

Synthesis of Lignophenol-Based Network Polymer with Hydrogel Property

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Lignophenols that was directly derived through the phase-separation system, and their derivatives chemically modified could be easily cross-linked with polyalkylene glycol diglycidyl ether. The resultant lignophenol-based network polymer had the properties of the hydrogel that absorbed and kept a good deal of water, in spite of what lignophenols had high aromaticity and hydrophobic property. The lignophenol-based hydrogel could be prepared from any lignophenols under the proper condition, independent of lignocellulosic species as softwoods, hardwoods and herbs. The water absorbed with cross-linked lignophenol was some tens times as much as their dried weights. Especially, the cross-linked gel from carboxymethylated lignophenol derivatives held the absorbing-water from some hundreds to approximately thousand times as much as their dried weights. For the water-absorbing ability, the intramolecular type of the cross-linkages existing in the lignophenol-based network polymer played more important part than the intermolecular cross-linkages among the molecules.

Key words: Phase-separation system, Lignophenol, Carboxymethylation, Cross-linkage, Hydrogel

1. INTRODUCTION

Native lignin in vascular plants assumes the role of mechanically important reinforcement agent and mainly exists as intra- and intercellular adhesions [1]. Usually with reference to this function, the utilization of conventional lignin has been carried out; nevertheless, which has not yet been successfully achieved. We remarked that native lignin assumes the roles not only as the plant element, but also as the soil element called the humic substance until becoming the fossil resources [2], because which is a long circulating material in the nature. One of them is the fact that the lignin partially biodegraded in the soil assumes the part of important forest roles such as which absorbing, holding and releasing rainwater. For getting out and emphasizing these functions to the lignophenols that were designed directly from native lignin for the utilization through the phase-separation system [3], the cross-linkage of them were performed. As the result, the water-absorbing network polymer based on lignophenols could be obtained. In the present paper are described the cross-linkage reaction of lignophenols and the water-absorbing functions and mechanisms of the resulting cross-linked gels.

2. MATERIALS AND METHODS

2.1 Lignocellulosics

Air-dried sample (100 μm screen pass), wood; Japanese beech (*Fagus crenata*) and herbs; rice (*Oryza sativa*) straw and husk, kenaf (*Hibiscus cannabinus*) and bamboo (*Phyllostachys bambusoides*), were extracted with ethanol-benzene (1:2, v/v) for 48 hr to remove extractives.

2.2 Synthesis of lignophenol

Using the phase-separation system (Two step process I) composed of phenols and 72 % sulfuric acid [3], lingo-*p*-cresols were synthesized. *p*-Cresol (3 mol/C₉) were sorpted to extractive-free lignocellulosics. Then 72 % sulfuric acid was added and the mixture was vigorously stirred at room temperature for 1 hr. The phenol-benzene solution (7:3, v/v) was added to the mixture with stirring. By stopping the stirring, the reaction mixture separated into the organic and aqueous phases. The organic phase was added dropwise to an excess amount of ethyl ether with vigorous stirring. The precipitates were dissolved in acetone and the acetone solution without insoluble substance was added dropwise again to an excess amount of ethyl ether. The precipitates (lignocresol) were collected by centrifugation and dried over P₂O₅ after evaporating the solvent.

2.3 Alkaline treatment (AT) of lignophenol

Under alkaline condition, aryl ether linkages in lignophenols were selectively cleaved, leading low molecular weights [4]. Lignocresol dissolved with 0.5 N NaOH in a stainless steel bomb was heated at 140 °C or 170 °C for 1 hr. The reaction mixture was acidified to pH 2 with 1 N HCl. After collecting and washing, the precipitates were dried over P₂O₅.

2.4 Carboxymethylation (CM) of lignophenol

Lignocresols and their AT-derivatives were suspended in isopropanol, to which 40 % NaOH was added. The mixture was stored at room temperature more than 3 hr, and then isopropanol was added to it again. The mixture was stirred at 50 °C, to which monochloroacetic acid (1 mol/mol of hydroxyl group in lignophenol) in isopropanol was dropwise added for 1 hr, and then the

reaction was kept at 50 °C for 2 hr. After the treatment, the precipitates were collected by centrifugation, dissolved with water, and acidified to pH 2. The insoluble fractions were removed by centrifugation and the solution including CM-lignocresol was purified by dialysis, and freeze-dried.

2.5 Preparation of cross-linked lignophenol

Lignocresol and their modified derivatives were dissolved with diluted NaOH solution, to which was added water-soluble cross-linkage reagent, polyalkylene glycol diglycidyl ether with stirring at the prescribed temperature. The reaction was kept until the reaction mixture started having much highest viscosity and completely formed a gel. The then viscosity was measured by digital viscometer on a TOKYO SEIKI DVR-E. To the gelatinous mixture was added excess distilled water to stop the reaction. The gels were repeatedly washed with water, and absorbed water at the same time. The amounts of the absorbed water (W_{Water}) were measured from the difference between the weights of gels with reaching the swelled equilibrium state and that with freeze-drying (W_{Dry}). The water-absorbing ability was determined from the ratio of $W_{\text{Water}} / W_{\text{Dry}}$.

2.6 Structural analysis of lignophenols

The amounts of combined phenols and hydroxyl groups in lignophenols were calculated by $^1\text{H-NMR}$ spectra of the acetylated derivatives [5] on a JEOL JNM-LA300 FT-NMR. The extents of the carboxymethylation were estimated by FT-IR (KBr disks, JASCO FT/IR-8900 μ) and NMR spectroscopy. The existences of cross-linkages were confirmed by FT-IR spectroscopy. The average molecular weights of lignophenols were measured by gel permeation chromatograms on a JASCO GULLIVER 1500 system, PU-1585, UV-1575 with three columns (Shodex KF602, KF603, KF604) and THF was used as the eluent.

3. RESULTS AND DISCUSSION

3.1 Properties of lignocresol and its derivatives

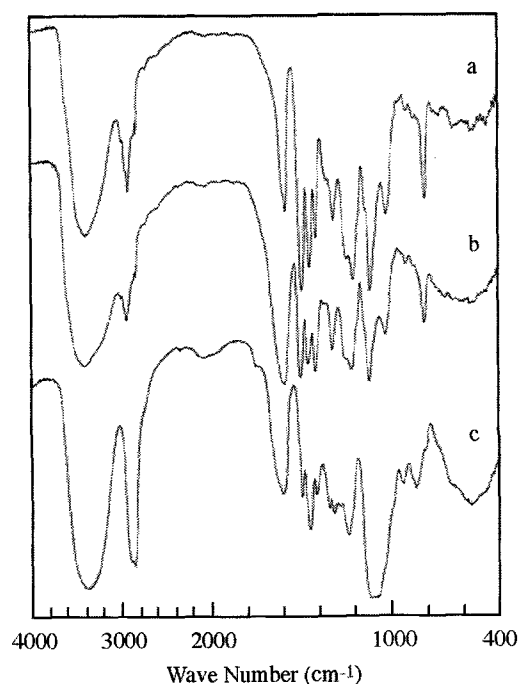
Each characteristic was slight difference among the species (Table I). However, as for the main properties, original lignocresols had large amounts of hydroxyl groups, especially phenolic hydroxyl groups in the molecule, because of high frequency of phenol grafting

Table I Properties of lignocresols.

Ligno-cellulose	Ligno-cresol	\bar{M}_w	Hydroxyl groups (mol/C ₉)		Grafted cresol (mol/C ₉)
			Aliphatic	Phenolic	
Beech	Original	3810	0.88	1.41	} 0.90
	AT der.*	1390	0.82	1.47	
	AT der.**	1150	0.80	1.47	
Rice straw	Original	4590	0.43	1.10	0.52
Rice husk	Original	8300	0.73	1.12	0.52
Kenaf	Original	8000	0.89	1.20	0.89
Bamboo	Original	8810	0.70	1.28	0.71

* Alkaline treatment at 140 °C

** Alkaline treatment at 170 °C



a: Lignocresol (Beech)
b: CM-lignocresol (Beech)
c: Cross-linked CM-lignocresol (Beech)

[Cross-linkage condition]
Sample 100 mg, 0.5 N NaOH 0.5 ml, Ethylene glycol diglycidyl ether 0.4 ml, 50 °C, 175 min

Fig. 1 IR spectra of lignocresols and their cross-linked derivatives.

to C1-position of phenylpropane units in native lignin during the phase separation system [5]. Using these functionalities, lignocresols were chemically modified. By the alkaline treatment, the hydroxyl groups of which cresols grafted to lignocresol attacked adjacent C2-carbon, leading to the cleavage of C2-O-aryl ether linkages [6]. The resultant AT-lignocresol derivatives had lower molecular weights than the original (Table I). Moreover, the hydroxyl groups in lignocresol were substituted with carboxymethyl ether groups. CM-lignocresols have high water solubility and were extensively dissolved in aqueous solutions with pH of 1-14. The carboxymethyl groups in them were recognized by $^1\text{H-NMR}$ and IR spectrum. Signals at δ 4.6 in the NMR spectra of CM-lignocresols, which were absent in the spectra of the originals, were due to the methylene protons of the $-\text{OCH}_2\text{COOH}$ groups. Bands around 1600-1710 cm^{-1} and 1425 cm^{-1} in the IR spectra of them were more intensively increased in comparison with those of the original, which were due to the overlap of absorptions for introduced carboxyl groups with those for aromatic nuclei contained in the originals (Fig. 1).

3.2 Cross-linkage reaction of lignophenols

The aliphatic, phenolic and carboxylic hydroxyl groups of lignocresol and CM derivative reacted with the epoxy groups of cross-linkage reagent to form the network structure through the resulting ether and ester bonds. The intensive increase of bands around 1000-1200 cm^{-1} that were due to absorptions for aliphatic ether and bands around 2850-2930 cm^{-1} for methylene in

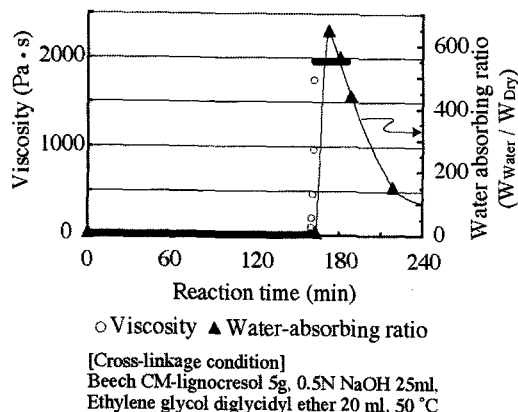


Fig. 2 Viscosity of cross-linkage reaction system and water-absorbing ratio of cross-linked lignophenols.

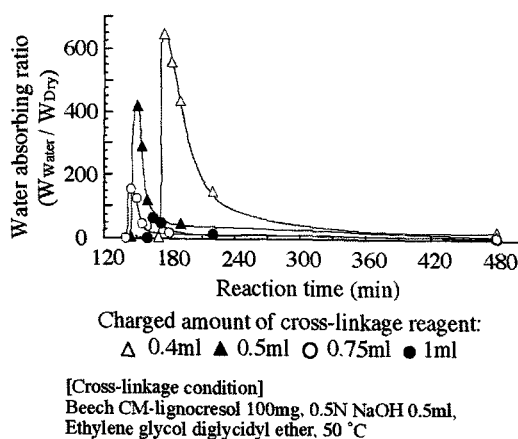


Fig. 3 Effect of charged amount of cross-linkage reagent on reaction time and water-absorbing ability.

the IR spectra suggested presence of cross-linkage reagent combined in the network structure (Fig. 1). When the network structure gradually grown just after starting the reaction began to hold water in the reaction system, in the moment the viscosity of the system dramatically increased and the reaction mixture were completely gelled (Fig. 2). At that time, the ability for absorbing water of the resultant cross-linked lignocresol was a maximum, after which it rapidly decreased with the reaction time because of higher density of the cross-linkage in the network molecule. The obtained cross-linked lignocresols until the point were not hydrogels but water-soluble polymers. The optimum reaction time for getting the hydrogel with a maximum water-absorbing ability was different in the reaction conditions. The reaction rates increased, but the maximum water-absorbing abilities of hydrogels decreased with increasing the charged amounts of cross-linked reagent (Fig. 3) and sodium hydroxide (Table II), because the accelerated reaction formed higher densities of cross-linkages. The hydrogels were readily gained at the temperature from 20 °C to 60 °C (Table III). The cross-linkage reactions took place at under 20 °C, but extremely slowed down. The increase of temperature were accelerated the gelation of cross-linked lignocresols. But under the condition of over 60 °C, the

Table II Effect of charged amount of sodium hydroxide on reaction time and water-absorbing ability.

Concentration of NaOH (N)	Reaction time (min)	Max. water-absorbing ratio ($W_{\text{Water}} / W_{\text{Dry}}$)
0.5	175	643
1	103	580
2	60	512
3	45	32

[Cross-linkage condition]
Beech CM-lignocresol 100 mg, NaOH 0.5 ml,
Ethylene glycol diglycidyl ether 0.4 ml, 50 °C

Table III Effect of temperature on reaction time and water-absorbing ability.

Temperature (°C)	Reaction time (min)	Max. water-absorbing ratio ($W_{\text{Water}} / W_{\text{Dry}}$)
20	865	417
40	195	643
50	103	580
60	80	512
70*	150	1277
80**	15	195

[Cross-linkage condition]
Beech CM-lignocresol 100 mg, 1N NaOH 0.5 ml
(*: 0.25N NaOH 0.5ml, **: 2N NaOH 1ml),
Ethylene glycol diglycidyl ether 0.4 ml (*: 0.5ml,
**: 1ml)

cross-linkage reaction competed with the degradation reaction that was the same reaction that lignocresol was alkaline-treated, so that the other condition in addition to the temperature also had to be established empirically and severely.

3.3 Water-absorbing ability of cross-linked lignophenol

The water-absorbing ability of cross-linked lignophenol gel from CM-lignocresol was higher in comparison with from which the original (Table IV). The reason why is as follow; The CM-lignocresol, which had many hydrophilic carboxymethyl groups that the original do not have, is water-soluble, and the ester types of cross-linkages formed between the carboxyl groups and epoxy groups of cross-linkage reagent and the partially remaining carboxymethyl groups in its gel that had not be used for cross-linkage have more important water-absorbing roles than the hydroxyl groups and the ether types of linkages formed between the hydroxyl groups and epoxy groups. The cross-linked products from AT-lignocresol and its CM-derivative that had lower molecule weights did not have hydrogel properties but water solubility (Table IV), indicating that these network structures did not extend till which had hydrogel property and the linkage with water-soluble reagent made them be water-soluble. Further, the cross-linkage types between AT-derivative molecules were expected intramolecular linkages rather than intermolecular linkages held a dominant position because the number of reactive site with epoxy groups,

Table IV Effect of modification for lignophenol on water-absorbing ability.

Modified lignocresol	Reaction time	Max. water-absorbing ratio (W _{Water} / W _{Dry})
Beech original lignocresol		
Original	60 min	27
Carboxymethylated	50 min	82
Beech alkaline-treated lignocresol at 140 °C		
Original	60 hr	Water-soluble
Carboxymethylated	60 hr	Water-soluble
Beech alkaline-treated lignocresol at 170 °C		
Original	60 hr	Water-soluble
Carboxymethylated	60 hr	Water-soluble

[Cross-linkage condition]
Sample 100 mg, 2 N NaOH 1 ml, Ethylene glycol diglycidyl ether 0.4 ml, 50 °C

Table V Effect of lignocellulosics species on water-absorbing ability.

Lignocellulosics	Max. water-absorbing ratio (W _{Water} / W _{Dry})
Beech	580
Rice straw	332
Rice husk	415
Kenaf	200
Bamboo	304

[Cross-linkage condition]
Beech CM-lignocresol 100 mg, Ethylene glycol diglycidyl ether 0.4 ml, 0.5 N NaOH 0.5 ml, 50 °C

Table VI Effect of length of alkylene chain of cross-linkage reagent on water-absorbing ability.

Cross-linkage reagent	Length of alkylene chain	Max. water-absorbing ratio (W _{Water} / W _{Dry})
Polyethylene glycol diglycidyl ether	n = 1	128
	n = 2	115
	n = 4	402
	n = 9	449
	n = 13	631

[Cross-linkage condition]
Beech CM-lignocresol 100 mg, Polyethylene glycol diglycidyl ether 0.4 ml, 2 N NaOH 0.5 ml, 50 °C

which one molecule of low molecular AT derivative has is little. In other words, the holes formed by intramolecular linkage between a lignophenol molecule and a cross-linkage reagent function importantly for the water-absorbing ability of cross-linked lignophenol gel.

The cross-linked lignophenols from any lignocellulosics could have hydrogel properties (Table V); nevertheless the water-absorbing abilities differed respectively on account of difference of native lignin structure remaining intact within lignophenol.

The cross-linked reagents could be used two types of water-soluble compounds, polyethylene (PEG-GE) and polypropylene glycol diglycidyl ether (PPG-GE), which were classified by the length of alkylene chain. The lignophenols cross-kinked with PEG-GEs and PPG-GEs

that had severally polymerization degree until 13 and 3 had hydrogel properties. The hydrogels with PPG-GEs under the same reaction condition as PEG-GEs were hardly obtained good yields (a few % of lignophenols), because the reactivity of PPG-GEs had lower reactivity and more hydrophilic property than PEG-GEs. The water-absorbing abilities for hydrogels of CM-lignocresol cross-linked with PPG-GEs increased with extending the length of ethylene chain in them (Table VI). This is due to what the holes formed intramolecular linkage in the gels were enlarged by the extension of chain length in used cross-linkage reagent, as a result water-absorbing capacities of hydrogels increased.

4. CONCLUSION

The cross-linkage of lignophenols derived through the phase-separation system and their modified derivatives were carried out with polyalkylene glycol diglycidyl ether. The resultant lignophenol-based network polymer had the properties of the hydrogel that absorbed and kept a good deal of water, in spite of what the original lignophenol used for cross-linkage had higher phenolic structure than the native lignin and usually the cross-linked aromatic polymers have hydrophobic and waterproof property. The lignophenol-based hydrogel could be prepared from any lignophenols on the proper condition, independent of lignocellulosic species as woods and herbs. The water-absorbing abilities of hydrogels were some tens times as much as their dried weights. And especially the hydrogel from carboxymethylated lignophenol that had hydrophilic property and water-solubility exhibited the excellent abilities for absorbing water, the absorbed amounts were from some hundreds to approximately thousand times as much as their dried weights. The intramolecular type of the cross-linkages existing in the lignophenol-based network polymer played more important part for the water-absorbing ability than the intermolecular cross-linkages. The absorbed water were hold by the holes formed between mother structures of lignophenol and intramolecular linkage

These easy cross-linkage technique of lignophenols and the unique features of the hydrogels would provide a new field for utilization of lignin and be used in the various fields such as an industry, an agriculture, an environment and medical care, etc.

5. REFERENCE

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