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Practical research of wood-like thermoplastic using lignin extracted by high pressure hydrolysis process

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Abstract

Japanese cedar (*Cryptomeria japonica*) as softwood and Japanese beech (*Fagus crenata*) as hardwood were also treated in subcritical water and supercritical water. The methanol-soluble portion of the extract maintained the typical structure of lignin.

Lignin was extracted from wood under HPH-subcritical condition, and mixtures of the HPH-lignin with natural fibers were prepared to obtain a granulate which could be processed on a small injection moulding machine. The mechanical properties of the test samples were measured and found to be comparable to those found for the wood-like thermoplastic with normal lignin from the current paper making process.

The extraction conditions of lignin from wood were chosen as 5 MPa at 250℃ and the separation condition of lignin from hot water was chosen as 0.3 MPa at 120℃. In the case of the throughput of 1t-wood/h (160kg-lignin/h), the extraction cost of the lignin was estimated at 110 yen/kg-lignin.

In summary, the wood-like thermoplastic by HPH-process has good mechanical properties, and HPH-process is feasible.

Keywords: subcritical, lignin, extraction, plastic

1. Introduction

High Pressure Hydrolysis (HPH) process to treat biomass renounces additional chemicals. The renunciation causes different ecological and economical benefits in processing, but is also advantageous referring the received raw materials, which can be thus described to be as close as possible to nature. Primary products are native lignins(HPH-lignin), hemicellulose and partially delignificated pulp, similar to the products of cellulose- and paper industry, but without any chemical modification. The HPH-lignin can directly used for thermoplastic products, just as synthetic thermoplastic materials to replace partially products out of plastics, or treated in subsequent treatments to chemicals like aromatics, pharmaceutical and medical products, e.g. vanillin. In subsequent processes, also the hemicellulose can be converted to furfural and finally to furfuryl-alcohol, useable as a solvent or to be form the resin of natural fibers in laminated natural composite materials. At least, the partially delignificated pulp can be offered to the paper industry to save chemicals and energy or to produce natural long and short fibers for technical applications, e.g. in the thermoplastic composites.

Thus approach of the chemical industry, that they would use more chemicals and raw materials received from biomass if only the process technologies become more efficient, the mass of extracted substances increase and the quality would be improved, is legitimated. At present, less than 10% of the chemicals and raw materials offered by the chemical industry were generated out of biomass. Consequently, it is necessary to open new ways to receive raw materials and chemicals for technical products and consumables.

In thus situation, "practical research of wood-like thermoplastic using lignin extracted by high pressure hydrolysis process" was carried out. Concretely, the following research items were carried out.

(1) Research on the thermoplastic using the lignin extracted by HPH process
- (a) Fundamental research of the lignin extraction
- (b) Research on the lignin extracted by HPH process
- (c) Research on the thermoplastic using the lignin extracted by HPH process

(2) Research on the adaptability of the HPH process
- (a) Investigation of biomass as raw materials and applications of the thermoplastic
- (b) Development of the products using the thermoplastic
- (c) Concept design and feasibility study of HPH process

2. Experimental

2.1 Research on the thermoplastic using the lignin extracted by HPH process

2.1.1 Fundamental research of the lignin extraction

Japanese cedar (*Cryptomeria japonica*) as softwood and Japanese beech (*Fagus crenata*) as hardwood were treated in subcritical water and supercritical water. The treated woods were, then, fractionated to the water-soluble portion, methanol-soluble portion and methanol-insoluble residues as shown in Fig.1.

The molecular weight distribution (M_W) of methanol-soluble portion was estimated by gel permeation chromatography (GPC) on the HPLC system (Shimadzu LC-10A) with refractive index detector. HITACHI G-7000M and M-9000 Gas Chromatograph 3-Dimensional Quadrupole Mass Spectrometer (GC-MS) was used for identifying the monomeric products in the methanol-soluble portion. The fourier transform-infrared (FT-IR) spectra were recorded in the IR-8000 spectrophotometer (Shimadzu Co.) using KBr pellet technique.

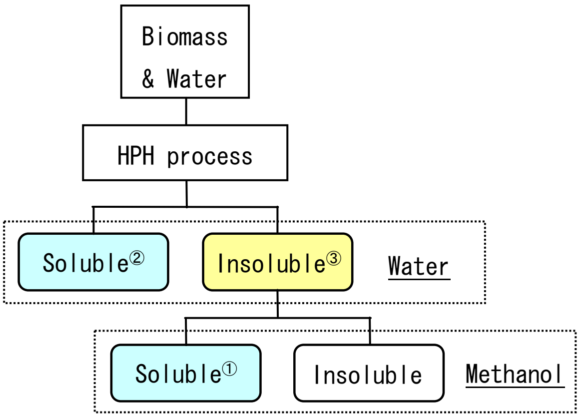


Fig.1 Fractionation scheme of treated lignocellulosics

2.1.2 Research on the lignin extracted by HPH process

A laboratory scale batch equipment was used to extract the lignin from wood for generating granulates for injection molding and obtaining test samples for material testing. It operates at working conditions of:

- Temperature range: 200 to 220°C
- Pressure range: to max. 40 bar
- Solvent: pure water
- Additives: (none)
- Solid biomass feed: 800 g
- Water volume: 3 - 10 l
- Pump feed: 3 l/mim
- Residence time 10 - 25 min

Separation of the might run by:

ultrafiltration, → rotational evaporation → vacuum drying

2.1.3 Research on the thermoplastic using the lignin extracted by HPH process

The extruders to produce granules made from lignin, fiber and additives have single or twin screws which transport, compact, melt (or soften), mix, shape and finally bring out the melt which then cools down and solidifies. For the preparation of the granules a special technique is used, which allows its preparation without inducing heat stress to the natural components, and differs from the preparation of plastic granules in the standard extrusion process.

The processing of the lignin compound granules runs on industrial injection molding machines with the screws as normal as shown in Fig.2. The temperature can be below 170 °C and the nozzle temperature can be a between 155 and 170 °C using an open nozzle. The back pressure must be kept high enough to enable a smooth rotation of the screw. The injection pressure is relatively (150 MPa) high and so is the injection speed. Pictures of samples of the HPH lignin to measure mechanical properties are shown in Fig.3.

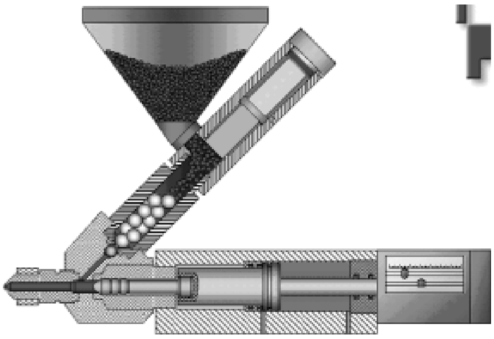


Fig.2 The injection molding machine

Fig.3 Samples of the HPH lignin

2.2 Research on the adaptability of the HPH process

2.2.1 Investigation of biomass as raw materials and applications of the thermoplastic

Biomass as raw materials and applications of the thermoplastic were mostly investigated by literature and interview.

2.2.2 Development of the products using the thermoplastic

Several commercial samples were made by injection moulding machine, and the samples were demonstrated to several Japanese companies.

2.2.3 Concept design and feasibility study of HPH process

The extraction condition and separation condition of the lignin determined by batch experiment and semi-batch experiment, and material balance and energy balance were calculated by process simulator "HYSYS.process" (supplied by Aspen Technology, Inc.). The total equipment cost in the equipment list was estimated, and total investment cost of the HPH plant was estimated by cost factored method.

3. Results and Discussion

3.1 Research on the thermoplastic using the lignin extracted by HPH process

3.1.1 Fundamental research of the lignin extraction

Nineteen guaiacyl-type compounds in methanol-soluble portion from softwood, and 15 syringyl-type monomeric compounds in that from hardwood were identified by GC-MS analysis as shown in Table1. The structure of identified products was not only phenyl propane (C6-C3) units but also C6-C2 and C6-C1 units. Besides, the infrared spectra suggested that the methanol-soluble portion maintains the typical structure of lignin, though it shows richness in condensed-type linkages and changes in propyl side chain. These results indicate that the supercritical water treatment cleaved not only ether linkages but also part of propyl side chains in lignin to give various aromatic compounds. These lines of evidence would provide a clue as to efficient utilization of lignin-derived products for not only wood-like thermoplastics but also value-added useful chemicals.

Table 1 Lignin-derived monomeric products in the methanol-soluble portion

No.	Product name	Structure*	Detection**	
			Japanese cedar	Japanese beech
1	Guaiacol	G	+	+
2	Methylguaiacol	G-C	+	+
3	Ethylguaiacol	G-C-C	+	+
4	Vinylguaiacol	G-C=C	+	–
5	Syringol	S	–	+
6	Vanillin	G-CHO	+	–
7	Eugenol	G-C-C=C	+	–
8	Propylguaiacol	G-C-C-C	+	+
9	Methylsyringol	S-C	–	+
10	Isoeugenol (*cis*)	G-C=C-C	+	+
11	Homovanillin	G-C-CHO	+	+
12	Isoeugenol (*trans*)	G-C=C-C	+	+
13	Acetoguaiacone	G-CO-C	+	+
14	Propioguaiacone	G-CO-C-C	+	+
15	Ethylsyringol	S-C-C	–	+
16	Guaiacylacetone	G-C-CO-C	+	+
17	Vinylsyringol	S-C=C	–	+
18	Propylsyringol	S-C-C-C	–	+
19	2-Methoxy-4-(1-hydroxypropyl)phenol	G-C-C-C-OH	+	–
20	Allylsyringol	S-C-C=C	–	+
21	Syringaldehyde	S-CHO	–	+
22	Propenylsyringol (*cis*)	S-C=C-C	–	+
23	Homovanillic acid	G-C-COOH	+	–
24	Synapylalcohol (*cis*)	S-C=C-C-OH	–	+
25	Synapylalcohol (*trans*)	S-C=C-C-OH	–	+
26	Propenylsyringol (*trans*)	S-C=C-C	–	+
27	2-Methoxy-4-(prop-1-en-3-one)phenol	G-CO-C=C	+	–
28	Synapylaldehyde (*cis*)	G-C=C-CHO	–	+
29	Acetosyringone	S-CO-C	–	+
30	Coniferylaldehyde (*trans*)	G-C=C-CHO	+	–
31	Propiosyringone	S-CO-C-C	–	+
32	Syringylacetone	S-C-CO-C	–	+
33	Felulic acid	G-C=C-COOH	+	+
34	Synapylaldehyde (*trans*)	S-C=C-CHO	–	+

* G and S represent guaiacyl and syringyl nuclei, respectively. ** Plus (+) and minus (–) correspond to detection and non-detection by GC-MS, respectively.

3.1.2 Research on the lignin extracted by HPH process

The obtained lignin consist of fine particles which are composed of spheres of 200 nm size. Their NIR and IR do not substantially differ from those of other types of lignin. The molecular weight distribution contains only of the lower molecular weight peaks from those found in commercial lignin. Mean values of the molecular weight is listed in the following Table 2.

3.1.3 Research on the thermoplastic using the lignin extracted by HPH process

Fig.4 illustrates a nearly linear dependence of the tensile strength on the content of fibers in wood-like plastic for hardwood. At about 45% content of fiber the maximum of increase of Young’s modulus is obtained. Other properties depending on the fiber content are illustrated by the Fig.5-6. The dependence of the indentation hardness (Fig.7) and the impact strength (Fig.8) on the fiber contents, however, is less pronounced. The data of mechanical properties are very close to those of wood-like plastics with commercial lignin.

Table 2 The average molecular weight distributions for various types of lignin

Sample	Mn	Mw	MP	Mz+1	Poly-dispersity
Kraft-Lignin I	**623**	**1240**	**933**	**2954**	**1,988968**
Kraft-Lignin C	**664**	**1345**	**1059**	**3404**	**2,024828**
Organosolv Lignin	**666**	**1467**	**1135**	**4531**	**2,203520**
HPH-Lignin	**505**	**750**	**525**	**1554**	**1,485042**

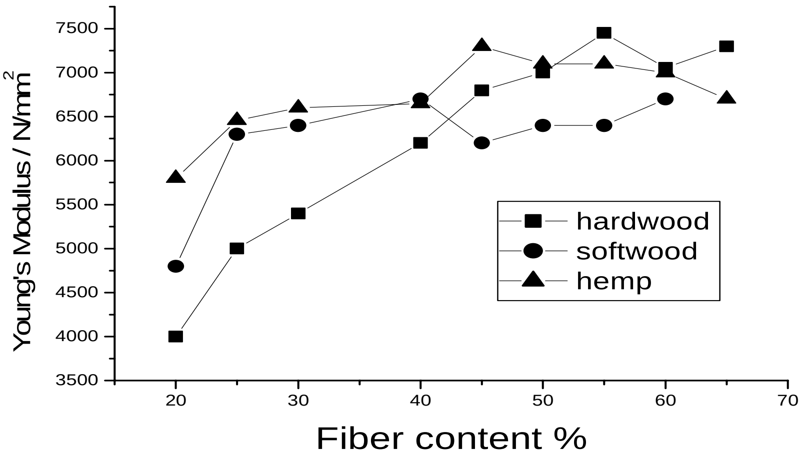
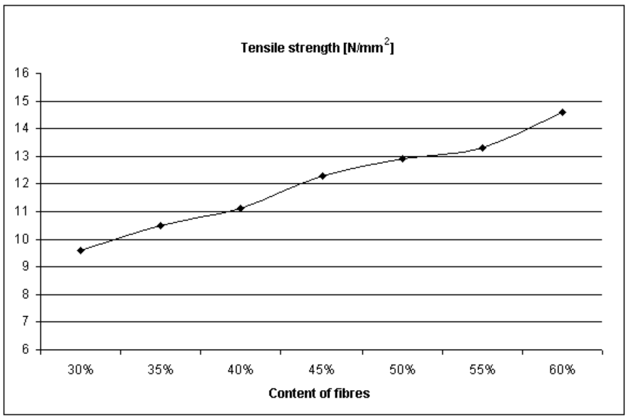


Fig.4 Young's modulus



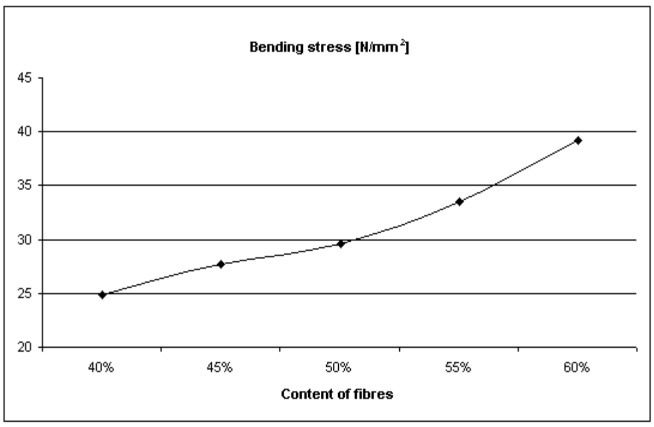


Fig.5 Tensile strength **Fig.6 Bending stress**

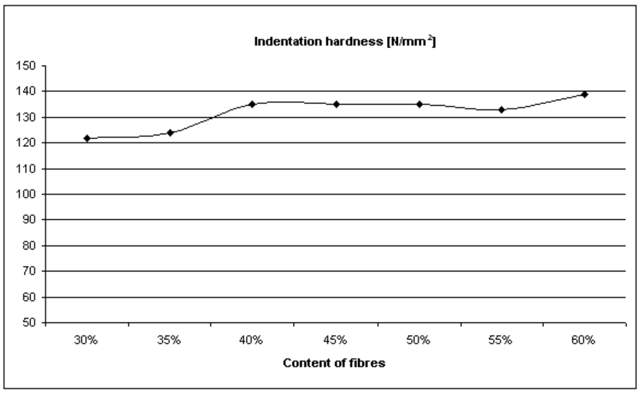


Fig.7 Indentation hardness

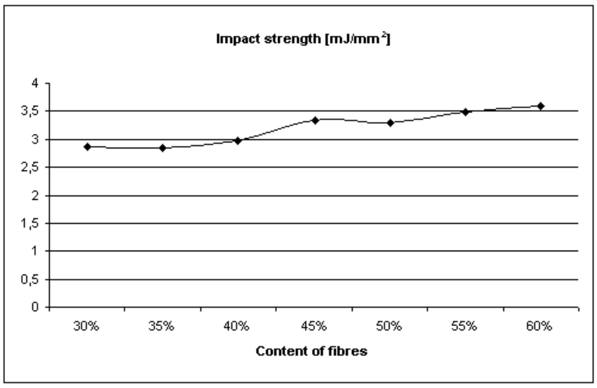


Fig.8 Impact strength

3.2 Research on the adaptability of the HPH process

3.2.1 Investigation of biomass as raw materials and applications of the thermoplastic

The quantities annually produced and available of the lignin in Japan are shown in Table 3. The potential of wood-like thermoplastic from lignin (12,637,000 t/year) is as much as the annual output of thermoplastic resins (12,232,000 t/year). The available mass of wood-like thermoplastic from lignin (2,529,000 t/year) is almost as much as engineering thermoplastic resins (2,209,000 t/year) which are PET resin, ABS resin, Polycarbonate, Polyamide, Metacrylic resin, Polyvinyl alcohol and Polyvinyl acetal.

Regarding wood powder compound, the market size was 9000 tons a year in 2001, and over 10000 tons a year was forecasted in 2002. As remarkable application of wood-like thermoplastic, the interior and wall of building was taken up on Japanese market, the requested properties became apparent. The research for "M wood" as typical wood powder compounds was carried out. "M wood" was developed by Misawa Homes Co. and Zeon Kasei Co. in 1993, and its share on wood powder compound was estimated 50.5%. This material has a good performance for molding, secondary processing and mechanical properties, but it included synthetic thermoplastic such as polyvinylchloride, polypropylene, polystyrene. This is the great target when we bring the wood-like plastics into the market in the future.

Table 3 Available mass and potential of lignin resin

Promising wastes containing lignin			Quantity of biomass dry-Tt/year	Available mass dry-Tt/year	Quantity of lignin dry-Tt/year	Available mass of lignin dry-Tt/year	Quantity of lignin resin dry-Tt/year	Available mass of lignin dry-Tt/year
From agliculture and forestry	Agricultual wastes	Chaff	1,830	502	494	135	618	169
		Rice Straw	8,649	414	1,384	66	1,730	83
		Wheet Straw	783	297	125	48	157	59
		Bagasse	120	120	19	19	24	24
	Forestry wastes	Remainder of the forest	2,178	480	610	134	762	168
		Wood from thinning	2,070	1,182	580	331	725	414
		Factory waste wood	7,500	1,296	2,100	363	5,250	454
Wastes	Industrial wastes	Black liquor	7,840	0	1,568	0	1,960	0
		Construction waste wood	1,962	1,236	549	346	687	433
		Floral residues	2,073	2,073	580	580	726	726
Total			35,005	7,600	8,010	2,023	12,637	2,529

3.2.2 Development of the products using the thermoplastic

There were various model applications. They concerned consumer good, toys, parts for electronic and automotive industries(Fig.9). In the electronic area was searched a model products which could be made from lignin. A loudspeaker(Fig.10) was developed to present and demonstrate the possibilities to use lignin in technical application. Some tests with the loudspeaker were done, with successful advantages of the sound and frequency, important aspect for the use of new material in this area. For the electronic industries it is of high interest that the lignin based material does not need any flame retardants.

Fig. 9 Mass consumer model products

Fig. 10 Loudspeaker model products

3.2.3 Concept design and feasibility study of HPH process

The operation conditions of HPH process(Fig.11) are mentioned below.

(1)Extraction conditions : 5MPaG at 250℃

16wt% : Extraction ratio of lignin against wood solid

14wt% : Extraction ratio of glucose against wood solid

(2)Separation condition : 0.3MPaG at 120℃(liquid-liquid separation)

The supply of wood, the supply of slurry and the output of lignin are mentioned below.

(1)Supply of wood : 1667kg/h containing 40wt% of water (1000kg-wood solid/h)

(2)Supply of slurry : 10000kg/h containing 10wt% of wood solid (1000kg-wood solid/h)

(3)Output of lignin : 160kg-lignin/h

Operation conditions of the HPH plant to do feasibility study are shown below.

(1)Operating hour : 24h/day x 330days/year = 7920h/year

(2)Depreciation expenses : 9%/year of investment cost of the plant

(3)Repair expenses : 2%/year of investment cost of the plant

(4)Personnel expenses : 6 million yen/person・year × 6 persons

The investment cost and production cost was estimated as shown below when the treatment fee of waste wood is 0 yen/kg and the waste water treatment cost is 0 yen/kg.

Investment cost ;870 million yen

Production cost ;110 yen/kg-lignin

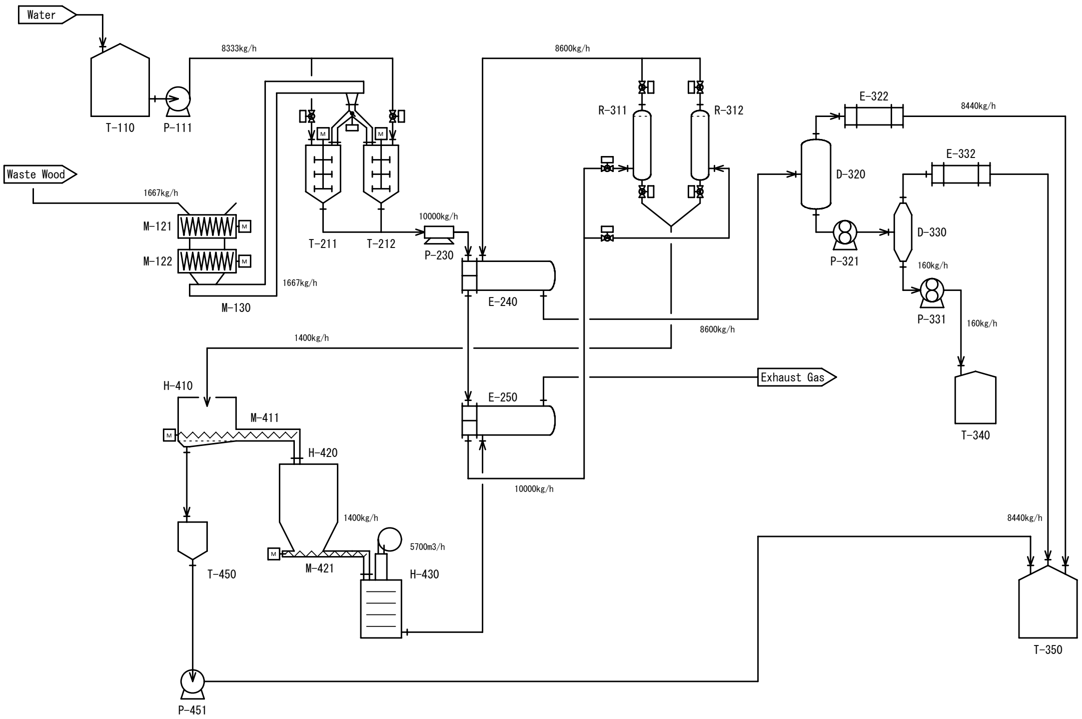


Fig.11 Process flow diagram of lignin extraction plant

4. Conclusions

Lignin was extracted from wood under HPH-subcritical condition, and mixtures of the HPH-lignin with natural fibers were prepared to obtain a granulate which could be processed on a small injection moulding machine. The mechanical properties of the test samples were measured and found to be comparable to those found for the wood-like thermoplastic with normal lignin from the current paper making process.

The extraction conditions of lignin from wood were chosen as 5 MPa at 250℃ and the separation condition of lignin from hot water was chosen as 0.3 MPa at 120℃. In the case of the throughput of 1t-wood/h (160kg-lignin/h), the extraction cost of the lignin was estimated at 110 yen/kg-lignin.

In summary, the wood-like thermoplastic by HPH-process has good mechanical properties, and HPH-process is feasible.

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[3] Shiro Saka, 26th Symposium on Biotechnology for Fuels and Chemicals, Chattanooga USA(2004/5)

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[1] JP Appl.No.2005-080607 “Separation method of lignin”(2005/3/18)

Award (total 1)

[1] Helmut Nägele, Material Excellence 2002 in Material connexion(USA), “Arboform” Category: naturals