

Refining of fiberboards through the phase-separation system

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The Potential as molecular materials of fiberboards through the phase-separation system was examined. Fiberboards were separated rapidly and quantitatively into carbohydrates and lignophenols through the phase-separation system composed of phenol derivatives and acid. Although the plant cell walls form IPN (Interpenetrating Polymer Network) structure, fibrillated lignocellulosics (fiberboard) had high accessibility for the reagents, thus acid hydrolysis of carbohydrates and phenol grafting to native lignin were accelerated. The resulting lignophenols and sugars from fiberboards had almost the same properties as those from wood meal, although a slight amount of the urea-melamine resin adhesive component were contained in the lignophenol. These results indicated that the fiberboard are preferable to original wood as aliphatic and aromatic material sources, and should be adapted to the molecular level recycling through the phase-separation system.

Key words: fiberboard, lignin, cellulose, hemicellulose, lignophenol, phase-separation system

1. INTRODUCTION

In recent years, plant biomaterials have attracted lots of attention as sustainable petroleum substitute again. Especially polylactic acid as a biodegradable plastic from corn or sweet potato and biodiesel oil from soybean oil or palm oil have already been commercialized. But utilization of these plant biomaterials causes a price increase in food. Thus it is important to use lignocellulosics which does not compete with food are proceeding as petroleum substitute.

After adoption of Kyoto protocol, many companies plant fast-growing trees as clean development mechanism (CDM) in order to prevent global warming. For example it is said that eucalyptus, acacia, radiata pine, falcata can use for about 10 years. The utilization of these fast-growing trees is proceeding. In particular, the use to fiberboard has expanded.

The fiberboards are classified by density. A fiberboards with specific gravity between 0.50 and 0.80 is classified as medium density fiberboard (MDF) and a fiberboard with specific gravity greater than 0.80 is classified as hardboard. The MDF has some good benefits. For example the MDF is homogeneous structure without fiber direction and smoothing surface suitable for print etc. Recently the application of MDF to furniture, residential material etc.

The MDF production process involves in the first steps debarking and chipping. Cleaned chips are cooked in a digester and refined into wood fibers which are then mixed with resin and wax. The mixture of wet fiber, resin and wax is dried and transported to the mat former before it is pressed to produce a continuous mat. In the final processing stage it is trimmed, sanded and cut to

specified dimensions.¹

A lot of lignocellulosics wastes are generated through the these process. Especially fiber wastes applied adhesive (process waste), edgings and mill ends can be rarely recyclable as MDF fiber. The used MDF (product waste) is also difficult to recycle for wood material because of many adhesive and fiber deterioration. Most of these MDF waste are combusted for thermal recycle.

However the lignocellulosics is accumulated in the forest ecosystem over a long period of time. Thus long time cascade utilization of the lignocellulosics is importance.

Recently a new process for separating lignocellulosics into lignin and carbohydrate moieties with the conversion to highly reactive forms at room temperature was developed.²⁻⁴ This process includes a phase-separative reaction system composed of phenol derivatives and concentrated acid which are immiscible with each other. In the process the concentrated acid is not only a solvent for carbohydrate, but also works as a catalyst for the fragmentation and phenolation of lignin, whereas phenol derivatives act as phenolation agents, a barrier to minimize the attack of acid on the lignin and a solvent for the lignin fractions. The separated lignin derivatives (lignophenol) have several unique functions, which conventional lignins do not have, in spite of retention of the original interunit linkages: these include highly phenolic property, no conjugated system, light color comparable with native lignin, solid-liquid transformation and high immobilization capability for proteins.³ These original functions are due to the selective hybridization of monomeric phenol derivatives at

C-1 positions, leading to linear type structures composed mainly of 1,1-bis(aryl)propane-type units.

In this study, the potential as molecular materials of fiberboards through the phase-separation system was examined.

2. EXPERIMENTAL

2.1 MDF materials

Soft wood MDF board (fiber / urea-melamine adhesive / wax = 100 / 18 / 1) was utilized. After surface layer (preure layer) of MDF board was ground, the MDF board internal material was obtained by drill cutting. As fiber material, raw fiber, milled fiber (60 mesh pass) and fiber blended with urea-melamine resin were used. As control material, softwood chip for MDF board and Western hemlock (*Tsuga heterophylla*) were used. These materials were pulverized by Ultra Centrifugal Mill ZM 100 and a part of materials were extracted with ethanol / benzene = 1/2 solution for 48h (Table 1).

The MDF boards and their materials were provided from Tokushima Prefectural Industrial Technology Center.

2.2 Lignin contents

Lignin contents were determined on Klason method.⁵

2.3 Phase-separation treatment 1step process

p-Cresol (10 ml/g wood) was added to wood meals with stirring at room temperature. After 10 min, 72% sulfuric acid (20 ml/g wood) was added to the mixture and the vigorous stirring was continued at 30°C for 60 min.

The reaction mixture was rapidly separated into the organic and aqueous phases by centrifugation. The organic phase was taken up and added dropwise to an excess amount of ethyl ether with vigorous stirring. The precipitates were dissolved in acetone and insoluble materials were removed by centrifugation. The acetone solution was then concentrated under reduced pressure and added dropwise to an excess amount of ethyl ether with stirring. The precipitated lignin derivative (lignophenol) was collected by centrifugation.

2.3 Molecular weight distribution of lignophenol

Gel permeation chromatography (GPC) of lignophenols were determined on a JASCO PU-1580 equipped with JASCO MD-1515 multi wavelength detector. Shodex GPC KF-801,802,803,804 (8 mm ID x 300 mm) was connected in series and THF used as an eluent [flow rate; 1.0 ml/min].

Table 1. MDF and control samples

raw samples	milled	extraction	sample name
softwood chips	○	○	S-chip
raw fiber	-	-	Raw fiber
fiber	○	○	Fiber
fiber blended with urea-meramin resin	○	-	UM-F
preure layer	-	-	Precure
MDF board	○	-	MDF board
western hemlock	○	○	Western hemlock

2.4 FT-IR of spectra of fractionated lignophenols

FT-IR spectra of fractionated lignophenols were determined on Perkin Elmer Spectrum GX FT-IR Spectroscopy using KBr discs. The spectra were recorded from 400 to 4000cm⁻¹.

2.5 Thermomechanical analysis (TMA) of fractionated lignocresols

Thermomechanical analyses of fractionated lignophenols were performed on a SEIKO EXSTAR 6000 TMA/SS. About 5 mg of a powdered sample was placed in an aluminum pan (5 mmφ x 2 mm) and aluminum plate (2 mm x 2 mm) was put on the sample. The sample was compressed with the quartz probe with a 5 g load under a nitrogen stream and heating rate was carried on 2°C/min.⁶

2.6 Carbohydrate composition

The aqueous phase after phase-separation treatment was diluted to 3% sulfuric acid concentration with distilled water, and was boiled for 4 hours. After cooling, ribose as an internal standard was added. The solution was neutralized and desalted by barium hydroxide octahydrate and saturated barium hydroxide solution, and the solution was analyzed by the SHIMADZU HPLC Reducing Sugar Analysis System. (HPLC condition)

Column: Shim-pack ISA-07/S2504. Eluent: A; 0.1 M potassium borate buffer (pH8.0), B; 0.4 M potassium borate buffer (pH9.0), Flow rate: 0.6 ml/min. Gradient: A 100% to B 100% (2%/min). Temp: 65°C. Detect; reaction reagent; 1% *L*-arginine, 3% Boric acid, 0.5 ml/min. Reaction temp.; 150°C, detection wave; Ex-320 nm, Em-430 nm

2.7 Molecular weight distribution of carbohydrates

The aqueous phase after phase-separation treatment was neutralized and desalted by barium hydroxide octahydrate and saturated barium hydroxide solution. The solution was analyzed by GPC.

(GPC condition)

Column: Asahipak GS-620HQ, GS-520HQ, GS-320HQ, GS-220HQ (7.6 mm ID. × 30 cm L.)
Eluent: H₂O. Flow rate: 0.6 ml/min. Temp: 50°C.
Detect: RI. Standard: Pullulan, maltose, maltotriose, maltopentaose, maltoheptaose

3. RESULTS AND DISCUSSION

3.1 Lignin contents

Table 2 shows lignin contents of MDF samples and wood meals. The total lignin contents of UM-fiber and MDF board higher than softwood chip. Because acid-insoluble lignins contain

Table2. Lignin contents of wood meals and MDF samples

Species	Lignin contents (% of wood)		
	Acid-insoluble	Acid-soluble	Total
Western hemlock	29.79	0.22	30.00
S-chip	29.98	0.29	30.27
Fiber	32.72	1.31	34.02
UM-F	31.08	4.73	35.81
MDF board	32.57	2.22	34.77

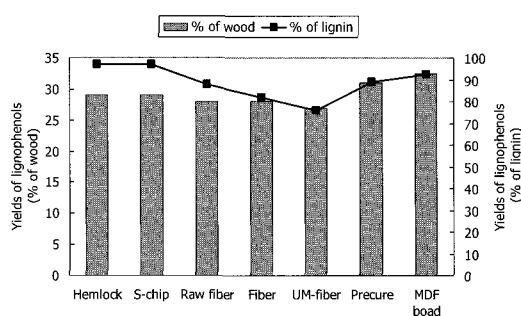


Fig. 1. Yields of lignophenols from MDF samples and wood meal

urea-melamine resin.

3.2 Yields of lignophenols

In the phase-separation system, an excess amount of cresol was added milled wood, followed by the addition of 72% sulfuric acid. The reaction mixture of milled wood turned light green and its viscosity began to increase after 30 s, reaching a maximum after 2-3min, after which it decreased rapidly to its original value. However the viscosity of reaction mixture of milled sample from fiber, UM-fiber and MDF board increased rapidly after addition of sulfuric acid, because cell wall structure of these fiber samples were collapsed and having high accessibility to reagents.

Figure 1 shows yields of lignophenols from MDF samples and wood meals.

The lignophenol yields per lignin of raw fiber, fiber and UM-fiber slightly reduced compared to S-chip. Because these fibers treated with steam during the fibrillation process, a part of lignin was depolymerized and dissolved in diethyl ether through the purification of lignophenol. Although the yields of lignophenol from MDF board and precure layer of MDF were higher than fiber, the lignophenol yields per lignin was lower than S-chip. Because the lignin content of MDF and precure layer contain polymerized urea-melamine resin.

3.3 Characterization of lignophenol separated from MDF board

3.3.1 Molecular weight distribution of lignophenol

The pattern of molecular weight distribution and average molecular weight of lignophenol from hemlock s-chip fiber had similar (Fig.2). However the lignophenols from UM-fiber and MDF board were contained peak of urea-melamine resin before curing at retention time 37 min. But the content of low molecular weight resin was small in amount and molecular weight distributions of lignophenol moiety were similar.

3.3.2 FT-IR spectra of lignophenol

The FT-IR spectra of lignophenols from hemlock, S-chip and raw fiber had similar peak pattern, the steam treatment had little influence on characterization of lignophenol. However the carbonyl absorption peak (1680cm^{-1}) was slightly appeared in lignophenols from UM-fiber and MDF

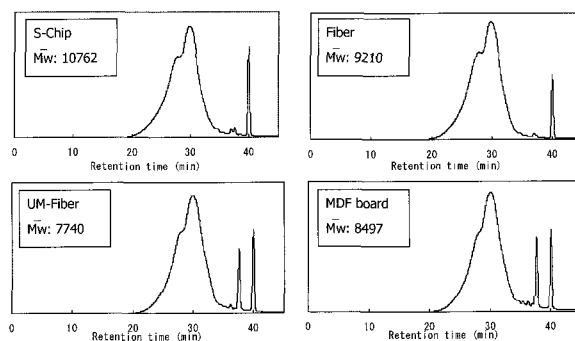


Fig. 2 GPC profiles of lignophenols from the MDF board and the control samples

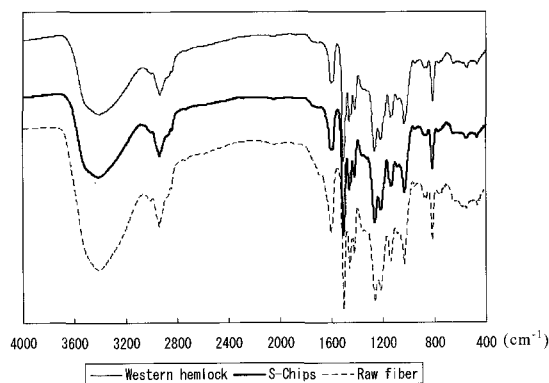


Fig. 3 FT-IR spectra of lignophenols from fiber board raw materials and control sample.

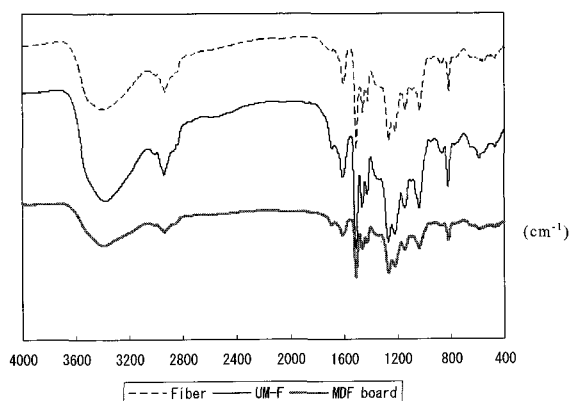


Fig. 4 FT-IR spectra of lignophenols from the fibers and the MDF board

board. It was thought that this absorption was based on the urea carbonyl group of urea-melamine resin. The other peak pattern of MDF board lignophenol had similar pattern to raw material.

3.3.3 TMA analysis of lignophenol

The lignophenol are converted to linear-type polymers with high frequency of 1,1-bis (aryl) propane-2-O-aryl ethers during the phase separation treatment, therefore lignophenol has thermal softening property. The TMA curves of lignophenol from MDF board and fibers revealed volume decreasing at 150°C - 170°C due to transformation of solid state to clear liquid state (Fig. 5). Although the UM-fiber lignophenol contained a small amount of urea-melamine resin

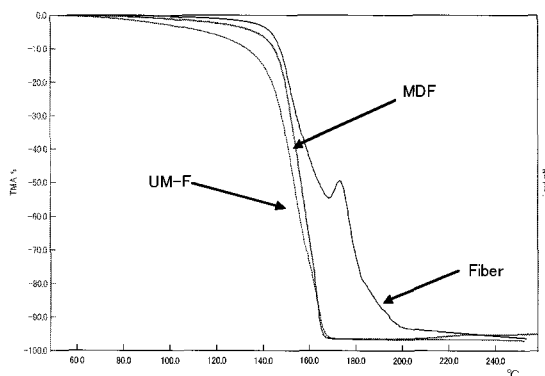


Fig. 5 TMA curves of lignophenols from from the fibers and the MDF board

before curing, contaminated urea-melamine resin had little influence on thermal softening property of lignophenol. It was thought that the peak of fiber lignophenol at 170°C was due to air trap during thermal softening process.

3.4. Carbohydrate

Figure 6 shows the carbohydrate composition of the aqueous phase after the phase separation treatment for 60 min. The carbohydrate content of softwood was generically about 70%. The sugar yields of the adhesive-free raw material similar to hemlock wood meal. But the sugar yields of MDF board and UM-fiber was slightly low value. Because about 18% of adhesive was contained in MDF board and a part of hemicellulose sugar (mannose, arabinose, galactose, xylose) was degradation through steam fibrillation process. Thus it is said that sugar yields of total carbohydrate was enough high level.

The carbohydrates in the sulfuric acid phase were consisted of high molecular weight fractions (more than $M_w=100,000$) and low molecular weight fraction (less than $M_w=2,000$) (Fig. 7). The molecular weight distributions of MDF board and its raw material were similar.

Separated carbohydrates were consisted of various sizes of oligosaccharide and high molecular weight water-soluble glucose polymers. The water-soluble polysaccharide and oligosaccharide can be use for thickening agent etc. and functional food, respectively. These carbohydrate components can be converted readily to simple sugars by dilute acid hydrolysis. The monosaccharides also convert to ethanol or lactic acid through fermentation. The monosaccharides from hemicellulose are expected as pharmaceuticals, for example xylitol.

The lignophenol derived from MDF board had appropriate features, for example thermal softening property and no conjugated system, although it contained a small amount of adhesive.

Thus the fiberboard are preferable to original wood as aliphatic and aromatic material sources, and should be adapted to the molecular level recycling through the phase-separation system.

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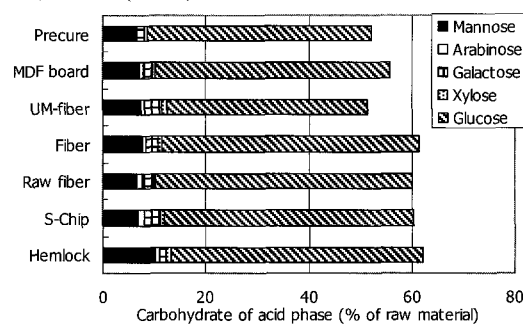


Fig. 6 Neutral sugar compositions of the aqueous phase through the phase-separation system from the control materials and the MDF samples.

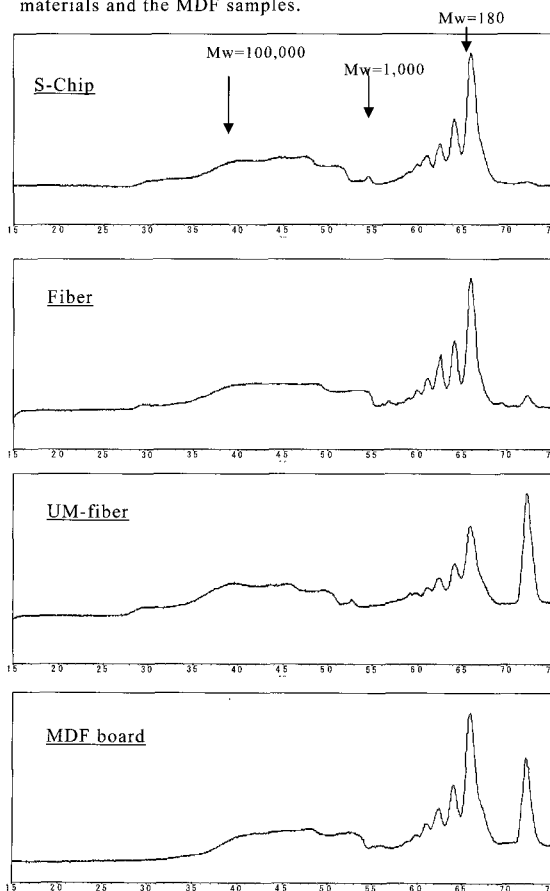


Fig. 7 GPC profiles of carbohydrate of the aqueous phase through the phase-separation system from the control materials and the MDF samples.