ELSEVIER

Novolak PF resins prepared from phenol liquefied *Cryptomeria japonica* and used in manufacturing moldings

Wen-Jau Lee [*], Yi-Chun Chen

Department of Forestry, National Chung-Hsing University, 250, Kuo Kuang Road, Taichung 402, Taiwan

Abstract

The wood of Japanese cedar (*Cryptomeria japonica*) was liquefied in phenol with H_2SO_4 and HCl as catalysts. The liquefied wood was reacted with formalin to prepare the novolak PF resin. The results showed that the reaction of liquefied Japanese cedar with formalin was an exothermic reaction, and formed a solid-like resin without extra heating. Two novolak PF resins were prepared from the liquefied wood which were identified as SF and CF that using the liquefied wood with H_2SO_4 and HCl as catalyst respectively. The novolak PF powder displayed thermo-melting characteristic. The resins of SF and CF had weight average molecular weight of 3638 and 3941 respectively and melting temperature of 149.4 °C and 127.5 °C respectively. Both of the novolak resins could be used to make moldings with good performance by mixing the novolak resin with wood powder, hardener and zinc stearate at the weight ratio of 60:30:10:1 and hot-pressed under 200 °C for 10 min.
© 2007 Elsevier Ltd. All rights reserved.

Keywords: *Cryptomeria japonica*; Liquefied wood; Moldings; Novolak PF resin

1. Introduction

Solvent liquefaction is one of the effective methods to convert the wood materials from solid to liquid. Liquefaction wood materials in phenol or polyhydric alcohol with inorganic acid as a catalyst were one of the major methods nowadays. The acid catalyst can degrade the wood components to small ingredients. And then, these ingredients react with phenol or polyhydric alcohol to form a derivative and dissolve in the liquefaction solvent. The liquefied products can be used as raw materials for the synthesis of resins.

Zhang et al. (2006) researched the liquefaction mechanism of cellulose in phenol. They indicated the pyranose that decomposed from cellulose could combine with phenol to form a hydroxyl benzyl form derivative. It retained the characteristic of phenolic functional group. Lin et al. (2004) examined the mechanism of cellulose in the presence of phenol under acid catalysis too. Acemioglu and Alma (2002) examined the kinetic of wood phenolation in the presence of HCl as a catalyst. Lee and Ohkata (2003) indicated wood could be rapidly liquefied at the supercritical temperature of phenol. Under this condition, over 90% of wood was liquefied for 0.5 min, and the properties of the products were similar to those obtained by conventional liquefaction methods. Honglu and Tiejun (2006) used the imidazole-based ionic liquid as wood liquefaction agent, they found using this method a rapid and complete liquefaction could be acquired at 120 °C for 25 min without acid catalyst. Lee et al. (2002a,b) used the phenolated wood to prepare the resol type PF resin, and liquefied wastepaper to prepare the novolak type phenolic PF. Kishi et al. (2006) used resorcinol to replace phenol to liquefy wood and indicated the products could react with epichlorohydrin to prepare the epoxy resin. In our previous study (Lee et al., 2004, 2006; Lee and Liu, 2001, 2003), resol type PF resins had prepared from the liquefied wood and bark and those were used in the manufacturing of plywood and particleboard.

[*] Corresponding author. Tel.: +886 4 22840345x126; fax: +886 4 22873628.
E-mail address: wjlee@dragon.nchu.edu.tw (W.-J. Lee).

Novolak PF resins are synthesized from phenol with an insufficient amount of formaldehyde under acidic conditions to form a linear prepolymer. They are a thermoplastic resin without hydroxymethyl group in the molecular structure. Cross-linking agent such as hexamine is needed for them to form a three-dimensional networks structure under heating. Alma et al. (1996) investigated the flowability of phenolated wood and using it directly as a novolak resin. But it needed the extra process to remove the un-reacted phenol. Furthermore, the temperature needed to flow the dry liquefied wood was too high to practical use. However, the acid catalyzed phenolated wood has high acidity and possesses the constituents which can react with formaldehyde. For example, the free phenols those are un-reacted and rich in the liquefied wood and the derivatives those formed by the reaction of wood component with phenol, both of them can react with formaldehyde. In addition, lignin, one of the major wood components including the hydroxyl–benzyl structure, has the potential to react with formaldehyde.

For all these characteristics, the formalin was added directly to the acidic phenol liquefied *C. japonica* wood to prepare the novolak type PF resin in this study. The properties of the prepared novolak PF resins and the feasibility of using them as raw materials for moldings were also researched.

2. Methods

2.1. Materials

Japanese cedar (*C. japonica*) was air-dried and ground to powder in a hammer mill with a 2 mm diameter screen. The wood powder with a dimension passing 20 meshes was used for liquefaction, and passing 200 meshes were used as filler for moldings. All the wood powder was dehydrated in an oven at 105 °C for 12 h. Chemicals such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), phenol, formalin (37% aq), methanol, acetic anhydride, pyridine, dichloromethane, hexamine ($C_6H_{12}N_4$), zinc stearate and acetone were the reagent grade and were used without further purification. Tetrahydrofuran (THF) was HPLC grade, used as solvent and eluant for the gel permeation chromatography. Potassium bromide (KBr) was used for FT-IR spectrometry.

2.2. Liquefaction of Japanese cedar

To liquefy the wood of Japanese cedar, phenol and acid catalyst were premixed thoroughly in a 1000 mL separable glass flask equipped with a stirrer, thermometer, and reflux condenser. The wood powder was added gradually to the reaction flask after the temperature reached 110 °C. For the liquefaction using H_2SO_4 as a catalyst, the weight ratio of phenol/wood/H_2SO_4 was 2.5/1/0.125 and heating under 130 °C for 60 min to carry out the liquefaction reaction, the liquefied product was identified as S. For the liquefaction using HCl as a catalyst, the weight ratio of phenol/wood/

HCl was 3/1/0.3 heated under 110 °C for 60 min, and the liquefied product was identified as C.

2.3. Characterization of liquefied wood

2.3.1. Residue content

About 5 g of liquefied wood was weighted and diluted with 100 mL of methanol, and then filtered through a G3 glass filter in vacuum. The residue was dried to a constant weight in a heating oven at 103 ± 2 °C. The residue content was calculated by the following equation: $R\,(\%) = W_R/W_O \times 100$. Where W_R is the oven-dry weight of the solid residue, and W_O is the oven-dry weight of the starting wood.

2.3.2. Viscosity

The viscosity of liquefied wood was measured with a Brookfield rotary viscometer at 25 ± 2 °C.

2.3.3. Nonvolatility

About 2 g of liquefied wood was weighted and dried using a rotary vacuum evaporator heating at 180 °C to remove the un-reacted phenol and calculated by the following equation: $S\,(\%) = W_S/W_1 \times 100$. Where W_S is the weight of the nonvolatility, and W_1 is the weight of the sample.

2.3.4. Combined phenol and free phenol

The combined phenol and free phenol were used to show the phenol existing in the liquefied wood that were combined with wood components or free in the system, respectively. Both the combined and free phenol were calculated from the nonvolatile content in the liquefied wood. The combined phenol was calculated by subtracting the content of wood used in the liquefaction system from the nonvolatile content after liquefaction. The free phenol was calculated by subtracting the content of combined phenol from the content of phenol used in the initial liquefaction system.

2.3.5. GPC molecular weight measuring

Liquefied wood was acetylated by acetic anhydride/pyridine (1/1; v/v). The molecular weight and weight distributions of acetylated and unacetylated liquefied woods were determined using a Hitachi L-6200A gel permeation chromatograph (GPC) equipped with the Shodex KF-802 column. The chromatograms were monitored with a UV detector at a wavelength of 280 nm. THF was used as the solvent and eluant. The concentration of testing sample was 0.1%, and filtrated with a 0.45 μm filter film. The flowing rate and injection volume were 1 mL/min and 20 μL, respectively. The monodisperse polystyrenes were used as the standards for calibrating the molecular weight.

2.4. Preparation of novolak PF resin

For preparing novolak PF resin, the molar ratio of free phenol in liquefied wood to formaldehyde was set at 1/0.8.

The calculated amount of liquefied wood and formalin were charged in a beaker with a thermocouple. The total weight of reactant measured was W_1 and no extra acid catalyst was needed. After stirring the reactant without any external heating, the exothermic reaction underwent with heat release. After this, the reactant formed a solid-like resin and the weight measured as W_2. The yield of resin was calculated by $W_2/W_1 \times 100$. The novolak PF glue powder was gained after dehydrating the solid-like resin with heating under 105 °C and grinding to pass a 100 mesh screen. The weight of novolak PF in the measured glue powder was W_3 and the yield was calculated by $W_3/W_1 \times 100$.

2.5. Analysis of the reactivity of liquefied wood with formaldehyde by DSC

The liquefied wood was mixed with formalin as described in the previous section. About 0.5 mg of the mixture was sealed quickly in an aluminum capsule that had a laser hole in the cover and measured by differential scanning calorimetry (Perkin-Elmer DSC-7). Two stages of the detecting program were used for DSC analysis. First, the sample was detected with an isothermal program that kept at 30 °C for 90 min. And then the sample would be scanning with the heating rate of 10 °C/min up to 500 °C. The heat flow variation at these two stages was detected.

2.6. Measuring the properties of nonolak PF glue

The melting point of novolak PF glue powder was observed using the Electrothermal IA9200 melting point apparatus at a heating rate of 10 °C/min. The GPC analysis of the novolak PF resins were the same as described in the previous section. The DSC analysis was used a heat scanning program. Three kinds of sample were tested, including the novolak PF glue powder, glue powder with hexamine and glue powder with wood filler, hexamine and zinc stearate.

2.7. Manufacturing of moldings

For the moldings manufacture, the novolak PF glue powder, Japanese cedar wood powder and hexamine were used as a binder, filler and cross-linking hardener respectively. The zinc stearate was added to advance the flowability. The weight ratio of novolak PF glue powder to wood filler to hardener to zinc stearate was 60:30:10:1. After all the components were mixed completely, the flat moldings with a dimension of $10 \times 10 \times 0.4 \text{ cm}^3$ and density of 1.0 g/cm^3 were made by hot-pressing using a temperature of 200 °C for 10 min under a pressure of 20 kgf/cm^2.

2.8. Measuring the properties of moldings

The produced flat moldings were cut into specimens with dimensions of $2 \times 2 \times 0.4 \text{ cm}^3$ and used for testing density, internal bonding strength and water immersion testing. The internal bonding strength was carried out using the universal strength testing machine (Shimadzu UEH-10) with a load vertical to the surface of the flat molding at a crosshead speed of 2 mm/min. The water immersion testing was carried out by dipping the specimens into water, and measuring the rate of water absorption and thickness swelling after 2 h, 24 h and 36 h. Furthermore, the produced moldings were ground to a powder and dried with a vacuum oven at 60 °C for 24 h. About 0.2 g of the powder was immersed into 20 mL of acetone for 24 h followed by filtrating and calculating the weight retention.

3. Results and discussion

3.1. The properties of liquefied Japanese cedar

Table 1 shows the properties of phenol liquefied Japanese cedar. The liquefied wood of S that used H$_2$SO$_4$ as a catalyst had the unliquefied wood residue lower than C that used HCl as a catalyst. This result indicated Japanese cedar liquefied with H$_2$SO$_4$ as a catalyst had a better liquefaction effect than HCl. But the former had viscosity higher than the latter.

The proportion of wood in the liquefaction system at the initial stage for liquefied wood S and C was 27.6% and 23.3%, respectively. After liquefaction, the nonvolatile content in the liquefied wood was 74.8% for S and 43.3% for C. These higher value of nonvolatility might be caused by some of the phenol would combine with the wood component to form a derivative. The combined phenol and free phenol calculated from the nonvolatile content were 47.2% and 21.8% for liquefied wood S, and were 20.0% and 49.8% for liquefied wood C. It indicated the kind of catalyst used for liquefaction would influence the type of phenol existing in the liquefied wood. The combined phenol was the main type for the liquefied wood using

Table 1
Properties of liquefied Japanese cedar

Code of liquefied wood[a]	Catalyst	Residue (%)		Viscosity (cps)	pH	Nonvolatility (%)	Combined phenol (%)	Free phenol (%)
		Base on liquefied wood	Base on wood					
S	H$_2$SO$_4$	1.4	5.1	99,600	0.28	74.8	47.2	21.8
C	HCl	4.2	18.1	7610	0.15	43.3	20.0	49.8

[a] S: the weight ratio of phenol/wood/H$_2$SO$_4$ used for liquefaction was 2.5/1/0.125. C: the weight ratio of phenol/wood/HCl used for liquefaction was 3/1/0.3.

H_2SO_4 as a catalyst, but it had more free phenol for the liquefied wood that using HCl as a catalyst.

3.2. The reaction characteristic of liquefied Japanese cedar with formaldehyde

Zhang et al. (2006) indicated the cellulose would be degraded to oligosaccharide and glucose in phenol with an acid catalyst under a high temperature. The pyranose ring would decompose further and combine with phenol to form derivatives. The derivatives formed had the hydroxyl benzyl group but not the phenoxyl-form. Because the phenolic functional group that kept in the derivatives had the similar reactivity as phenol. So, the cross-linking and polymerization reaction with formaldehyde could be expected by the active position in the combined phenol. However, in our preliminary experiment, if the full liquefied wood was hypothesized as phenol and used the molecular weight of phenol as a basis to sample the liquefied wood and formalin. The reaction between the liquefied wood and formalin with the molar ratio of formaldehyde to phenol at 0.8/1 was too drastic. This formed insoluble and infusible cured products very quickly. So, the free phenol in liquefied wood was used to calculate the equivalent weight of formaldehyde in this study. As the equivalent weight of liquefied wood and formalin was blended, an exothermic reaction took place without external heating.

Fig. 1 shows the temperature variation of the two kinds of liquefied wood after formalin was blended. The SF and CF indicated the resin prepared from liquefied woods those using H_2SO_4 and HCl as a catalyst, respectively. Comparing these two resins, SF showed a faster exothermic reac-
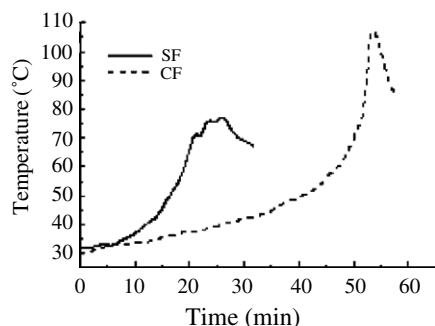
tion than CF. The temperature of SF would rise to 76 °C at 26 min after blending the liquefied wood with formalin. However, such exothermic reaction was slower for CF resin, which had a significant temperature increasing until 45 min after the formalin was added. However, the maximum temperature of CF could reach 106 °C. The faster reaction for SF might contribute to the higher acidity of liquefied wood S. But the higher maximum temperature of CF might be caused by much more formaldehyde being blended with liquefied wood C because it had higher content of free phenol. So, it could undergo more polymerization reaction and much more reaction heat would be released. After achieving the maximum temperature, the exothermic reaction of both resins slowed down and gradually formed a solid-like product.

As shown in Table 2, the yield of resin after synthesis was 96.7% and 88.6% for SF and CF, respectively. However, after drying and grinding, the yield became 85.4% and 67.2% for SF and CF, respectively. The CF resin had lower yield than SF, which might be caused by two reasons. One was the higher temperature achieved for CF than SF, which might cause some of the unreacted formaldehyde lost by evaporation. The other reason was more formalin was added in CF because of its higher free phenol content. This meant that more water would exist in the reaction system which brought with the formalin and produced by the condensation reaction, thus reducing the yield of products. The melting point of SF and CF measured was 149.4 °C and 127.5 °C, respectively.

Fig. 2 shows the DSC thermograms of liquefied wood blended with formalin. In our previous discussion, blending liquefied wood with formalin had an obvious exothermic reaction. But in diagram A, an isothermal analysis with DSC under 30 °C, the appearance of heat release was not obvious except in the initial stage. However, DSC thermal scanning after 90 min of isothermal reaction, as shown in diagram B, no exothermic phenomenon caused by the cross-linking reaction had been found. It indicated the reaction between liquefied wood and formaldehyde had completed under the period of isothermal reaction. However, because the molar ratio of free phenol in liquefied with the formaldehyde used was 1/0.8, it meant the formaldehyde was not enough to form a three-dimensional network cured resin. So, the products were a novolak type resin without hydroxymethyl group and could not undergo an advanced cross-linking reaction. But the heat flow in DSC thermograms displayed the phenomenon of glass

Fig. 1. Temperature variations of liquefied Japanese cedar after mixing with Formalin.

Table 2
Exothermic temperature and yield of resins by the reaction of liquefied Japanese cedar with formalin

Code of resin	Code of liquefied wood	Time to achieve maximum temperature (min)	Maximum temperature (°C)	Yield of resin[a] (%)	Yield of novolak PF glue powder[b] (%)	Melting point (°C)
SF	S	26	76	96.7	85.4	149.4
CF	C	54	106	88.6	67.2	127.5

[a] Weight percent of the resin products measured after the reaction of liquefied wood with formalin.
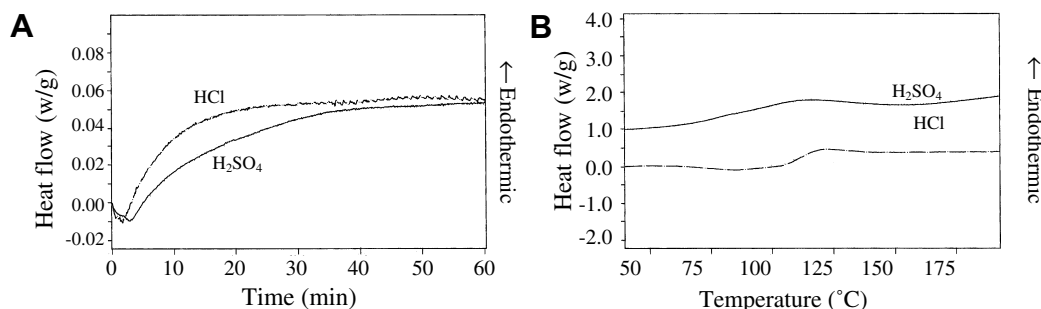[b] Weight percent of novolak PF glue powder measured after the resins was dried under 105 °C.

Fig. 2. DSC thermograms of liquefied Japanese cedar blended with formalin. A: isothermal reaction at first stage; B: thermal scanning at second stage.

Table 3
Glass transition temperature of cured novolak resins

Code of resin	T_g (°C)	Onset temperature (°C)	End temperature (°C)	Temperature range[a] (°C)
SF	89.5	54.8	113.3	58.5
CF	110.2	101.7	118.1	16.4

[a] The range of temperature for phase transition.

Table 4
Average molecular weight and polydispersity of the liquefied Japanese cedar and Novolak PF resin

Sample	Acetylated			Unacetylated		
	Mn[c]	Mw[d]	Mw/Mn	Mn[c]	Mw[c]	Mw/Mn
S	205	1298	6.3	74	1116	19.9
SF[a]	252	2530	10.1	166	1745	10.5
SF-105[b]	285	3638	12.8	155	1938	12.5
C	224	1101	4.9	37	743	19.9
CF[a]	278	3592	12.9	167	2254	13.5
CF-105[b]	419	3941	9.4	216	3354	15.6

[a] Resin products after the reaction of liquefied Japanese cedar with formalin.
[b] Novolak PF glue powder after dehydrated under 105 °C.
[c] Number average molecular weight.
[d] Weight average molecular weight.

transition. Table 3 shows the correlating temperature parameter of the glass transition. The isothermal cured CF resin had onset temperature and T_g temperature higher than SF, but the temperature range for phase transition was narrower than SF. It indicated that CF resin had lower thermal activity than SF after the polycondensation reaction of liquefied wood with formaldehyde. This result might be caused by the liquefied wood with HCl as catalyst had higher content of free phenol, and then more formaldehyde was added in the system to undergo the reaction. This made CF resin had a higher degree of polymerization.

3.3. GPC molecular weight of liquefied Japanese cedar and novolak resins

The extent of solvation of PF resins in tetrahydrofuran would influence the accuracy of molecular weight analysis. Yazaki et al. (1994) indicated the hydroxyl group in the PF resins would form the hydrogen bond with the packing gels in the analysis column and prolong the retention time. Chen and Hatano (1990) indicated the high molecular weight components of bark extractive would not really dissolved in tetrahydrofuran, and might be excluded at the stage of filtration. For these reasons, the samples used for GPC analysis in this study were acetylated by anhydride/pyridine, and the results would be compared with the unacetylated samples.

The average molecular weight (Mn and Mw) and polydispersity (Mw/Mn) of liquefied Japanese cedar and novolak PF resins are summarized in Table 4. The unacetylated samples had an average molecular weight lower than the acetylated samples, but had a higher molecular weight polydispersity. Comparing the molecular weight between liquefied wood S and C, the former had a weight average molecular weight higher than the latter. After reacting with

formaldehyde, both the novolak PF resins (SF and CF) had a molecular weight higher than the liquefied wood, indicating the liquefied wood had reacted with formaldehyde. The novolak resin prepared from liquefied wood C had the weight average molecular weight that was about three times higher than liquefied wood. But it was only two times of molecular weight increment for the novolak resin that prepared from liquefied wood S. This result indicated Japanese cedar liquefied with HCl as a catalyst had reactivity higher than with H_2SO_4 as a catalyst. After heating under 105 °C to dehydrate, the weight average molecular weight of novolak PF resins would increase further and a similar value would be achieved for both SF and CF. They were 3638 and 3941 for SF-105 and CF-105, respectively. It illustrated the liquefied wood with H_2SO_4 as catalyst had reactivity lower than HCl, and a higher temperature was needed to promote the reaction.

Fig. 3 shows the molecular weight distribution of liquefied Japanese cedar and the novolak resins. As shown in these figures, the molecular weight of unacetylated samples (diagrams of B1 and B2) concentrated at the low molecular weight region. But after being acetylated (diagrams of A1 and A2), they would shift to a higher molecular weight, and the molecular weight of novolak PF resin would be divided into two regions. Those were the molecular weight lower than 8000 and between 8000 and 25,000. After drying with 105 °C to dehydrate, the content of high molecular
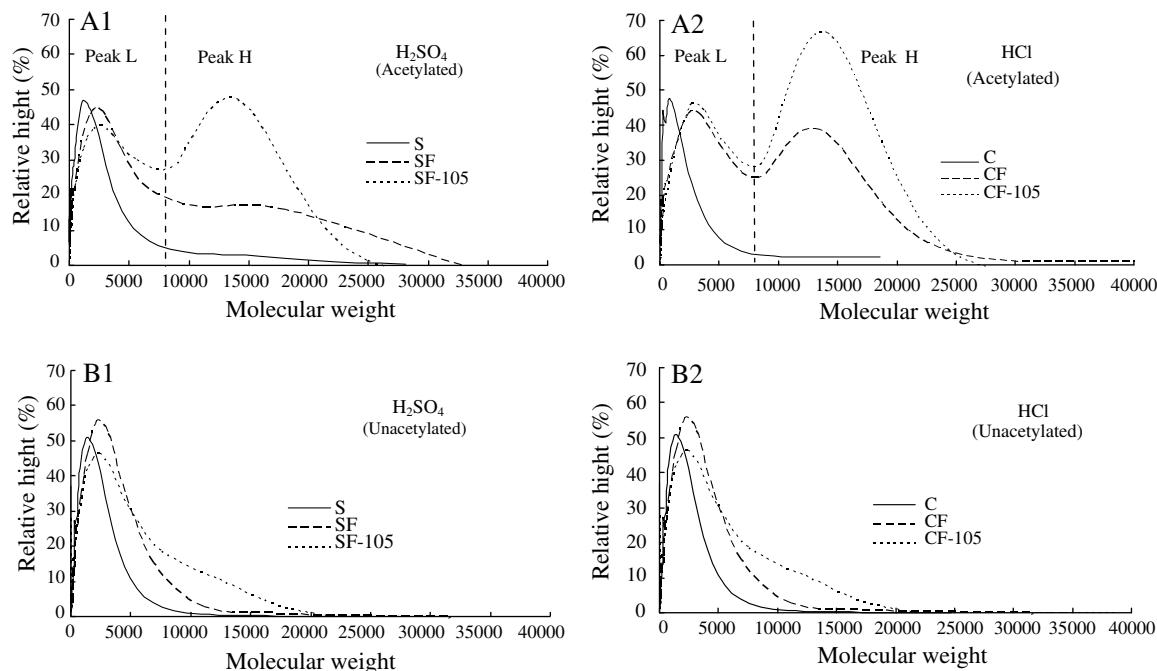
Fig. 3. Molecular weight distribution of liquefied Japanese cedar and Novolak PF resins. A1, B1: liquefied with H_2SO_4 as Catalyst; A2, B2: liquefied with HCl as Catalyst. A1, A2: Acetylated samples; B1, B2: Unacetylated samples.

Table 5
Average molecular weight and percentage of high and low molecular weight region of acetylated Novolak PF resins

Sample	High molecular weight region				Low molecular weight region			
	Mn[c]	Mw[d]	Mw/Mn	Percentage (%)	Mn[c]	Mw[d]	Mw/Mn	Percentage (%)
SF[a]	11,783	14,645	1.2	48.9	223	1731	7.8	51.1
SF-105[b]	12,707	13,581	1.2	67.9	364	1908	5.2	32.1
CF[a]	11,089	12,014	1.1	42.3	218	1598	7.3	57.7
CF-105[b]	10,822	12,795	1.2	70.8	211	1655	7.5	29.2

[a] Resin products after the reaction of liquefied Japanese cedar with formalin.
[b] Novolak PF glue powder after dehydrated under 105 °C.
[c] Number average molecular weight.
[d] Weight average molecular weight.

weight increased significantly, indicating the reaction between liquefied wood and formaldehyde really existed.

Table 5 shows the average molecular weight, molecular weight polydispersity and the percentage of the high and low molecular weight region of acetylated novolak PF resins. The weight average molecular weight for the high and low molecular weight region was 12,014–14,645 and 1598–1908, respectively. Comparison the molecular weight of novolak PF resins before and after heating to dehydrate, the novolak resin before dehydrating (SF and CF) had higher percentage of low molecular weight than high molecular weight. But after heating to dehydrate (SF-105 and CF-105), the percentage of high molecular weight increased substantially. This result indicated the molecular chain would grow continually during the period of heating to dehydrate. Compared with the average molecular weight of acetylated liquefied wood shown in Table 4, it could be speculated the major constitution of low molecular weight

region was connected with two molecules of liquefied wood, but the high molecular weight region was connected with about ten molecules of liquefied wood.

3.4. DSC thermal analysis of novolak PF resins

Novolak PF resins are prepared from phenol with an insufficient amount of formaldehyde under acidic condition to form a linear prepolymer without hydroxymethyl group. It needs adding a cross-linking agent such as hexamine to form a three-dimensional network curing structure under heating. Fig. 4 shows the DSC thermograms of novolak PF resins prepared from the liquefied Japanese cedar. The exothermic peak caused by the curing reaction had not been found in diagram A that without hexamine added at the period of heating. This was because these resins lacked the hydroxymethyl group used for cross-linking reaction in their molecular structure. But in diagram B,
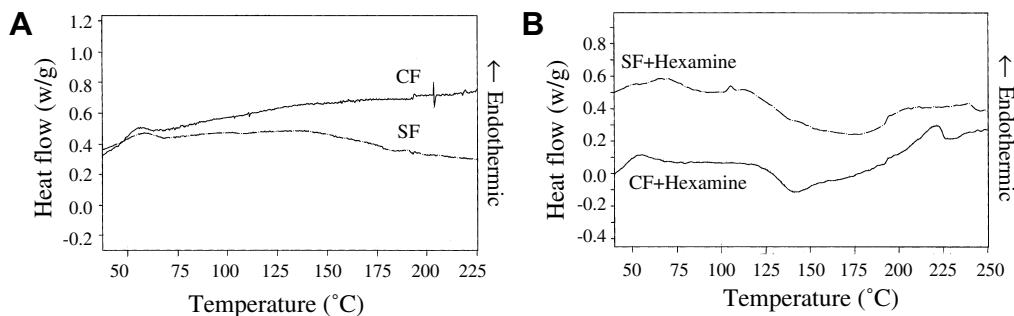
Fig. 4. DSC thermograms of novolak PF resins prepared from liquefied Japanese cedar. A: Without hexamine; B: With hexamine.

Table 6
DSC thermosetting parameters of novolak PF resins blending with hexamine

Resins	Onset temperature (°C)	Temperature at maximum height of exothermic peak (°C)	Height of exothermic peak (W/g)	Reaction heat (J/W)
SF + Hexamine	102.6	157.7	−0.195	−68.0
CF + Hexamine	125.5	143.4	−0.204	−85.7

both SF and CF those blended with hexamine displayed an obvious exothermic peak caused by the curing reaction. Table 6 shows their DSC thermosetting parameter. The novolak PF resin of SF had a broader temperature range for its exothermic peak. The onset temperature for starting the curing reaction was at 102.6 °C and the temperature at the maximum height of exothermic peak was at 157.7 °C. On the other hand, CF resin had a narrower temperature range for its exothermic peak. It had higher onset temperature and lower temperature at maximum height of peak and larger curing reaction heat.

Fig. 5 shows the DSC thermograms of novolak PF resins which blended with hexamine, wood filler and zinc stearate. As shown in diagram A, a strong endothermic peak appeared at around 275 °C. It might be caused by the thermo-degradation of wood filler. Diagram B amplified the signal of heat flow before the thermo-degradation temperature, an obvious exothermic peak caused by the curing reaction was found. The exothermic peak for CF resin was larger than SF significantly. The onset temperature for SF and CF was 143.1 °C and 127.9 °C, respectively. The temperature at the maximum height of exothermic peak was

237.2 °C and 223.7 °C for SF and CF, respectively. But comparison with Table 6, the curing reaction shifted to a higher temperature. These results indicating the great quantity of wood filler would influence heat conductivity, and a higher temperature would be needed for heat curing.

3.5. Properties of moldings made from the novolak resin

The properties of moldings made with the formula of novolak PF resin: wood filler: hexamine: zinc stearate as 60:30:10:1 by weight, and hot-pressed under 200 °C for 10 min are shown in Table 7. The weight retention after acetone soaked for the moldings made with SF and CF was 95.3% and 97.6%, respectively. The internal bonding strength of the moldings was 15.9 kgf/cm² and 11.5 kgf/cm² for SF and CF, respectively. These results indicated the novolak PF resins those prepared from liquefied Japanese cedar had a high degree of gelation and strong combining action with the wood powder after hot-pressing. As shown in Table 7, the Japanese cedar solid wood had a high water absorption rate and thickness swelling. After 2 h and 24 h of water soaking, the water absorption rates were
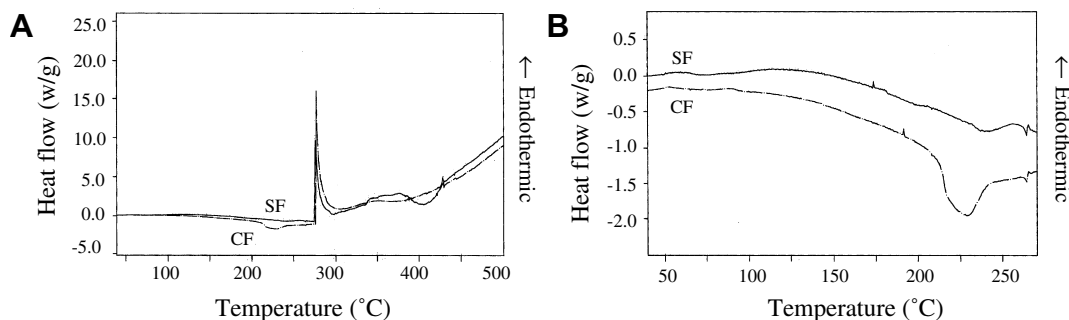

Fig. 5. DSC thermograms of the novolak PF resins blended with hexamine, wood filler and zinc stearate. * Weight proportion of novolak PF resin:wood filler:hexamine:zinc stearate blending was 60:30:10:1.

Table 7
Properties of moldings made with novolak PF resins

Resin[a]	Density (g/cm^3)	Weight retention (%)	Water absorption rate (%)			Thickness swelling (%)			Internal bonding strength (kgf/cm^2)
			2 h	24 h	36 h	2 h	24 h	36 h	
SF	0.97	95.3	1.8	6.2	7.4	0.8	1.3	1.3	15.9
CF	0.94	97.6	2.2	6.4	7.6	0.3	1.3	1.3	11.5
Wood[b]	–	–	35.3	70.6	–	4.2	7.7	–	–

[a] Weight proportion of novolak PF resin: wood filler: hexamine: zinc stearate blending was 60:30:10:1.
[b] Solid wood of Japanese cedar.

35.3% and 70.6% respectively, and the thickness swelling was 4.2% and 7.7%, respectively. However, the moldings made with SF and CF had lower water absorbency and higher dimensional stability. After 36 h of water soaking, the thickness swelling of the moldings was only 1.3%, and the water absorption was only 7.4% and 7.6% for SF and CF, respectively. These results showed the novolak PF resin prepared from the liquefied Japanese cedar could be used in manufacturing moldings with good performance.

4. Conclusion

This study using phenol liquefied Japanese cedar to prepare the novolak resin. The novolak resin blended with wood powder, hexamine and zinc stearate would be used as the materials for moldings. The results showed that Japanese cedar liquefied in phenol with H_2SO_4 as the catalyst had a better effect than with HCl. The phenol liquefied Japanese cedar could react with formalin by an exothermic reaction without extra heating and formed a solid-like novolak PF resin. After dehydration by heating, the weight average molecular weight of novolak PF resin was 3638 and 3941 for SF and CF, respectively. The novolak PF resins prepared could be melted under heating. The melting temperature were 149.4 °C and 127.5 °C for SF and CF, respectively. When hexamine was added into the novolak PF resins as a cross-linking agent, the resins would become insoluble and infusible under heating. The novolak PF resin mixed with wood powder, hexamine and zinc stearate at the weight ratio of 60:30:10:1, and hot-pressing under 200 °C for 10 min could produce the moldings with good performance.

References

Acemioglu, B., Alma, M.H., 2002. Kinetic of wood phenolysis in the presence of HCl as catalyst. J. Appl. Polym. Sci. 85, 1098–1103.

Alma, M.H., Yoshioka, M., Yao, Y., Shiraishi, N., 1996. The preparation and flow properties of HCl catalyzed phenolated wood and its blends with commercial novolak resin. Holzforschung 50 (1), 85–90.

Chen, C.M., Hatano, Y., 1990. Study of the molecular weight of bark extracts and products of their reaction with formaldehyde. Biomass 21, 65–74.

Honglu, X., Tiejun, S., 2006. Wood liquefaction by ionic liquids. Holzforschung 60, 509–512.

Kishi, H., Fujita, A., Miyazaki, H., Matsuda, S., Murakami, A., 2006. Synthesis of wood-based epoxy resins and their mechanical and adhesive properties. J. Appl. Polym. Sci. 102, 2285–2292.

Lee, W.J., Liu, C.T., 2001. Manufacture of phenol-formaldehyde wood adhesives using liquefied bark of *Cunninghamia lanceolata*. For. Prod. Ind. 20 (3), 217–226.

Lee, W.J., Liu, C.T., 2003. Preparation of liquefied bark-based resol resin and its application to particleboard. J. Appl. Polym. Sci. 87, 1837–1841.

Lee, S.H., Ohkata, T., 2003. Rapid wood liquefaction by supercritical phenol. Wood Sci. Technol. 37, 29–38.

Lee, W.J., Liu, C.T., Hou, C.H., 2004. Phenol-formaldehyde resin adhesives prepared from liquefied *Acacia confusa* wood. For. Prod. Ind. 23 (1), 43–53.

Lee, S.H., Teramoto, Y., Shiraishi, N., 2002a. Resol-type phenolic resin from liquefied phenolated wood and its application to phenolic foam. J. Appl. Polym. Sci. 84, 468–472.

Lee, S.H., Teramoto, Y., Shiraishi, N., 2002b. Acid-catalyzed liquefaction of waste paper in the presence of phenol and its application to novolak-type phenolic resin. J. Appl. Polym. Sci. 83, 1473–1481.

Lee, W.J., Chang, K.C., Sung, I.C., Chen, Y.C., 2006. Liquefaction of *Cryptomeria japonica* with phenol and utilized in the preparation of resol type PF resins. Q. J. Chin. For. 39 (4), 517–530.

Lin, L., Yao, Y., Yoshioka, M., Shiraishi, N., 2004. Liquefaction mechanism of cellulose in the presence of phenol under acid catalysis. Carbohyd. Polym. 57, 123–129.

Yazaki, Y., Collins, P.J., Reilly, M.J., Terrill, S.D., Nikpour, T., 1994. Fast-curing phenol-formaldehyde resins. part 1. Molecular weight distribution of PF resins. Holzforschung 48 (1), 41–48.

Zhang, Y., Ikeda, A., Hori, N., Takemura, A., One, H., Yamada, T., 2006. Characterization of liquefied product from cellulose with phenol in the presence of sulfuric acid. Bioresource Techn. 97, 313–321.