Molecular Response of Lignophenols for High Energy Input II 
- Plasticizing Performance of Low Molecular Weight Fractions -

Shimpei HORII, Mitsuura AOYAGI and Masamitsu FUNAOKA
Graduate School of Bioresources, Mie University, 1577 Kurimamachiya Tsu Mie 514-8507 Japan
Fax: 81-59-231-9591, e-mail: funaoka@bio.mie-u.ac.jp

Lignocresol was synthesized from Hinoki cypress (Chamaecyparis obtusa) through the phase-separation treatment with p-cresol and 72% sulfuric acid. Thermal responses of lignocresol were observed around 160°C, which is attributed to existence of unstable sites. Molecular rearrangements associated with the cleavages of benzyl aryl ether linkages improved thermal stabilities of lignocresols. Low molecular weight units formed by the molecular rearrangements work as plasticizer of lignocresol. The grass-transition temperatures (T_g) and solid-liquid transition temperatures of lignocresols were shifted down with increasing ratios of low molecular weight units. The results indicated that low molecular weight units have the function as plasticizer, forming a new application of lignophenol.

Key words: Lignophenol, Phase-separation system, Solid-liquid transition, The grass-transition, Plasticizer

1. INTRODUCTION
Recently, lignocellulosic biomass has been expected as sustainable resources. The carbohydrates, cellulose and hemicelluloses have been utilized as pulp and so on. However lignin, which is an aromatic network polymer, has been difficult to be utilized, because lignin is highly sensitive to given environments.
Through the phase-separation system, which was developed by Funaoa in 1988, both quantitative separation of the components and selective conversion of lignin structure can be achieved [1-3]. The separated lignin derivatives (lignophenol) have 1,1-bis (aryl) propane type structures. Lignophenols have the solid-liquid transition and the grass-transition temperature (T_g), indicating that the structures are of linear type.
In our previous studies, the structural responses of lignocresol for high energy input were revealed [4-7]. Thermal properties of lignocresole were affected by the existence of benzyl aryl ether linkages. By the alkaline treatment under ordinary pressure at room temperature, benzyl aryl ether linkages in phenolic units were cleaved. As a result, thermal stabilities of alkaline-treated lignophenol were improved. Moreover, thermal stabilities of lignophenol were improved by the elimination of low molecular weight (MW) units formed by heating. These results suggested that low MW units linked at benzyl positions through ether bonds worked as a plasticizer of lignophenol. Thus, the low MW units are the key element of lignophenol for thermal properties. In this work, the functions of low MW units for the control of thermal properties of lignophenols were discussed.

2. EXPERIMENTAL
2.1 Preparation of lignocresol
Extratcives in the wood meals of Hinoki cypress (Chamaecyparis obtuse, 60 mesh pass) were removed with benzene and ethanol (v/v = 2:1) using Soxhlet system for 48 hrs. Lignocresol (LC) was synthesized through the phase-separation system, using two step process II [3]. The wood meals (50 g) were immersed in acetone solution of p-cresol with a concentration of 3 mol / phenylpropane units (C_4 units). After evaporating acetone, 72% H2SO4 was poured into the wood meals at 30°C. Then, the mixture was stirred vigorously for 60 min. The mixture was poured into 5 L of deionized water with vigorously stirring. The precipitate was washed until neutral. After drying, the precipitate was dissolved in acetone, and the insoluble materials were removed by centrifugation and filtration. The acetone solution was concentrated under reduced pressure and added dropwise to an excess amount of diethyl ether with stirring. The precipitate (LC) was collected by centrifugation. The ether soluble fractions (ELC) were obtained by distilling away the solvent.

2.2 Alkaline treatment of lignocresol
LC was dissolved in 0.1 N NaOH under nitrogen atmosphere. The reaction mixture was kept at room temperature for 72 hrs. Then, it was acidified to pH 2 with 1 N HCl. The precipitate (ALC: Alkaline treated lignocresol) was collected by centrifugation and washed until neutral. The water soluble fractions (AELC: Alkaline treated ether soluble fractions) were extracted from the supernatant solution with diethyl ether.

2.3 Heating of lignocresol
LC was heated to 160°C at a rate of 2°C min⁻¹ under 200 mL min⁻³ of N₂ flow. Heated LC was dissolved in acetone. The acetone solution was added dropwise to excess amount of diethyl ether with stirring to remove low MW fractions. The precipitate (HLC: Heated lignocresol) was collected by centrifugation. The ether
soluble fractions (HELC: Heated ether soluble fractions) were obtained by distilling away of the solvent.

2.4 Blending of low MW units

ALC (45 mg) and ELC, AELC or HELC (5 mg) were dissolved into 1.0 mL of acetone (10 wt%). After completely dissolved, acetone was evaporated. Then, the composites were pulverized to fine powder in agate mortar. ALC and ELC were also blended with various ratio: 5, 7.5 and 20 wt%.

2.5 Analytical method

Thermo Mechanical Analysis (TMA) was carried out by TMA-SS (SH Inc.) at a rate of 2°C min⁻¹ under N₂ flow, using penetrating method. Thermogravimetry analysis (TGA) was also carried out by TG/DTA-6200 (SII Inc.) at a rate 2°C min⁻¹ under N₂ flow. Gel permeation chromatography (GPC) was carried out by LC-10 system (Shimadzu Co.) with four columns (KF801, KF802, KF803 and KF804, Shodex Co.), using tetrahydrofuran (THF). Weight average molecular weight (Mw) and Number average molecular weight (Mn) were calculated based on standard polystyrene. Differential scanning calorimeter (DSC) was carried out using Diamond DSC (Perkin Elmer Co.) in 7 mm diameter Al pan and lid at a rate 10°C min⁻¹ under N₂ flow. TG-GC/MS analysis was carried out by TG/DTA 8120 (Rigaku Co.), GC-2010 (Shimadzu Co.) and GC/MS-QP2010 (Shimadzu Co.). TGA was measured at a rate of 5°C min⁻¹ under N₂ flow. Temperature of the transfer tube connecting TGA and GC/MS was 250°C. GC/MS condition was as following; column: crosslinked methyl silicone capillary column, column temperature: 40-270°C at rate of 5°C/min, carrier gas: He, detector temperature: 280°C, Split ratio: 1/20, electron energy: 90 eV.

3. RESULTS AND DISCUSSION

3.1 Improvement of thermal stability of lignocresol by releasing low MW fractions

LC was obtained in 93.3% yield based on Klasson lignin content. The solid-liquid transition temperature of LC was 157.7°C by TMA (curve (a) in Fig. 1). TGA showed that Thermal degradation temperature when weight loss of 5% (T₅₀) and 10% (T₅₀) were 174.9 and 242.4°C, respectively (curve (a) in Fig. 2). In the previous study, it is revealed that thermal responses of LC at around 160°C are attributed to the existence of ether linkages at benzyl position [5-7]. HLC was obtained in 62.6% yield based on LC heated to 160°C, whose solid-liquid transition temperature was 148.9°C [5]. However, after removing the released low MW fractions, the temperature was shifted up to 184.7°C (curve (b) in Fig. 1). T₅₀ and T₅₀ of HLC were 220.3 and 269.4°C, respectively (curve (b) in Fig. 2). Thermal stabilities of ALC were higher than that of HLC. By the fragmentation during alkaline treatment, reactive sites, which are benzyl aryl ether bonds on phenolic units in LC were vanished and low MW fractions were removed [4, 5]. The solid-liquid transition temperature of ALC, which was obtained in 90% based on LC, was 194.2°C (curve (c) in Fig. 1). T₅₀ and T₅₀ of ALC were 281.1 and 298.5°C, respectively (curve (c) in Fig. 2). These results indicate that low MW lignin fractions give plasticizing performance to lignophenols.

3.2 The function of low MW lignin fractions as plasticizer

The average molecular weights of ether soluble fractions were shown in Table 1. Fig. 3 illustrated GPC profiles of low MW lignin fractions. It is confirmed that the released fractions consist of small molecules [5]. TMA profiles of ALC with low MW fractions were shown in Fig. 4. The solid-liquid transition temperatures of the composites were shifted down than original ALC. These results indicated that low MW lignin fractions worked as plasticizer of lignocresols. Lignophenols are bio-based thermo-plastics, self-providing plasticizer under high energy condition.

TGA profiles of the composites were shown in Fig. 5. Around 80°C, the weight losses of composites were observed. Pyrolysis gases in this temperature range were analyzed by TG-GC/MS. Only acetone derivatives were detected from pyrolysis gas of the composites. These
results indicated that the weight losses of composites in low-temperature range were attributed to acetone used for blending low MW fractions. \( T_g \) was also shifted down by blending low MW fractions. DSC profiles of ALC and composites were shown in Fig. 6. \( T_g \) of ALC was observed at 182°C, while those of composites with ELC, AELC and HELC were 122, 163 and 175°C, respectively. These changes of thermal properties accord with the results by TMA.

Table 1 Average molecular weights of low MW lignin fractions.

<table>
<thead>
<tr>
<th></th>
<th>( M_w )</th>
<th>( M_n )</th>
<th>( M_w/M_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELC</td>
<td>1100</td>
<td>470</td>
<td>2.3</td>
</tr>
<tr>
<td>AELC</td>
<td>580</td>
<td>280</td>
<td>2.1</td>
</tr>
<tr>
<td>HELC</td>
<td>1190</td>
<td>340</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Fig. 3 GPC profiles of low MW lignin fractions. (a) ELC, (b) AELC, (c) HELC

Fig. 4 TMA curves of composites of ALC and three kinds of low MW lignin fractions. (a) ALC, (b) ALC:ELC = 9:1, (c) ALC:AELC = 9:1, (d) ALC:HEL = 9:1

Fig. 5 TGA curves of composites of ALC and three kinds of low MW lignin fractions. (a) ALC, (b) ALC:ELC = 9:1, (c) ALC:AELC = 9:1, (d) ALC:HEL = 9:1

Fig. 6 DSC profiles of composites of ALC and three kinds of low MW lignin fractions. (a) ALC, (b) ALC:ELC = 9:1, (c) ALC:AELC = 9:1, (d) ALC:HEL = 9:1
3.3 Effect of blend ratio

The effect of the blend ratio on plasticizing performances was examined. Thermal properties of composites of ALC and ELC with various blend ratios were shown in Table 2. The TMA profiles were shown in Fig. 7. The solid-liquid transition temperatures of composites were shifted down with increasing blend ratio of ELC. In addition, the $T_g$ values measured by DSC were also shifted down. These results indicated that thermal properties of lignophenols can be controlled by changing the blend ratio of low MW lignin fractions. The plasticizer can be a new application for low MW lignin fractions derived from lignophenol.

Table 2 Thermal properties of composites of ALC and ELC with various blend ratios.

<table>
<thead>
<tr>
<th>Blend ratio (wt%)</th>
<th>$T_d5$</th>
<th>$T_d10$</th>
<th>Solid-liquid transition</th>
<th>$T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>213.4</td>
<td>252.8</td>
<td>183.9</td>
<td>135.4</td>
</tr>
<tr>
<td>7.5</td>
<td>172.8</td>
<td>218.4</td>
<td>173.7</td>
<td>125.3</td>
</tr>
<tr>
<td>10</td>
<td>164.6</td>
<td>226.1</td>
<td>164.6</td>
<td>122.3</td>
</tr>
<tr>
<td>20</td>
<td>155.9</td>
<td>194.3</td>
<td>162.0</td>
<td>119.3</td>
</tr>
</tbody>
</table>

4. CONCLUSION

Thermal properties of lignocresols can be controlled in two ways: First, by the control of frequency of ether linkages at benzyl positions. Alkaline treatments or heating up to 160 °C are effective. The removal of the low MW fractions released by alkaline treatment or heating dramatically improved the thermal properties. Lignophenol is a special polymer, releasing low MW lignin fractions as a plasticizer, corresponding to given environments. Second, by blending the low MW lignin fractions released from lignocresols. The solid-liquid transition temperature and $T_g$ of thermally stabilized lignocresols (e.g. alkaline-treated lignocresol) can be controlled. The changes of thermal properties of lignocresols are correlated with the blend ratio. This can be a new application of low MW lignin fractions derived from lignophenols.

5. ACKNOWLEDGEMENT

We thank Dr. Nonaka and Dr. Mikame for helpful discussion.

6. REFERENCES


(Received February 5, 2012; Accepted April 4, 2013)