Molecular Response of Lignophenols for High Energy Input
- Formation and Function of Low Molecular Weight Units -

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Lignocresol was synthesized from Hinoki cypress (Chamaecyparis obtusa) through the phase-separation system with p-cresol and 72% sulfuric acid. Molecular responses of lignocresol for heating were observed at around 160°C. These behaviors were caused by molecular rearrangement associated with the cleavages of benzyl aryl ether linkages. By the alkaline treatment under ordinary pressure at room temperature, benzyl aryl ether linkages with phenolic units are cleaved, and then low molecular lignin fractions are formed. After the alkaline treatment, thermal stability of lignocresol was improved. The glass-transition temperature ($T_g$) of lignocresol was shifted up by removing the low molecular weight units. The solid-liquid transition temperature was also shifted. These results indicated that the low molecular weight fractions released from lignocresol work as plasticizer. Lignophenols are bio-based thermoplastics, self-providing plasticizer through molecular rearrangement under high energy condition.

Key words: Lignin, Phase-separation system, Lignophenol, Solid-liquid transition

1. INTRODUCTION

Lignin, accounting for approximately 25-35% of lignocellulosics, is an aromatic network polymer. It is formed by the random radical coupling of phenylpropane type precursors, followed by the nucleophilic attack to the quinonemethides. Lignin is expected to serve as one of the alternatives to fossil resources. However, it has been difficult to utilize lignin as functional polymers, because lignin is highly sensitive to a given environment, and subjected to complicated molecular rearrangement during the isolation. Through the phase-separation system, which was developed by Funaoka in 1988, both quantitative separation of components and selective control of the structures of lignin can be achieved [1-3]. Lignocellulosics are rapidly separated under ordinary pressure at room temperature: carbohydrates are swollen and partially hydrolyzed, giving water-soluble saccharides. At the same time, linkages and functional groups formed by the nucleophilic attack to the quinonemethides are selectively released, and phenol derivatives are grafted at benzyl positions in lignin. Separated lignin (lignophenol), which has 1,1-bis (aryl) propane type structures, has the solid-liquid transition, indicating that the structures are linear type compared with native lignins and conventional lignins.

Thermal properties of biomaterials are important for utilization as industrial materials. Molecular response of lignocresol for high energy input was observed at around 160°C. In the previous study, lignophenol treated with alkaline solution under ordinary pressure at room temperature showed higher thermal stability [4]. This improvement of thermal stability was probably caused by elimination of the low molecular weight lignin fractions linked at benzyl positions during alkaline treatment. Namely, it is indicated that the formation of low molecular weight units could be dominating molecular response for high energy input to give low thermal stability. In the present work, the structural response for high energy input and the resulting functionality change of lignophenols were discussed.

2. EXPERIMENTAL

2.1 Preparation of lignocresol

The chips of Hinoki cypress (Chamaecyparis obtusa) were milled to 60 mesh. Extractives in the wood meals 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 method [3]. The wood meals (50 g) were immersed in acetone solution of p-cresol with concentration of 3 mol/phenylpropane units (C₉ 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 solution of 0.1 N NaOH under nitrogen atmosphere. 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 excess amount of diethyl ether with stirring. The precipitate (LC) was collected by centrifugation.

2.2 Alkaline treatment of lignocresol

LC was dissolved in 0.1 or 0.01 N NaOH under nitrogen atmosphere. The reaction mixture was kept at room temperature for 72 hrs. Then, it was acidified to
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pH 2 with 1 N HCl. The precipitate (ALC; Alkaline treated lignocresol) was collected by centrifugation and washed until neutral. The released water soluble fractions were extracted from the supernatant solution with diethyl ether.

2.3 Heating of lignocresol
LC was heated to 160, 170, 200°C at a rate of 2°C min⁻¹ under 200 mL min⁻¹ of N₂ flow. Using the similar technique, ALC was heated to 160, 200, 250°C. Heated LCs were dissolved in acetone. The acetone solution was added dropwise to excess amount of diethyl ether with stirring to remove low molecular weight fractions. The precipitate was collected by centrifugation.

2.4 Analytical method
GPC was carried out by LC-10 system (Shimadzu Co.) with four columns (KF801, KF802, KF803 and KF804, Shodex Co.), using tetrahydrofuran (THF). Mw and Mn were calculated based on standard polystyrene. TMA was carried out by TMA-SS (SII Inc.) at a rate of 2°C min⁻¹ under N₂ flow, using penetrating method for a measurement. TGA was also carried out by TG/DTA-6200 (SII Inc.) at a rate 2°C min⁻¹ under N₂ flow. DSC was carried out using Diamond DSC (Perkin Elmer Co.) in 7 mmϕ Al pan and lid at a rate 10°C min⁻¹ under N₂ flow. Dynamic Mechanical Analysis (DMA) was carried out using ARES (TA Instrument Inc.) with shear module using 20 mmϕ plates at a rate 2°C min⁻¹. The shear stress was 1 rad sec⁻¹.

3. RESULTS AND DISCUSSION
3.1 Alkaline treatment of lignocresol
LC was obtained in 93.3% yield based on Klason lignin. The solid-liquid transition temperature of LC was 157.7°C by TMA (curve (a) in Fig. 1). TGA showed that Td5 and Td10 were 174.9 and 242.4°C, respectively (curve (c) in Fig. 1). Thermal responses of LC at around 160°C are attributed to the existence of ether linkages at benzyl position, whose existence is estimated to be about 0.3 mol / phenylpropane units (C₉ units) in LC by ¹H-NMR [5]. The solid-liquid transition temperature of ALC was 194.2°C (curve (b) in Fig. 1). Td5 and Td10 were observed at 281.1 and 298.5°C, respectively (curve (d) in Fig. 1). Alkaline treatment under ordinary pressure at room temperature is one of the effective methods for the control of ether linkages at benzyl position. The fragmentation mechanism under alkaline condition was shown in Fig. 2. When the quinonemethide types structures are formed in phenolic units, benzyl aryl ether linkages were cleaved. By the fragmentation, unstable sites in LC vanished and low molecular weight fractions were removed. ALC was obtained in 90% yield based on LC by heating (Fig. 4). Fig. 5 showed the change of molecular weight distribution of ALC heated to 250°C. Depolymerization of ALC was not observed after heating to 250°C.
3.2 Control of the formation of low molecular weight units
Lignocresol treated with 0.01 N NaOH was obtained in 95.7% yield based on LC. LC was dissolved in 0.1 N NaOH perfectly. However, in the case of using 0.01 N NaOH, LC was partly dissolved. Degree of dissociation of phenolic hydroxyl group can be controlled by changing the pH of the treatment solution. Thermal stability of LC treated with 0.01 N was lower than that with 0.1 N (Fig. 6). These results indicated that it is necessary for improvement of thermal stability to control the formation of low molecular weight fractions. This supported that the improvement of thermal stability was caused by the fragmentation shown in Fig. 2.

3.3 Molecular response of lignophenol for high energy input
The solid-liquid transition temperature of ALC was higher than that of LC. These results indicated that the low molecular weight fractions released from lignocresol worked as plasticizer. Fig. 4 showed the change of molecular weight distribution of LC after heating. Benzyl aryl ether linkages were cleaved by heating, and low molecular weight fractions were formed. The low molecular fractions in LC heated to 160°C were removed with acetone and diethyl ether to reveal its function. The yield of lignocresol after removing low molecular weight fractions was 62.6%. Fig. 7 illustrated GPC profiles of lignocresols fractionated after heating. The fractions released by high energy input showed similar molecular weight distribution when treated in alkaline solution (Fig. 3). The solid-liquid transition temperatures of both LC and ALC heated to 160°C were 157.7 and 148.9°C, respectively (curve (a) and (b) in Fig. 8). This lower temperature of LC heated to 160°C was based on the existence of low molecular weight fractions formed by heating to 160°C. In comparison, after removing the released low molecular weight fractions, the solid-liquid transition temperature was shifted up to 185°C (curve (c) in Fig. 8). These results supported that low molecular weight units formed by high energy input have the function as plasticizer of lignocresol. To work as plasticizer was demonstrated by DSC. On the 1st scan of DSC of LC, exothermal peaks were observed (curve (a) in Fig. 9). These peaks are attributed to molecular rearrangement associated with the cleavages of benzyl aryl ether linkages [5]. The exothermal peaks have not been observed on the 2nd scan (curve (b) in Fig. 9). This indicated that reactive benzyl ether linkages were cleaved perfectly by heating. On the other hand, in the DSC profiles of ALC, the exothermal peaks have not been observed (curve (c) and (d) in Fig. 9), confirming
the cleavages of benzyl ether linkages. This higher thermal stability of ALC was kept in 2nd scan of DSC. The glass transition temperature (T_g) of LC was observed at 134°C on the 2nd scan, while that of ALC was 182°C. Low molecular weight fractions released at the high temperature remained with thermal stable fractions and worked as plasticizer. In the results of DMA, T_g of ALC was higher than that of LC as well as the results of DSC (Fig. 10). Dynamic loss tangent (tan δ) of LC was increased with a rise in temperature. On the other hand, tan δ of ALC was decreased with rising temperature. This means that ALC has elastic properties than LC. These results supported that the existence of the low molecular weight fractions give plasticizing performance to lignophenols.

4. CONCLUSION
Low molecular weight units were released from LC by both the alkaline treatment and high energy input. The formations are associated with the cleavages of benzyl aryl ether linkages. By removing the released low molecular weight units, thermal stabilities of LC were improved. These results indicated that thermal properties of lignophenols were controlled by the change of the formations of low molecular weight units. Variation of the glass transition temperature (T_g) and tan δ in DSC and DMA after alkaline treatment indicated that released low molecular weight fractions worked as plasticizer. Lignophenols are specific polymers, self-providing plasticizer under high energy input. Alkaline treatments are effective for functionality change of lignophenols.

5. ACKNOWLEDGEMENT
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6. REFERENCES

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