Design and Application of Functionality Controllable Lignin-Based Materials

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Through the phase-separation system composed of phenols and concentrated acid, lignin-based materials, lignophenols were synthesized. Under the alkaline condition, C1-phenoxide of 1,1-bis(aryl)propane type units attacked adjacent C2, followed by the cleavage of aryl ether linkages (switching function). Cellulose-lignophenol composites were prepared by the combination with cellulose powder and hydroxymethylated lignophenol through heating and pressing. Highly hydroxymethylated ligno-p-cresol gave a composite with higher density and higher water resistance, compared with ligno-2,4-dimethylphenol hydroxymethylated only in their terminal units. Ligno-p-cresol and ligno-2,4-dimethylphenol were separated from the composites using the switching function in 17% and 98% yields, respectively.

Key words: Lignin, Phase-separation system, Lignophenol, Cellulose-lignophenol composites, Recycle

1. INTRODUCTION

Lignocellulosics produced through the photosynthesis are the source of a wide range of organic materials. The essential resources for the modern society such as petroleum and coal are have been derived from them. But if we continue current mass production-consumption system, these fossil resources would be exhausted and the global ecological cycle of materials would lose their balance. In order to ensure a sustainable future, we should built utilization system of the lignocellulosics in the molecular level and recycle them as long as possible.

The plant cell wall has the complicated semi-IPN structure built up from cellulose, hemicellulose and lignin. These components cannot be separated by simple extraction processes. The drastic treatments for the separation result in the undesirable modification of components, especially lignin.

For the successive total utilization system of lignocellulosics, the phase-separation system composed of phenols and concentrated acid has been originally designed [1-3]. The key point of this system is that hydrophobic lignin and hydrophilic carbohydrates are into different phases within the cell wall, and are modified individually. In the organic phase, the lignin is hybridized with phenols at C1-position of phenylpropane to give the lignophenol with 1,1-bis(aryl)propane unit. On the other hand carbohydrates are hydrolyzed into soluble poly-, oligo- and mono-saccharides.

The resulting linear type polymers, lignophenols can be applied to various industries as raw materials. For the successive utilization, the functionality of lignophenols might be changed using the intramolecular switching function (Fig. 1) [4]. The switching function of lignophenols works as follows; C1-phenols hybridized to lignophenol at ortho position to their hydroxyl group attack adjacent C2-carbons by mild alkaline treatment. The C2-O-aryl ether linkages of lignophenol are cleaved with the exchange of phenolic functionality from C1-phenols to lignin nuclei.

In the present works, lignophenols were

hydroxymethylated, and use as the matrixes for binding cellulose. Mechanical characteristics of the resulting composites and their recycling properties using the switching functionality of were discussed.
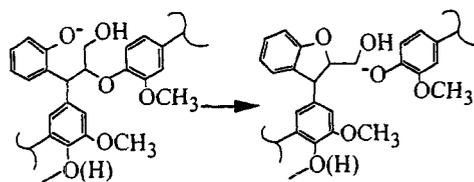

Fig. 1 Cleavage of C2-aryl ether linkages by C1-phenoxide ions in lignophenols.

2. EXPERIMENTAL

2.1 Synthesis of lignophenols.

Through the phase-separation system (2 step process II) composed of p-alkylphenols and seventy-two % sulfuric acid [5], ligno-p-cresol, and ligno-2,4-dimethylphenol were synthesized.

To extractives-free spruce *(Picea jezoensis)* and maple *(Acer japonicum)* wood meals (20-40 mesh size), the acetone solutions of p-cresol or 2,4-dimethylphenol (3 mol/C9) were sorpted. After 24 hr, the acetone was evaporated. Seventy-two % sulfuric acid was added to the phenol-sorpted wood meals and the mixture was stirred vigorously at room temperature. After 1 hr, the reaction mixture was poured in excess water. The precipitates were centrifuged off, and dialyzed to remove excess phenols and acid. After drying, the precipitates were extracted with acetone. The soluble fractions were added dropwise to an excess amount of ethyl ether with stirring. The precipitates (lignophenols) were collected by centrifugation and dried over P_2O_5 after evaporating the solvent.

2.2. Hydroxymethylation (HM) and polymerization of lignophenols

To a solution of ligno-*p*-cresol or ligno-2,4-dimethylphenol in 0.1 N NaOH was added 37 % formaldehyde solution (20 mol/C₀).

The mixtures were heated at 60 °C for 3 hr with constant stirring and bubbling of N₂. At the end of the reaction, they were acidified with 0.5 N HCl to pH 2. The precipitates were purified by dialysis, and dried over P₂O₅. Resulting HM-lignophenols were polymerized by heating (initial temp.; 70°C, final temp.; 150°C, rate; 2.0 °C/min, holding time; 60min)

2.3 Structural control of polymerized lignophenols using switching functionality

Polymerized lignophenols were placed into a stainless steel bomb, to which 0.5N NaOH was added. The mixture was heated in an oil bath. The reaction mixtures were filtrated. The soluble parts were acidified to pH 2 with 1 N HCl. The precipitates were collected by centrifugation and dried over P₂O₅.

2.4 Preparation of cellulose-lignophenol composites

Spruce lignophenol derivatives (HM-ligno-*p*-cresol and HM-ligno-2,4-dimethylphenol) (100 mg) dissolved in THF were added to 900 mg cellulose powder (nakarai tesque). The mixtures were stirred continuously until the THF were evaporated. Lignophenols-sorpted cellulose powders were pre-formed (ø 10 mm column), and then molded (initial temp.; 70 °C, rate; 1.5 °C/min, final temp.; 180°C, load; 100 kgf).

2.5 Mechanical properties of cellulose-lignophenol composites

Young's modulus (MOE) on compression (JIS Z2111) and Brinell hardness (JIS Z2117) of composites were measured.

Cellulose-lignophenol composites were soaked in water for 60 min at room temperature, and the changes in weight and dimension were measured.

2.6 Recycling of cellulose-lignophenol composites using the switching function of lignophenols

In the same way as section 2.3, ground cellulose-lignophenol composites were placed into a stainless steel bomb, to which 0.5N NaOH was added. The mixture was heated in an oil bath. The reaction mixtures were filtrated. The filtrates were acidified to pH 2 with 1 N HCl. The precipitates were collected by centrifugation and dried over P₂O₅. On the other hand, the insoluble cellulose was washed with deionized water.

2.7 Structural analyses of lignophenols

Lignophenols were acetylated with pyridine:acetic anhydride (1:1 v/v) at room temperature for 48 hr.

The amounts of hybridized phenols and hydroxyl groups in lignophenols were determined by ¹H-NMR spectra on a JEOL JMN-A500 fourier transform NMR. CDCl₃ and C₅D₅N-CDCl₃ were used as solvents for acetylated and original lignophenols, respectively.

The average molecular weights were measured by GPC on a SHIMADZU CRASS LC-10 system, LC-10AD. SPD-10A with four shodex columns (KF804, KF803, KF802 and KF801). THF was used as an eluent.

TMA was carried out with RIGAKU TAS-200 system equipped with RIGAKU Thermoplus TMA8310. Under

the 5 g loading, the solid-liquid transformation (Tm) of lignophenol was measured by heating from room temperature to 300 °C with 2 °C/min.

Distribution and combination modes of phenols grafted to lignophenols were analyzed by the combination of phenyl nucleus exchange and periodate oxidation technique [5].

3. RESULTS AND DISCUSSION

3.1 Properties of ligno-*p*-cresol and ligno-2,4-dimethylphenol

The structural characteristics of lignophenols were given in Table 1. For both ligno-*p*-cresol and ligno-2,4-dimethylphenol, the frequency of hybrid phenols were about 0.60 mol/C₀ in spruce lignophenol and 0.80 mol/C₀ in maple lignophenol. These grated phenols were confirmed to be mainly at C1-position in lignophenols by the combination of phenyl nucleus exchange and periodate oxidation technique. To maple lignin, more phenols were hybridized than spruce lignin, indicating that hardwood lignin is more reactive toward phenol than softwood lignin. This is in agreement with the fact that hardwood lignins have more non-condensed unit and aryl ether linkages and the molecule is more flexible [6].

During the phase separation reaction, hardwood lignins are subjected to the cleavage of C1-aryl ether intermolecular linkages to larger extent, leading to lower molecular fragment and higher frequency of phenol grafting.

The phase transformation points of spruce and maple lignophenols were at ca. 160-165 °C, indicating that ligno-*p*-cresol and ligno-2,4-dimethylphenol had similar structural properties in spruce and maple, respectively.

Table I Properties of lignophenols.

Lignophenol	$\overline{Mw}$	Tm (°C)	Grafted phenols (mol/C₉)
Spruce			
Ligno-*p*-cresol	16680	161	0.65
Ligno-2,4-dimethylphenol	17560	163	0.60
Maple			
Ligno-*p*-cresol	13740	163	0.79
Ligno-2,4-dimethylphenol	11220	165	0.76

3.2 Functionality control of lignophenols.

¹H-NMR spectra of Hydroxymethylated (HM) ligno-*p*-cresol and ligno-2,4-dimethylphenol acetates are given in Fig. 2. The signals at about 4.7-5.3 ppm are assigned to methylene protons of acetylated hydroxymethyl groups [7]. As ligno-*p*-cresols have a reactive site on the cresol nucleus as well as lignin phenolic nucleus in terminal units, they were hydroxymethylated to larger extent (spruce; 0.78 mol/C₉, maple; 0.50 mol/C₉). On the other hand, ligno-2,4-dimethylphenol was hydroxymethylated only at terminal lignin units (spruce; 0.15 mol/C₉, maple; 0.06 mol/C₉). The difference between spruce and maple lignophenols is due to the quantity of reactive lignin nuclei: spruce lignophenols

had much more guaiacyl units with C5-positions available for the reaction [6].

TMA curves of HM-lignophenols were shown in Fig. 3. HM-ligno-*p*-cresol had no Tm while HM-ligno-2,4-dimethylphenol had Tm at higher temperature. These

results indicate that HM-ligno-*p*-cresol and HM-ligno-2,4-dimethylphenol were polymerized by heating to the network-type and linear-type polymers, respectively.
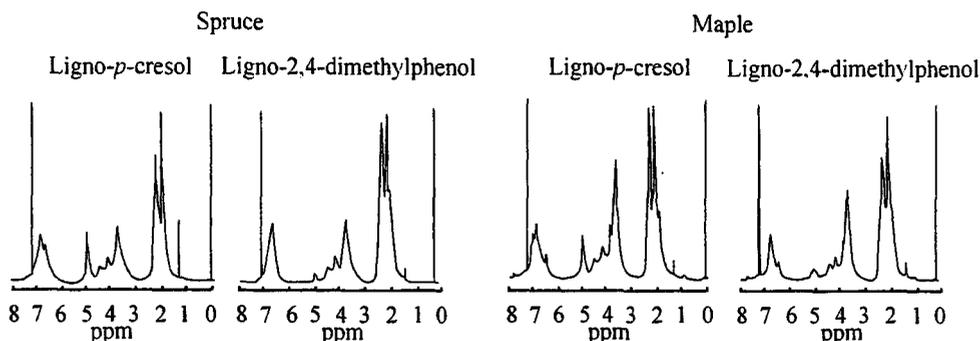
Spruce

Ligno-*p*-cresol   Ligno-2,4-dimethylphenol

Maple

Ligno-*p*-cresol   Ligno-2,4-dimethylphenol

8 7 6 5 4 3 2 1 0   8 7 6 5 4 3 2 1 0   8 7 6 5 4 3 2 1 0   8 7 6 5 4 3 2 1 0
ppm   ppm   ppm   ppm

Fig. 2 ¹H-NMR spectra of hydroxymethylated lignophenols. (acetylated)

Spruce

Maple

Hydroxymethylated
--- Ligno-*p*-cresol
— Ligno-2,4-dimethylphenol

Volume

100 140 180 220 260 300
Temperature (°C)

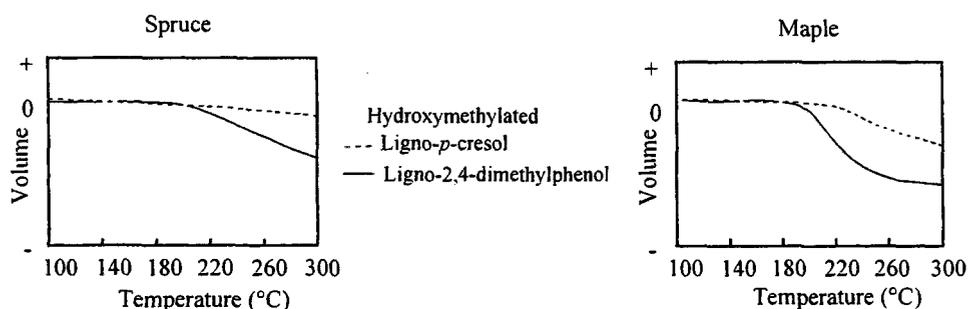100 140 180 220 260 300
Temperature (°C)

Fig. 3 Thermomechanical profiles of hydroxymethylated lignophenols.

Table II Solubility of lignophenols for acetone.

(Wt%)

	Original	HM	Heated**	Alkaline treated*
Spruce				
Ligno-*p*-cresol	100	57.7	0	30.7
Ligno-2,4-dimethylphenol	100	100	10.8	100
Maple				
Ligno-*p*-cresol	100	75.5	0	98.1
Ligno-2,4-dimethylphenol	100	100	47.6	100

[Condition]
Sample /Acetone: 10mg/2ml
25°C, 2hr
* 0.5N NaOH, 140°C, 60min
**RT ——→ 150°c 1hr
(2°c/min)

Although polymerized HM-lignophenols were little soluble for organic solvents such as ethanol, acetone and even THF, they could dissolve for acetone after using switching function (Table II). The functionality of ligno-2,4-dimethylphenol polymer was comparable to the original one because grafted 2,4-dimethylphenol had no linking point and worked as a switching device. Ligno-*p*-cresol polymer, however, had low solubility even after the switching treatment, due to the restricted mobility of cresolic nuclei by linking. These results indicate that through the controlled frequency of *p*-cresol- and 2,4-

dimethylphenol-units within lignophenol and arroying of both lignophenols, the reactivity, the frequency of intermolecular linkages and recycling properties of lignophenol materials can be controlled.

3.3 Mechanical properties of cellulose-lignophenol composites

60
50
40
30
20
10
0
0.4   0.6   0.8   1.0   1.2   1.4
Density (g/cm³)

Hardness (MPa)

O Control
■ HM-Ligno-*p*-cresol
□ HM-Ligno-2,4-dimethylphenol
▲ Hinoki (HRT)
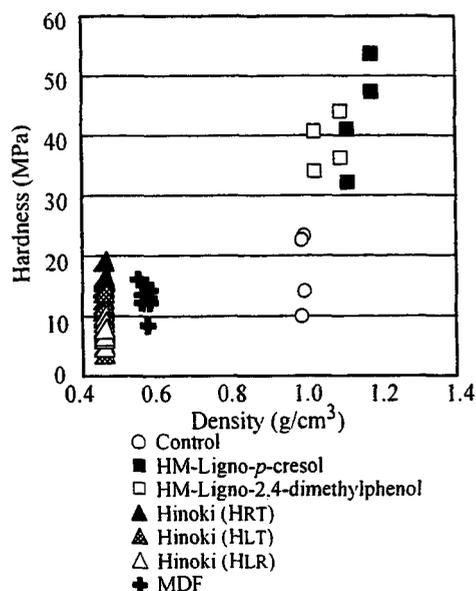▲ Hinoki (HLT)
△ Hinoki (HLR)
✦ MDF

Fig. 4 Hardness of cellulose-lignophenol composites.

Cellulose-lignophenol composites had light beige color, glossy surface, and allow to shaving and cutting. MOE of composites were all in the range of 40-60 MPa, comparable to wood and MDF.

Fig. 4 shows the relationships between the Brinell hardness and the density of cellulose-lignophenol composites. The hardness of all composites was higher than wood (hinoki) and MDF. Compared to cellulose control molds, cellulose-lignophenol composites had higher density and hardness by 2-5 times. Cellulose-ligno-*p*-cresol composite had the highest density and hardness of all, indicating that HM-ligno-*p*-cresol as a matrix formed network-type structure and held cellulose chains tightly. There was a good correlation between the density and the hardness of composites.

The dimensional stability of cellulose-lignophenol composites was greatly higher as compared to cellulose control mold (Fig. 5). Especially, cellulose-ligno-*p*-cresol composites had much lower volumetric swelling due to network-type polymerization of ligno-*p*-cresol. Both composites were recovered to about original dimensions by re-drying.
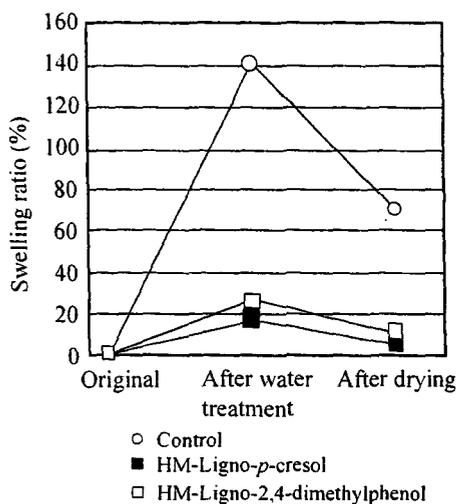

Fig. 5 Stability of cellulose-lignophenol composites.

3.4 Recycling property of cellulose-lignophenol composites

Using C1-cresol and 2,4-dimethylphenol units within lignophenol molecules as switching devices, the composites ware recycled to the constituents, cellulose and lignophenol. Table II shows the yields, molecular weight and dispersity index of recovered lignophenols. Ligno-2,4-dimethylphenol were almost quantitatively recovered from the composites as low molecular weight fragments. In the case of cellulose-ligno-*p*-cresol composites, however, the recovery of ligno-*p*-cresol was only 17%.

The limited recycling of cellulose-ligno-*p*-cresol composites was probably due to the penetrated network structure reveals cellulose of polymerized ligno-*p*-cresol. This insisted that the cellulose-ligno-*p*-cresol composite requires more drastic condition for switching functionality.

Table III Amounts of lignophenols recycled from composites using switching function.

Sample	Lignophenol reseparated as alkaline soluble fractions (%)
HM-Ligno-*p*-cresol	16.92
HM-Ligno-2,4-dimethylphenol	97.96

4. CONCLUSION

Lignin-based materials, lignophenols were synthesized directly from native lignins through the phase-separation system. C1-phenols in 1,1-bis(aryl)propane unit of lignophenols are derived from the phenol components of phase-separation system. When *p*-substituted phenols are grafted at C1 position in lignophenol, they nucleophilically attack adjacent C2, followed by the cleavage of aryl ether linkages (switching function).

Ligno-*p*-cresol and ligno-2,4-dimethylphenol had switching functionality and almost similar structural properties. Ligno-*p*-cresol with a reactive site on the cresolic nucleus was highly hydroxymethylated, giving a network-type polymer. While ligno-2,4-dimethylphenol was hydroxymethylated only on the terminal unit to give linear-type polymers. The resulting polymer chains were cleaved at the switching points to give low molecular weight subunits by the switching function.

Cellulose-lignophenol composites were prepared by combination with cellulose and HM- lignophenol. Ligno-*p*-cresol polymerized to the network-type structure gave a mold with higher density and higher water resistance than ligno-2,4-dimethylphenol. Using the switching function, ligno-*p*-cresol and ligno-2,4-dimethylphenol subunits were separated from the composites in 17% and 98% yields, respectively.

The controlled grafting of *p*-cresol and 2,4-dimethylphenol within the molecule and/or the arroying of both lignophenols would lead to the control of mechanical and recycling properties of the composites more accurate.

5. REFERENCES

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