

Synthesis and properties of resol-type phenol-formaldehyde resins prepared from H₂SO₄- and HCl-catalyzed phenol-liquefied *Cryptomeria japonica* wood

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Abstract

Wood of *Cryptomeria japonica* (Japanese cedar) was liquefied in phenol with H₂SO₄ or HCl as catalysts and used as raw materials to prepare phenol-formaldehyde (PF) resins. The curing behavior and adhesion properties of resins prepared were investigated. Wood liquefied with H₂SO₄ as a catalyst had better liquefaction effect than that with HCl; however, the reaction of resin synthesis was hard to control due to its quickly increasing viscosity. Differential scanning calorimetry analysis shows that PF resins prepared from HCl-catalyzed liquefied wood had higher reactivity than those of H₂SO₄-catalyzed wood. These PF resins were employed for manufacturing three-layer plywood. The wet bonding strength of plywood prepared with resins from HCl-catalyzed liquefied wood exceeded 0.7 MPa and fulfilled the requirement of the CNS 1349 standard.

Keywords: *Cryptomeria japonica*; curing behavior; differential scanning calorimetry (DSC); phenol-formaldehyde resins; phenol-liquefied wood; plywood.

Introduction

The cell wall of plants – containing the most abundant renewable resources on earth – are principally composed of the macromolecules cellulose, hemicelluloses, and lignin which form a 3D network with a unique supramolecular architecture (Salmén and Burgert 2009; Stevanic and Salmén 2009). Isolation and chemical utilization of the individual cell wall components is not a trivial matter; solubilization (liquefaction) is helpful in this context. In the past years, liquefaction in ionic liquids is an innovative approach under development (Xie and Shi 2006; Fasching et al. 2008; Nakamura et al. 2010), but for a long time, pyrolytic liquefaction of wood and bark (Amen-Chen et al. 2002a,b,c) and lique-

faction by means of phenols are in discussion (e.g., Lin et al. 2001a,b; Lee and Wang 2005; Asano et al. 2007; Lee et al. 2011). Liquefaction by means of acidic catalyzed phenolation has the unique advantage that liquefied products can be used without separation of its components for preparing phenol-formaldehyde (PF) resins. In the course of liquefaction, the degraded components form hydroxyl benzyl derivatives still maintaining the phenolic functional groups and thus they can react with formaldehyde just like monomeric phenols (Zhang et al. 2006). The acidic catalyzed phenol-liquefied wood can directly react with formaldehyde and gives rise to novolak-type PF resins (Lin et al. 1995a,b; Alma et al. 1996; Alma and Kelley 2000; Lee et al. 2000, 2002, 2009; Lee and Chen 2008; Pan et al. 2008, 2009). The preparation of resol-type PF resins is more complicated because these require alkaline conditions. Santana and colleagues (Santana et al. 1995; Santana and Baumann 1996) liquefied bark and tannin in phenol with H₂SO₄ as a catalyst. It was found that the liquefied products could be useful for preparing resol-type PF resins after NaOH was added. Lee (2003) liquefied corn bran in phenol with H₂SO₄ as a catalyst and the final product was methylolated by condensation with formaldehyde under alkaline condition. However, a milder condensation condition was required compared with that for preparing the conventional resol resin to lower the viscosity. These resol-type PF resins were suitable for manufacturing of plywood and particleboard (Lee and Liu 2003; Alma and Baştürk 2006; Hassan et al. 2009).

More research is needed to better understand the influence of the catalyst on the liquefaction and on the synthesis conditions of resins, and the properties of resin prepared. In the present paper, the hypothesis was that other acids than H₂SO₄ could lead to raw materials better suitable to PF resins. Hence, the H₂SO₄- and HCl-catalyzed liquefied wood was taken as a basis for preparing resol-type PF resins. The aim was to scrutinize the reactivity during the period of resin synthesizing and to ascertain the properties of resins prepared as well as the bonding strength of plywood manufactured with the resins.

Materials and methods

Liquefaction of Japanese cedar

Heartwood (HW) and sapwood (SW) of Japanese cedar (*Cryptomeria japonica* D. Don) with dimensions passing 20-mesh were liquefied in the presence of phenol with H₂SO₄ or HCl as catalyst. The holocellulose, pentosan, lignin, and alcohol-benzene extract were 63.9%, 7.8%, 32.5%, and 9.7%, respectively, for HW, and

Table 1 Properties of liquefied Japanese cedar heartwood (HW) and sapwood (SW).

Code of liquefied wood	Catalyst		Residue content (%)	Viscosity (cps)	Non-volatile content (%)	Average molecular weight		
	Acid	Dosage (%)				Mn	Mw	Dispersity Mw/Mn
H ₂ SO ₄ -HW	H ₂ SO ₄	5	1.0	36 100	60.6	812	2790	3.4
H ₂ SO ₄ -SW	H ₂ SO ₄	5	0.6	88 200	61.3	809	2156	2.7
HCl-HW	HCl	10	5.3	39 900	46.2	652	2307	3.5
HCl-SW	HCl	10	4.9	48 500	48.7	792	1810	2.3

67.7%, 8.5%, 33.0%, and 4.3% for SW, respectively. The wood powders were oven-dried at 105°C for 12 h prior to liquefaction. The weight ratio of phenol to wood was 3:1, and the dosage of H₂SO₄ and HCl added was 5% and 10% (based on the weight of phenol), respectively. The liquefaction was conducted in a 1000-ml four-neck round-bottom glass reactor equipped with stirrer, thermometer, and reflux condenser under a constant stirring for 60 min at 110°C and 130°C, as described previously by Lee and Chen (2008).

Properties of liquefied woods

The residue was determined by diluting the liquefied wood with methanol, followed by filtering through a G3 glass filter. The residue was dried in an oven at 103 ± 2°C and the yield was then calculated. The viscosity was measured in a Brookfield viscosimeter at 25°C. The non-volatile matter content – consisting of wood components, and phenol combined with wood components – was determined by evaporation of the residues of 2-g liquefied wood in a rotary vacuum evaporator (heating at 180°C to constant weight). The molecular weight was detected by gel permeation chromatography (GPC; Hitachi L-6200A) equipped with a Hitachi GL R-430 column and a UV detector with the sample concentration of 0.1%; the injection volume was 20 µl; tetrahydrofuran (THF) was used as eluant with flowing rate of 1 ml min⁻¹. The liquefied wood for GPC analysis was acetylated with acetic anhydride/pyridine (1:1; v/v) followed by vacuum evaporation to remove free phenol, unreacted acetic anhydride, and pyridine.

Synthesis of PF resol-resins based on liquefied wood

The liquefied woods – as a basis for PF resins – were assumed for calculations to have a molecular weight as phenol (94 g mol⁻¹). The molar ratio of formaldehyde to liquefied wood (F/P) was set at 1.8:1 and 2.0:1, whereas the molar ratio of NaOH to liquefied wood (NaOH/P) was set at 0.6:1. The liquefied wood, formalin, and one-third of the NaOH_(aq) were put into the round-bottom reactor and heated to 85°C within 30 min and the temperature was maintained for 10 min while the remaining two-thirds of NaOH_(aq) was gradually dropped into the reaction batch. Then, the reaction proceeded at 85°C until the viscosity of the reactant exceeded 200 cps. If the viscosity did not reach 200 cps after 90 min, the reaction was nevertheless stopped. The normal PF resins for comparison were prepared under the same conditions, except that the molar ratio of NaOH/P was set at 0.4:1.

Properties of synthesized PF resins

The properties of synthesized PF resins were measured according to the CNS 12001 standard (non-volatile content: by drying at 135°C for 60 min; viscosity: Brookfield viscosimeter at 25°C; pH at 25°C). The gel time was measured with 10 g of resin in a glass

tube (heated to 135°C in oil bath) equipped with a thin wire. The time at which the tube could be lifted up by pulling the wire was identified as the gel time. The unreacted formaldehyde was measured using the hydroxylamine hydrochloride titration method. For this test, 10 g of resin was diluted with 150 ml of distilled water, followed by adjusting the pH to 4. Then, 50 ml of hydroxylamine hydrochloride with pH of 4.0 was added and reacted for approximately 5 min. Finally, the sample was titrated with a 0.5-N NaOH_(aq) until the pH value reached 4.0.

DSC thermosetting analysis of PF resins

The thermosetting properties of PF resins were determined by differential scanning calorimetry (DSC; Perkin-Elmer DSC-7) with a large-volume O-ring sealed stainless steel sample pan. The sample was heated from 30°C to 275°C at a heating rate of 10°C min⁻¹ under nitrogen environment.

Bonding strength of PF resins

Lauan veneer was bonded to three-layer plywood. To avoid an over-penetration due to the low viscosity, the resin was mixed with 15% bark powder to adjust the viscosity to 1000–2000 cps prior to glue application. The amount of glue for a single glue line was 200 g m⁻². The plywood was made by hot pressing at 135°C for 3.5 min under a pressure of 10 kg cm⁻². The tensile shear bonding strength was done under dry and wet conditions, according to the CNS 1349 standard by means of a universal strength testing machine (Shimadzu UEH-10) at a loading speed of 1 mm min⁻¹. For the wet bonding strength, specimens were immersed in water under two conditions prior to testing: (i) immersion in 60°C water for 3 h and (ii) immersion in boiling water for 4 h, followed by drying in an oven at 60°C for 20 h, and finally immersion in boiling water again for 4 h. The wood failure of testing samples was estimated by the naked eye to the nearest 5% of shear area. Eight specimens were tested for each test set.

Results and discussion

Properties of liquefied Japanese cedar

During liquefaction of wood, both the carbohydrates and lignin undergo degradation by hydrolysis and other reactions leading to monomeric and oligomeric compounds, which react with phenol, and the formed derivatives are then dissolved in the free phenol (Lin et al. 2001a,b, 2004; Zhang et al. 2006). Table 1 shows the properties of liquefied woods. The contents of residue and non-volatiles serve as indicators for the efficiency of liquefaction. Woods liquefied with H₂SO₄ as a catalyst (H₂SO₄-HW and -SW) has less residue

and more non-volatiles than those with HCl as a catalyst (HCl-HW and -SW). Accordingly, H_2SO_4 has a better efficiency in the conversion than HCl, i.e., it promotes better the decomposition of wood components and their derivatization with phenol.

The wood content was 24.1% (with H_2SO_4) and 23.3% (with HCl) at the initial stage of liquefaction. The non-volatile content of liquefied woods was higher than the initial wood content, indicating that the phenol reacted with wood, in accordance with the literature (Alma et al. 1995a,b, 1996). It is also known that carbohydrates undergo transglycolation to form furfural or hydroxymethyl furfural which reacts with phenolic compounds (Alma and Baştürk 2001). Lignin is cleaved to a variety of phenolic compounds, which react with formaldehyde formed and undergo further condensation reactions (Adler 1977; Alma and Acemioglu 2004). The higher non-volatile content of reaction with H_2SO_4 is due to its stronger acidic character which leads to more active sites and to the formation of combined phenols. HW has more residue content, less non-volatile content, and higher molecular weights (Mn between 652 and 812, Mw between 1810 and 2790) than SW.

Properties of PF resins prepared

As well known, at the first step, addition reaction takes place between formaldehyde and phenol to form methylol phenol, followed by a condensation reaction of methylol phenol with phenol and/or methylol phenol to form oligomers at the second step. The further condensation reaction will take place at a higher temperature to form a highly branched cured resin. Figure 1 shows the variation in viscosity of PF resins prepared under various conditions during synthesis. PF-1.8 and PF-2.0, the normal PF resins as reference, show moderate viscosity increments ending up with 77 cps and 50 cps viscosities at 90 min, respectively. Expectedly, the viscosity increased rapidly for resins prepared with liquefied woods because of their higher average molecular weights.

Resins prepared with H_2SO_4 -HW or -SW show higher viscosity increments than those with HCl-catalyzed liquefied wood. For instance, H_2SO_4 -HW-1.8 had the viscosity of 319 cps at the reaction time of 45 min, whereas HCl-HW-1.8 had the viscosity of 217 cps at the reaction time of 75 min. These results are obvious considering the non-volatile contents and molecular weight data discussed above. Resins prepared with the F/P molar ratio of 2.0:1 have higher viscosities than those with P/F ratios of 1.8:1. In addition, these results are self-evident because the presence of more formaldehyde as cross-linking promotes molecular growth.

Table 2 shows the properties of synthesized PF resins. The non-volatile content of resins was measured via oven-dried at 135°C for 60 min. During this heating period, resins undergo condensation reaction to form cured resins accompanied with water evaporation and induced condensation reaction. The resins based on liquefied wood have less non-volatile contents than the normal PF resins, as the former were prepared with a NaOH/P ratio of 0.6:1, whereas this ratio was 0.4:1 for normal PF resins. The $NaOH_{(aq)}$ was submitted in 40% solution; therefore, more water was introduced

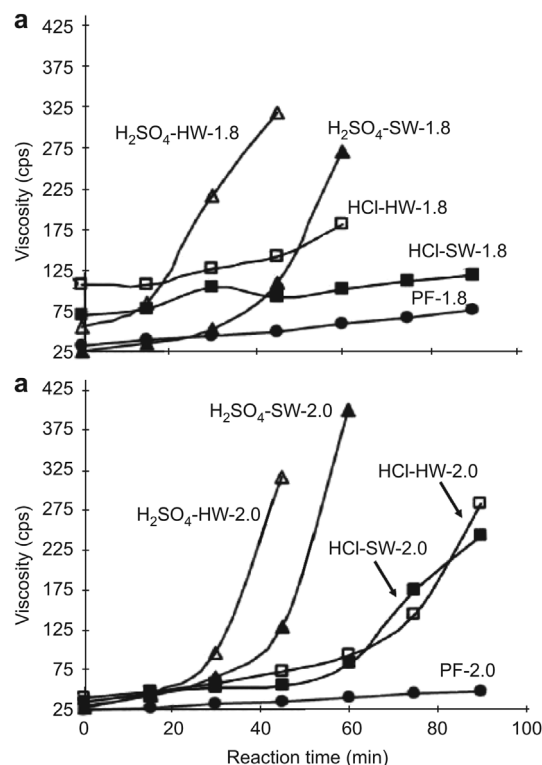


Figure 1 Variation in viscosity of PF resins prepared from liquefied wood during the period of synthesis. (a) Prepared with the F/P molar ratio of 1.8:1; (b) Prepared with the F/P molar ratio of 2.0:1.

into the system in the case of wood-based experiments resulting in less non-volatile content. In addition, resins synthesized with the F/P molar ratio of 2.0:1 have less non-volatile content than those with the F/P molar ratio of 1.8:1. The explanation is similar to that given above: formalin was supplied as a 37% aqueous solution, thus the higher the F/P molar ratio the more water is introduced into the reaction system.

The non-reacted formaldehyde in resins is predominantly influenced by the type of liquefied wood reacted with. PF resins prepared with HCl-HW or -SW have almost no non-reacted formaldehyde. By contrast, PF resins prepared from H_2SO_4 -HW or -SW still contain some formaldehyde, regardless of the rapid viscosity increment of these resins. Accordingly, the molecular propagation of these resins was less uniform than those prepared with HCl-catalyzed liquefied wood.

The gel time of PF resins based on liquefied wood is shorter than that of the PF resins reference at 135°C. The molar ratio of F/P plays a predominant factor for influencing the gel property of wood-based PF resins: F/P molar ratios of 2.0:1 have a shorter gel time than those of 1.8:1.

Thermosetting properties of PF resins

The addition and condensation reactions taking place during resin formation are exothermic, whereas the former takes place at a lower temperature than the latter. Figure 2 shows

Table 2 Synthesis conditions and properties of PF resins prepared from phenolated Japanese cedar.

Code of resins	Synthesis conditions		Properties of PF resins				
	F/P (molar ratio)	Reaction time (min)	Non-volatile (%)	pH	Viscosity (cps)	Gel time (min)	Non-reacted F (%)
H ₂ SO ₄ -HW-1.8	1.8:1	45	45.5	11.6	319	9.2	2.1
H ₂ SO ₄ -SW-1.8	1.8:1	60	43.5	10.9	563	10.6	3.6
HCl-HW-1.8	1.8:1	75	45.2	11.4	217	13.1	0.1
HCl-SW-1.8	1.8:1	90	44.8	11.5	93	13.0	0.0
PF-1.8 ^a	1.8:1	90	51.9	11.5	77	14.6	0.0
H ₂ SO ₄ -HW-2.0	2.0:1	60	41.5	10.8	768	10.3	4.9
H ₂ SO ₄ -SW-2.0	2.0:1	60	41.7	10.8	445	6.8	5.0
HCl-HW-2.0	2.0:1	90	42.7	10.7	378	9.8	0.1
HCl-SW-2.0	2.0:1	90	42.6	10.6	243	9.2	0.1
PF-2.0 ^a	2.0:1	90	46.7	11.6	50	13.7	0.1

^aReference: a traditional PF resin.

For explanation of abbreviations, see Table 1.

DSC curves of various PF resins prepared. As seen in Figure 2a, PF resins prepared from HCl-HW or -SW have heat flow curves similar to those of normal PF resins. They exhibit only one exothermic peak during thermosetting. However, as seen in Figure 2b, PF resins prepared from H₂SO₄-HW or -SW have different heat flow curves. Herein, H₂SO₄-HW-2.0 and H₂SO₄-SW-2.0 show exothermic peaks at 100°C and 94°C, respectively. In addition, H₂SO₄-HW-1.8 has a clear exothermic peak at 116°C, and another less distinct exothermic peak at 150°C. From this observation, it follows that their addition reactions were not entirely finished during res-

in synthesis. The residual formaldehyde reacts during DSC heating in the lower temperature range, followed by the condensation reaction of curing at higher temperatures.

The onset temperature, peak temperature, and reaction heat of thermosetting for various types of PF resins are listed in Table 3. The PF-1.8 and PF-2.0 have reaction heats of 190 W g⁻¹ and 212 W g⁻¹, respectively, which are much higher than those of liquefied wood-based PF resins, indicating a minor crosslinking reaction activity in the latter case. PF resins prepared from HCl-HW and -SW have onset temperatures lower than those with H₂SO₄-HW and -SW. Probably, the H₂SO₄-catalyzed liquefied wood dispose of more condensed phenols, which leads to lower reactivity in the course of curing.

Bonding strength of plywood

Table 4 shows the shear bonding strength of plywood made with Lauan veneers. According to the CNS 1349 standard,

Table 3 DSC thermosetting parameters of PF resins prepared from phenolated Japanese cedar.

Code of resins	Onset temperature (°C)	Peak temperature (°C)	Reaction heat (W g ⁻¹)
HCl-HW-1.8	112	144	103
HCl-SW-1.8	112	146	99
HCl-HW-2.0	117	135	78
HCl-SW-2.0	102	138	90
H ₂ SO ₄ -HW-1.8	132	144	16
	(111) ^b	(116) ^b	(31) ^b
H ₂ SO ₄ -SW-1.8	136	141	94
H ₂ SO ₄ -HW-2.0	136	142	72
H ₂ SO ₄ -SW-2.0	128	133	25
PF-1.8 ^a	117	145	191
PF-2.0 ^a	121	147	212

^aReference: traditional PF resin.

^bThe exothermic peak appeared at lower temperature.

For explanation of abbreviations, see Table 1.

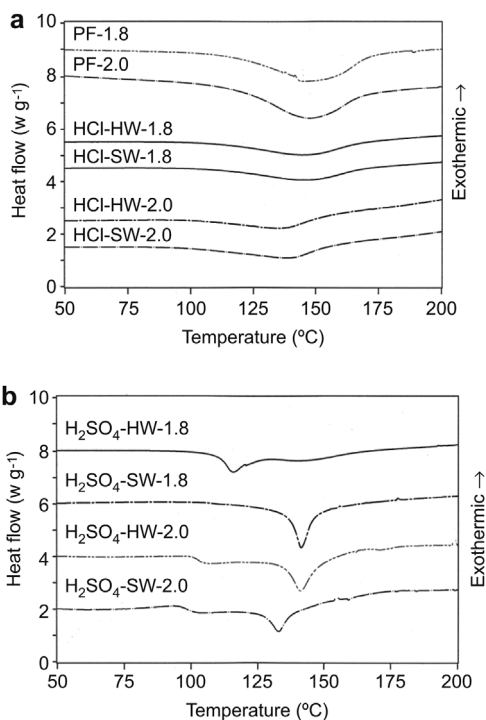
**Figure 2** DSC thermograms of PF resins prepared from liquefied wood. (a) Wood liquefied with HCl as the catalyst; (b) wood liquefied with H₂SO₄ as the catalyst.

Table 4 Bonding strength of plywood made with various PF resins prepared from phenolated Japanese cedar.

Code of resins	Shear bonding strength (MPa) ^a					
	Dry		30° water immersed		Boiling-dry-boiling cycling treated	
HCl-HW-1.8	1.3±0.3	(3)	0.9±0.1	(4)	0.7±0.1	(0)
HCl-SW-1.8	1.5±0.2	(28)	1.0±0.1	(0)	0.8±0.1	(0)
HCl-HW-2.0	1.4±0.2	(20)	1.0±0.1	(3)	0.8±0.2	(0)
HCl-SW-2.0	1.5±0.2	(2)	1.0±0.1	(0)	0.8±0.1	(0)
H ₂ SO ₄ -HW-1.8	1.2±0.2	(23)	0.7±0.1	(4)	0.6±0.1	(0)
H ₂ SO ₄ -SW-1.8	1.0±0.4	(1)	0.5±0.1	(0)	0.3±0.1	(0)
H ₂ SO ₄ -HW-2.0	0.8±0.2	(0)	0.7±0.1	(1)	0.5±0.1	(0)
H ₂ SO ₄ -SW-2.0	1.0±0.2	(1)	0.6±0.2	(2)	0.5±0.1	(0)
PF-1.8	1.5±0.6	(46)	1.6±0.6	(63)	1.0±0.4	(55)
PF-2.0	1.2±0.3	(93)	1.3±0.1	(55)	1.1±0.2	(70)

^aWood failure percent is in parentheses.

For explanation of abbreviations, see Table 1.

the bonding strength of Luan plywood should exceed 0.7 MPa. As demonstrated, plywood made with PF resins made of HCl-catalyzed liquefied wood has higher dry and wet bonding strength than the other experimental set. After repeated boiling-drying-boiling treatment, the former still meets the bonding strength requirement of the CNS standard. Resins made of H₂SO₄-HW and -SW have lower wet bonding strength. These results are not unexpected either, based on their lower thermosetting reactivities as described in the DSC analysis. In addition, comparing the impact of the wood species and the molar ratio of F/P for PF resins prepared from HCl-HW and -SW, the results show that with SW as raw material and synthesis with a molar F/P ratio of 2.0:1 a better wet bonding strength could be achieved.

Conclusions

Wood of Japanese cedar liquefied in phenol with H₂SO₄ or HCl as catalysts could be employed as raw materials for preparing PF resins. In H₂SO₄-catalyzed experiments, the viscosity of synthesizing resins increased rapidly and the reaction was difficult to control. In the case of HCl-catalyzed experiments, the resins had an adequate viscosity with higher thermal reactivity. The resins fulfilled wet bonding strength requirements of CNS 1349 standard for plywood.

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