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Manufacture of recyclable composites from lignocresol and cellulosic fibers

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Through the phase separative system composed of *p*-cresol and 72% sulfuric acid, lignocresols were synthesized directly from black pine and maple native lignins, and were sorpted to cellulosic fiber molds. The functions of the resulting composites as bio-based recyclable materials were investigated.

Lignocresols were highly phenolic and hydrophobic lignin derivatives, including 0.6-0.9 mol/C_9 of cresolic nuclei in the molecules, about 80% of which were linked to lignin $C\alpha$-positions through carbon-carbon linkages, about 15% to $C\gamma$-positions, and the remaining 5% etherified to lignin side chains through its phenolic hydroxyl groups. Lignocresols had 6500 and 3700 of the molecular weights ($\overline{M}w$) and the melting points around 170 and 130 °C in black pine and maple, respectively.

The mechanical strengths of cellulosic fiber molds were greatly improved by the sorption of lignocresol: the modulus of rupture of cellulosic fiber-lignocresol (5:1) composites was 2.5 times higher, compared with cellulosic fiber molds without lignocresol. It was further increased by heating at 170 °C. The water absorptions of fiber molds were greatly decreased with the sorption of small amount of lignocresol, due to the hydrophobic function of lignocresol. The composites were rapidly and perfectly separated into lignocresol and fiber moieties by the treatment with acetone. There was no structural difference between original and recovered lignocresols.

1. INTRODUCTION

Tremendous amounts of products in human life have so far been derived from petroleum. Also, coal, oil sand and oil shale have become of major interest lately as postpetroleum. However, these natural resources are fossil and will have become either exhausted or so scarce that they will be too expensive in the future. On the other hand, synthetic materials are generally resistant to microbiological attack and have been accumulated on the earth without being incorporated in the ecological system. Therefore, in order to keep the sound ecological system and to continue the material production for human life forever, it is of most importance to produce biodegradable materials, which are incorporated in the material cycle in nature, from renewable resources. In this connection, the forest provides excellent materials in both quantity and quality, cellulose, hemicellulose and lignin.

Wood is an aggregation of fibrous cells, in which lignin forms semi-interpenetrating polymer network (IPN) with polysaccharides, cellulose and hemicellulose. The best matching of a hydrophobic, random network polymer, lignin, and hydrophilic, linear polysaccharides gives woods a variety of distinctive properties, for example a high modulus of elasticity in fiber direction at a low specific gravity and the strength temperature-independent over a wide range, which artificial materials do not have. However, the utilization of wood as composites has produced enormous amounts of wastes during the processing and wood-based products themselves have been discarded as wastes after the use, in spite of almost no change in fundamental chemical structures and properties of cell wall materials.

We have designed a new process for separating lignocellulosic wastes into phenolic lignin derivatives and hydrolyzed carbohydrates [1]. This process includes the phase separative reaction system composed of phenol derivative and concentrated acid. Through this process, native lignins are modified primarily at $C\alpha$-positions, the most reactive sites, to give highly phenolic, light colored diphenylmethane type biopolymers (lignophenol derivatives) which still retain original interunit linkages formed by the dehydrogenative polymerization during the biosynthesis [2]. In the present work, waste biofibers, which are discharged from human life in tremendous amount, were reassembled using the functions of lignophenol derivatives. The properties of the resulting lignin-fiber composites as bio-based recyclable materials were discussed.

2. EXPERIMENTAL

2.1. Synthesis of lignocresol

p-Cresol was dissolved in acetone and added to extractive-free wood meals [black pine (*Pinus thunbergii*) and maple (*Acer japonicum*)], and the mixture was stirring for several hours. After acetone was evaporated, 72% sulfuric acid was added to the cresol-sorpted wood meals and the mixture was vigorously stirred at room temperature for 60 min. The reaction mixture was poured dropwise to excess water with stirring, and the insoluble fractions were collected by centrifugation, and were freeze-dried after acid and excess cresol were removed by dialysis. The acetone was added and the acetone soluble fraction was then concentrated under reduced pressure and added dropwise to excess ethyl ether with stirring. The precipitated lignin (lignocresol) was collected by centrifugation and dried over P_2O_5 after evaporating the solvent (Fig. 1).

2.2. Structural analysis of lignocresol

The amounts of combined cresol were calculated based on the signal intensity of its methyl protons on ^{1}H-NMR spectra of original lignocresols. The hydroxyl group contents were determined from acetoxyl proton signals on ^{1}H-NMR spectra of acetylated lignocresols. *p*-Nitrobenzaldehyde was used as the internal reference for the determination. The combination modes of cresolic nuclei were analyzed by combined nucleus exchange and $NaIO_4$ oxidation techniques [2]. The molecular weights ($\overline{M}w$) were calculated from gel permeation chromatograms using Shodex columns, KF802 and KF804.

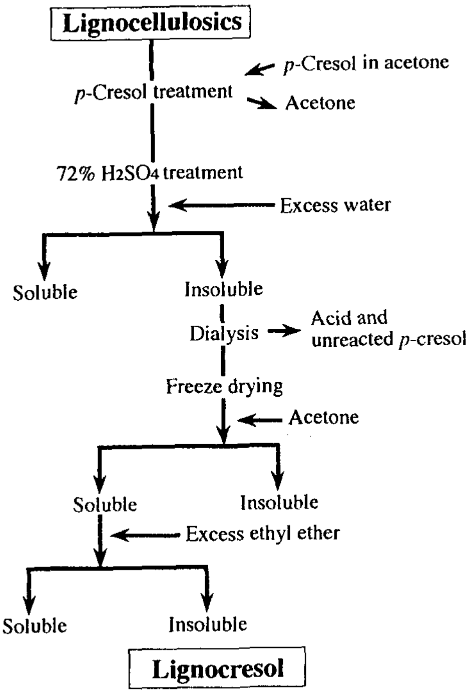

Fig. 1. Synthesis of lignocresol by phase-separation process. (Two step process)

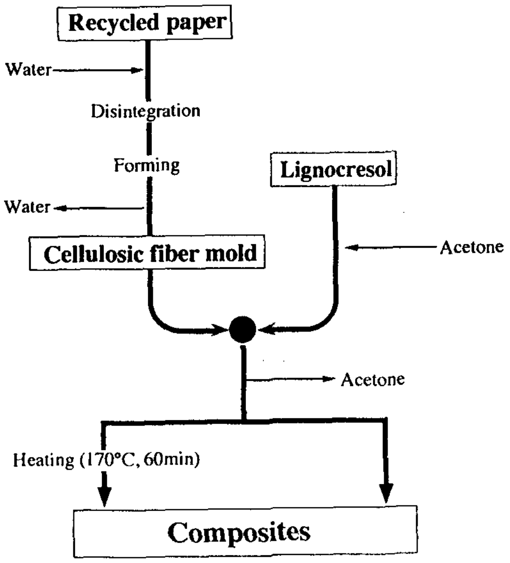

Fig. 2. Production of lignocresol - cellulosic fiber composites.

2.3. Production of lignocresol - Fiber composites

Recycled papers were swollen in excess water and disintegrated with a homogenizer. From the resulting pulp slurry, fiber molds (100mm diameter) were prepared and dried at 80 °C.

Lignocresol was dissolved in acetone, to which the fiber molds were dipped overnight. The thickness of composite was adjusted to 9mm and acetone was evaporated (Fig. 2).

2.4. Properties of the composites

For the bending test, the specimen (90mm length, 20mm width) was cut off from the composite. The moduli of rupture and elasticity were measured.

The specimen (20mm square) was dipped 30mm below the water at room temperature for 60 min. Excess water on the surface of specimen was quickly removed on filter papers, and the weight and volume were measured. Based on the differences in them between before and after water dipping, the water absorption and volumetric swelling were calculated.

The composite was dipped in acetone for several hours. The acetone soluble fraction (recovered lignocresol) was separated from the composite, and was weighed and analyzed after evaporating acetone.

3. RESULTS AND DISCUSSION

3.1. Properties of lignocresol

Lignocresols were highly phenolic and hydrophobic lignin derivatives. The phenolic OH contents were 1.3-1.5 mol/C_9, whereas that of native lignin was 0.1-0.2 mol/C_9 [3,4]. Lignocresols included 0.6-0.9 mol/C_9 of cresolic nuclei in the molecules, about 80% of which were linked to lignin $C\alpha$-positions through carbon-carbon linkages, about 15% to $C\gamma$-positions, and the remaining 5% etherified to lignin side chains through its phenolic hydroxyl groups. In black pine and maple, the molecular weights ($\bar{M}w$) of lignocresols were 6500 and 3700 and the melting points were ca.170 and ca.130 °C, respectively. Lignocresols had almost no conjugated system in the molecules, so it was pinkish white, its brightness comparable to milled wood lignin. Lignocresols were quickly dissolved in methanol, ethanol, acetone, etc., in addition to solvents such as dioxane and pyridine.

3.2. Physical properties of lignocresol - fiber composites

In the present work, lignocresol-fiber composites were prepared by the mold sorption process, in which the fiber mold was formed, then lignocresol was sorpted. In this process, sorpted lignocresols were migrated toward the surface of fiber mold during the solvent evaporation, so that lignocresols were sorpted in higher concentration toward the composite surface (the gradient sorption).

Compared with the fiber mold without lignocresol (the control mold), the lignocresol-fiber composites had higher modulus of rupture: 2.5 times higher in the lignocresol-fiber(1:5) composite. As shown in Fig. 3, the relative strength of composite was also greatly increased with increasing sorption ratio of lignocresol. These mechanical strengths were further improved by heating the composite at 170 °C.

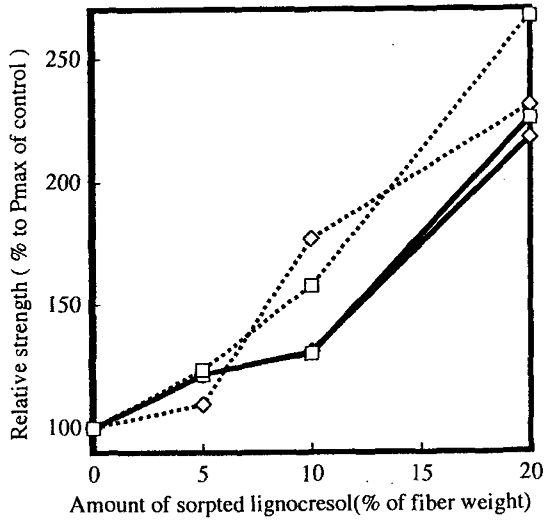

Fig. 3. Bending strength of lignocresol-cellulosic fiber composites.

□ : Black pine lignocresol sorpted
◇ : Maple lignocresol sorpted
——: Original
········ : Heated(170°C,60min)

The control mold indicated high water absorption. On the other hand, the presence of lignocresol in the small amount within the fiber mold suppressed it to a great extent, due to the hydrophobic function of lignocresol: from 270 to 20% with 5% sorption of lignocresol (Fig. 4).

The volumetric swelling of composite by water dipping was decreased with increasing sorption ratio of lignocresol: 1/2-1/3 and 1/6 of the control mold with 5 and 20 % sorptions of lignocresol, respectively. After heating at 170 °C, the volumetric swelling was further decreased. After re-drying, the composite was recovered to the original volume.

3.3. Re-separation of the composite into lignocresol and fibers

When the composite was dipped in acetone, lignocresols were quickly dissolved, the surface of composite getting lighter. After 15 hours, sorpted lignocresols were almost quantitatively recovered from the composite. There was almost no difference in the molecular weight between original and recovered lignocresols.

4. Concluding remarks

Highly phenolic lignin derivatives (lignocresol), in which the reactive groups of native lignin were replaced by cresol, were synthesized through the phase-separative system composed of *p*-cresol and 72% sulfuric acid. The original composites were prepared from only lignocresol and cellulosic fiber. Compared with conventional fiber molds, the lignocresol-fiber composites had much higher mechanical strength, dimensional stability, and water resistance. Furthermore, the composites were quantitatively re-separated into lignocresol and fibers by simple solvent treatment.

The raw materials of this composite, lignocresol and cellulosic fiber, both were derived from wastes in the present wood industry. The composites can be reconstructed any time to different shapes or to composites with different properties, because of its re-separable function. Also, the separated component itself may be utilized for other purposes. This type of forest biomass utilization leads to decreasing the utilization of original woods, to suppressing the forest destruction for wood utilization, and finally to environmental protection.

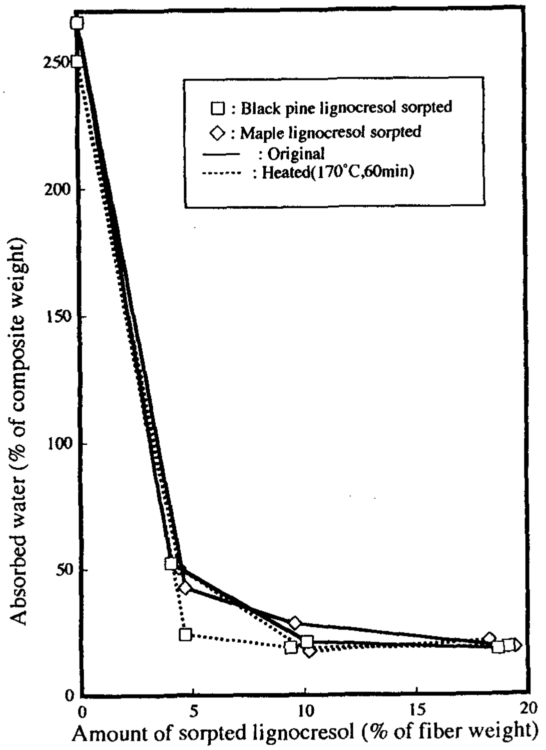

Fig. 4. Water resistance of lignocresol-cellulosic fiber composites.

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