

Functionality Control of Lignocellulosics through the Phase-Separation System

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Abstract: Through the phase-separation system composed of phenol derivatives and phosphoric acid, properties of lignocellulosics were modified: cellulose microfibrils (assembled celluloses) were separated to individual chains and the lignin networks were degraded to give linear type subunits, leading to the thermoplastics-like lignocellulosics in the yield of 70-90%. This composite can be modified to new types of functionality controllable materials through the acetylation and /or the linking of lignophenols.

Key words: Phase-Separation System, Lignophenol, Thermoplastic, IPN Structure, Resources circulation

1. INTRODUCTION

Recently, the lignocellulosic biomass (phytomass) has been expected to replace fossil resources such as petroleum and coal, which will be exhausted in the near future. As the wood has the interpenetrating polymer network (IPN) structure within the cell wall, the processing is limited and the constituents cannot be separated through evaporation and/or extraction. As a result, the present wood industries have generated a large amount of wastes during the processing. Aiming at achieving total utilization of lignocellulosics, new technologies have been developed (1-7). However, in those processes lignocellulosics components are modified to large extent. It is impossible to separate the wood constituents from the resulting composites after the use.

We have developed a new process for separating lignocellulosic components into carbohydrates and a new type of lignin derivative (lignophenol). This process includes the phase-separation system composed of phenol derivatives and sulfuric acid. Through the process, cellulose microfibrils (assembled celluloses) are hydrolyzed to give soluble saccharides, whereas lignin is converted to 1,1-bis (aryl) propane-type polymers (lignophenols) (8-13)

In the present work, woods were treated through the phase-separation system composed of phenol derivatives and phosphoric acid with the lower acidity, compared with sulfuric acid. The properties of the resulting composites were investigated in comparison with the wood.

2. EXPERIMENTAL

2.1 Materials

Air-dried wood meals [hinoki (*Chamaecyparis obtusa*), Douglas fir (*Pseudotsuga menziesii*) and beech (*Fagus crenata*)] were finely milled to pass through an 80-mesh screen. The wood meals were extracted with ethanol-benzene (1:2, v / v) for 48 hours, and then were subjected to determinations of the lignin contents (acid insoluble- and soluble-lignins, Tappi T222 om-83, UM-250).

Acid insoluble lignin contents of hinoki, Douglas fir and beech wood meals were 30.40, 27.97 and 25.69%, respectively.

2.2 Phase-separation treatment

2.2.1 Functionality control of lignocellulosics

The wood meals were mixed with phenol derivative (*p*-cresol /acetone solution), and then, acetone was evaporated. Ninety-five % phosphoric acid (10ml/g wood) was added to the mixture, which was vigorously stirred at 50°C for 1hour. The reaction mixture was poured to excess water, and the precipitates were collected by centrifugation, washed with water and dried under reduced pressure.

2.2.2 Extraction of lignophenol fractions

The phase-separation treated composites were extracted with acetone. The acetone extract was concentrated under reduced pressure and added dropwise to an excess amount of ethyl ether with stirring. The precipitates (lignophenol fractions) were collected by centrifugation and dried over P₂O₅ under reduced pressure after evaporating the solvent.

2.3 Modification of phase-separation treated composites

2.3.1 Acetylation

Pyridine (70ml) and acetic anhydride (70ml) were added to phase-separation treated composites (7g), and were stirred for 96 hours. The reaction mixture was added dropwise to cooled water, and the precipitates were collected by centrifugation, washed with water, and dried under reduced pressure.

2.3.2 Hydroxymethylation

After 0.5N NaOH was added to phase-separation treated composites, an excess amount of formaldehyde was added. The solution was stirred in the presence of N₂ at 60°C for 3 hours. Then, the reaction mixture was acidified with 1N HCl to pH2, and the insoluble fractions were collected by centrifugation, washed with

water and dried under reduced pressure.

2.4 Preparation of the composite molds

The composite molds were prepared from phase-separation treated composites using SHIMAZU flow tester CFT-500D (Load: 50kgf, Initial temperature: 70°C, Rate: 1.5°C/min, Final temperature: 180°C for original materials, 130°C and 150°C for acetylated materials, 180°C for 20 min for hydroxymethylated materials).

2.5 Physical properties of the composite molds

2.5.1 Stability of the composite molds

The composite molds were placed in water (depth: 3cm) at the room temperature for 60min. The surface-attached water of the composite mold was removed with filter papers, and the weight and volume were measured. The composite molds were dried at 60°C for 3 days. The water absorption (Aw) and volumetric swelling (Vs) were calculated as follows:

$$Aw(\%) = (Wt' - Wt) / Wt \times 100 \quad (\% \text{ of sample weight})$$

Whereby

Aw(%): water absorption (%)

Wt: weight of original composite mold

Wt': weight of composite mold after water absorption

$$Vs(\%) = (V' - V) / V \times 100 \quad (\% \text{ of sample volume})$$

Whereby

Vs(%): volumetric swelling (%)

V: volume of original composite mold

V': volume of composite mold after water absorption

2.5.2 Measurement of Brinell hardness

The Brinell hardness of the composite molds was measured according to JISZ-2117 by SHIMAZU AG-1. A steel ball of 10mm-diameter was pushed on the composite mold. The pressure (P) when the cave was $1/\pi \approx 0.32\text{mm}$ was measured. Hardness (HB) of the composite mold was calculated following:

$$HB \text{ (MPa)} = P \text{ (N)} / 10$$

2.6 Analysis

Thermal analysis of phase-separation treated

composites and lignophenol fractions were carried out by means of TMA (thermomechanical analysis). Measurements were taken over the temperature range of 20 to 250°C with the rate of 2°C/min and the load of 5g.

Number-average and weight-average molecular weights of lignophenols were determined by gel permeation chromatography (GPC) using JASCO TRIROTAR and JASCO 807-IT integrator. The conditions were as follows: Eluent: THF, Column: Shodex KF801, KF802, KF803 and KF804, Temperature: 40°C, Flow rate: 0.5ml/min, Detector: UV 280nm, Pressure: 50kgf/cm².

3. RESULTS AND DISCUSSION

3.1 Phase-separation treatment of lignocellulosics

Table I shows the yields of composites treated through the phase-separation system. The yields of the resulting composites were more than 98% and 77% in softwood and hardwood, respectively. They contain 11% and 21% of lignophenol fraction (the acetone extract), respectively. The difference in the yields between softwood and hardwood is due to the dissolution of carbohydrate fractions, mainly hemicelluloses. Compared with the softwood, the hardwood contains more hemicelluloses, which are labile in the acid solution and readily dissolved.

Thermomechanical properties of lignocellulosics are showed in Fig.1. Original wood meals did not show clear softening below 230°C, whereas the phase-separation treated composites began to soften at 150-180°C. Lignophenol fractions extracted from composites had clear solid-liquid transformation points at 150-180°C. There is a clear relationship between the thermoplastic properties of lignophenol fractions and phase-separation treated composites.

Table I Yields of phase-separation treated composites.

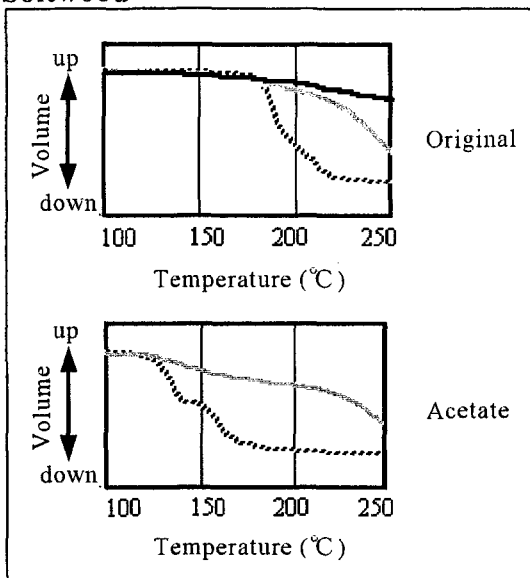
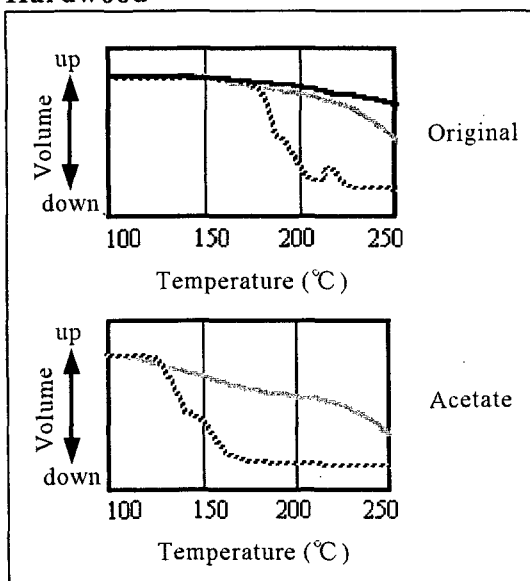
Species	% of original lignocellulosics
Softwood	98.36
Hardwood	77.42

Table II Yields of lignophenol fractions.

Species	% of phase-separation treated composites	% of original wood meal
Softwood	11.6	11.4
Hardwood	21.3	16.3

Table III Average molecular weights of lignophenol fractions.

	\overline{M}_n	\overline{M}_w	$\overline{M}_w/\overline{M}_n$
Softwood			
Original	3,490	9,960	2.85
Acetate	4,750	14,660	3.09
Hardwood			
Original	2,390	4,700	1.97
Acetate	2,840	6,410	2.25

Softwood**Hardwood**

— Original wood meals
 - - - Phase-separation treated composites
 Lignophenol fractions

Fig.1 Thermomechanical profiles of softwood and hardwood samples.

Acetylated lignophenol fractions had solid-liquid transformation points at 100-150°C, which were more clear and 40-50°C lower than original lignophenols. Solid-liquid transformation points of acetylated phase-separation treated composites also agree with those of acetylated lignophenol fractions. The improved thermoplasticity by acetylation would be due to the blocked hydrogen bonding between lignophenols, and between lignophenol and carbohydrate.

From these results, the modification of lignocellulosics during the phase-separation treatment with phenol derivatives and phosphoric acid would be explained as follows: cellulose microfibrils were swollen with partial hydrolysis, leading to the liberation of intimate association of cellulose chains by hydrogen bonding. The lignin networks were selectively degraded to give linear type subunits (lignophenols), resulting in the polysaccharides - lignophenol complexes. Within the composites lignophenol fractions would act as an effective plasticizer.

Lignophenol (*p*-cresol type) fractions have reactive sites on cresolic nuclei in addition to phenolic nuclei of lignin. Therefore, hydroxymethylated lignophenol can be polymerized to give network type-polymers within the composites by heating.

3.2 Physical properties of the composites

The all composite molds had very smooth surfaces with beige color. The acetylated composite molds had highest density (1.21) in spite of lowest molding temperature (130°C and 150°C), because of pronounced thermoplasticity. On the other hand, although the hydroxymethylated composite molds were prepared at higher temperature (180°C for 20 min), the resulting composite molds had the lowest density (0.71). This indicates that the linking of lignophenol fractions by heating inhibited the flow of materials, resulting in the composite molds with lots of pores. As shown in Table IV, the composites from hardwood had higher density than those from softwood. As shown in Table III, the weight-average molecular weights of lignophenol fractions, which act as an internal plasticizer in the composites, were lower

Table IV Physical properties of phase-separation treated composite molds.

Sample	Density (g/cm ³)	Brinell hardness (MPa)
Softwood		
Original	1.01	—
Acetylated (150°C)	0.21	—
Acetylated (130°C)	0.99	31.90
Hydroxymethylated	0.71	18.18
Hardwood		
Original	1.18	—
Acetylated (150°C)	1.22	—
Acetylated (130°C)	1.20	52.81
Hydroxymethylated	0.87	25.27

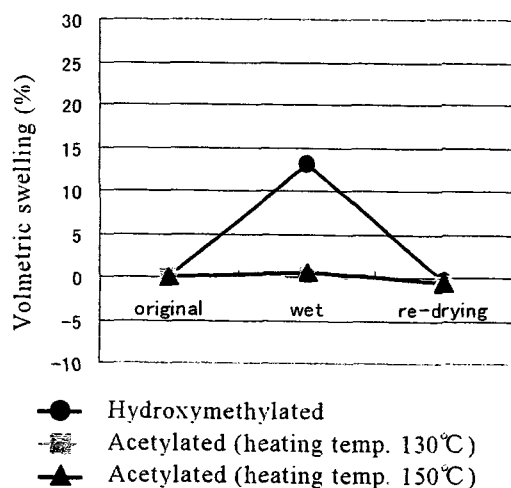


Fig.2 Stability of the softwood composite molds.

in hardwood than in softwood. Therefore, hardwood lignophenol fractions can flow more smoothly, leading to the compact composite molds.

By water soaking for 20min, softwood original composite molds were cracked, and were broken after re-drying. On the other hand, acetylated and hydroxymethylated composite molds hardly changed in appearance and were very stable.

In acetylated samples, 150 °C of molding temperature gave the molds with higher density and lower water absorption than 130 °C. The acetylated composite molds had pronounced stability (lowest volumetric swelling and dimensional stability) (Fig.2).

Although the hydroxymethylated composite molds had higher water absorption (17%) and volumetric swelling than acetylated ones because of the presence of lots of pores, they got back to the original shapes by drying, showing excellent stability (Fig.2).

As shown in TableIV, the Brinell hardness of the composite molds increased with the density. The Brinell hardness of hardwood is 10-60MPa for the transverse section, 5-34MPa for the tangential section and 4-29MPa for the radial section (14). The hardness of the composite molds (18-32MPa in softwood, 25-53MPa in the hardwood) is comparable or superior to the wood.

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