5-min by an injection molding machine (IMCA300, Imoto Machinery Co., Ltd. Japan). The obtained pellets were hot-pressed at 5.0 MPa for 10 min at 130 °C so they could be molded into films with about 100- $\mu\text{m}$  thickness.

#### 4.10 Thermo-gravimetric analysis

Thermogravimetric (TG) analysis was conducted using a Rigaku Thermo plus EVO2 TG8121 system heated for 10°C  $\text{min}^{-1}$  under an air atmosphere. The 5% and 50% decomposition temperature ( $T_d$ ) as an index of heat tolerance on the composites was defined.

## Author Contributions

Kazuhiro Shikinaka: Data curation, Investigation, Methodology, Formal Analysis, Validation, Conceptualization, Funding acquisition, Project administration, Writing - original draft. Yuichiro Otsuka: Project administration, Resources, Writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

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