

STUDY ON PREPARATION AND PROPERTIES OF PHENOL-FORMALDEHYDE-CHINESE FIR LIQUEFACTION COPOLYMER RESIN

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In memoriam of Dr. Manfred SCHWANNINGER

ABSTRACT

A new zero-waste and zero-pollution composite adhesive labeled Chinese fir-based adhesive for exterior plywood was synthesized by blending alkaline Chinese fir (*Cunninghamia lanceolata*) liquid with a small amount of phenol-formaldehyde (PF). The free phenol and free formaldehyde content of the Chinese fir-based adhesive were sharply decreased compared to normal PF resin by more than 50%. The synthetic adhesive show with excellent water resistance and environmental friendliness, which had a 28h boil-dry-boil wet bonding strength of 1,73MPa according to standard JIS K6806-2003 and a formaldehyde emission of 0,045mg/L according to standard JIS A1460-2003. The structural properties and their thermal properties of cured adhesives were evaluated using Fourier transform infrared (FT-IR) and differential scanning calorimetry (DSC). The FT-IR analysis confirmed the expected chemical structure as the Chinese fir liquid reacted with formaldehyde and phenol which occurred at the wavenumbers of 1733, 1698, 1652cm⁻¹ and 1077, 1048 cm⁻¹. Although the DSC results indicated that the Chinese fir-based adhesive's curing need higher temperature than the control PF resin, the higher curing temperature hardly cripple the availability of Chinese fir-based resin in the plywood production.

Keywords: Chinese fir-based adhesive, formaldehyde, bonding properties, FT-IR, DSC.

INTRODUCTION

The petrochemical-based phenol-formaldehyde adhesives, have commonly been used in the production of wood-based panels (Yang *et al.* 2009). However, the declining fossil fuel reserves combined with the increasing price of fossil fuel have become a barrier of wood composite boards (Klaas *et al.* 2009). Therefore, more and more exploitations aimed at applying natural and economical products as substitutes for conventional wood resin adhesives. In recent years, there have been many attempts to replace petrochemicals with renewable resources, such as lignin (Kouisni *et al.* 2011), cornstarch (Moubarik *et al.* 2009), tannin (Bisanda *et al.* 2003), protein (Wang *et al.* 2012), cashew nut shell (Papadopoulou and Chrissafis 2011), wheat straw (Chen *et al.* 2012) for wood resin adhesives. However, few of them can be further applied for industrial processes due to their inherent disadvantages in compromised adhesive strength, low water-resistance or high formaldehyde emission.

Wood, the most abundant biomass in nature, has been regarded as the most promising renewable resource. It is a complex bio-composite mainly consisting of three structural components: cellulose, hemicellulose and lignin (Binder *et al.* 2009) Lignin is of particular interest because of its phenolic formation from which a wide variety of phenols and phenol derivatives and aromatic chemicals can be derived. Cellulose and hemicellulose can be converted into polyols, aldehydes and other small molecule compounds under certain conditions (Liu *et al.* 2012). Hence, considerable attention has been given to the preparation of environmentally friendly polymeric products from liquefied woods and their derivatives.

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Until now, there were two main methods of wood liquefaction. The first liquefaction method is called phenolysis, involving phenol with acids as catalysts, which resulted in liquefaction products rich in combined phenolic compounds. Further application in the preparation of phenolic adhesives is similar to the conventional phenol resins (Wang *et al.* 2009), mouldings (Lee *et al.* 2011) and others. The second method was achieved in existence of alcohols, especially polyhydric alcohols, and the resulting products can be used as polyols for the preparation of polyurethane and epoxy products (Hajime *et al.* 2011, Niu *et al.* 2011). However, some research on the liquefaction of wood in alkaline medium show enormous potential (Yin *et al.* 2010, Moubarik *et al.* 2009). All of them reveal that alkaline treatment at elevated temperature is used to enhance the reactivity of the crystalline cellulose through decreasing DP (degrees of polymerization) and increasing accessibility of cellulose. Meanwhile, the lignin components depolymerize to form monomeric and oligomeric phenolic compounds. Therefore, liquefaction of wood combined with alkaline catalysts under high temperature appears to be an attractive way to obtain low molecular weight compounds in the further use.

The production of Chinese fir, which provides woody residues from furniture manufacturing, is increasing annually in South China. Only little of it is consumed in traditional applications such as using as an industrial fuel for boilers or as raw materials for particle boards. However, most of the residues are discarded and disposed of by burning in open fields. It is therefore worthwhile to develop potential uses for such residues. In this study, we evaluated the huge potential of waste Chinese fir as a biomass resource for the production of adhesives. In order to obtain a Chinese fir-based adhesive of desirable properties for bonding plywood in exterior use, the Chinese fir powder was liquefied in sodium hydroxide solution at 200°C for pretreatment, then co-polymerized with phenol-formaldehyde to synthesize biomass adhesive. The Chinese fir-based adhesives were formulated with high percents of Chinese fir liquefied resulting in the adhesive formulations that reduce the petrochemical dependency of conventional wood adhesives.

MATERIALS AND METHODS

Materials

Cunninghamia lanceolata Hook (collected in Guangdong Province, China) was ground into powder in a rotating disintegrator. The wood powder with a dimension passing 100 mesh was dehydrated in an oven at 105°C until oven-dried. Reagent grade phenol and formaldehyde (formalin, at concentration of 37%) solution were purchased from Guangdong Guanghua Chemical Factory Co. Ltd, China. Other analytical chemicals such as sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), absolute ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$), potassium iodide (KI), iodine (I_2), hydrochloric acid (HONH_3Cl), ammonium acetate ($\text{CH}_3\text{COONH}_4$), acetylacetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$) were obtained from Guangzhou chemical reagent factory, China.

Liquefaction of Chinese fir powder

The Chinese fir powder was liquefied in sealed reactor using a stainless steel autoclave reactor under the following conditions: column, 12cm×12cm×1,5cm (diameter×height×thickness); limit temperature, 500°C; limit pressure, 12MPa (figure 1). About 75g Chinese fir powder was loaded into the reactor. A concentration of 25% sodium hydroxide solution (300g in total) was gradually charged into the reactor with stirring. After all of the sodium hydroxide solution had been loaded, the reactor was sealed, and the mixture was kept in oil bath at 200±2°C for 15min. The liquefied resultant was cooled and preserved for synthesis. The residue rate of the liquefied product was only 0,65wt % (base on the total mass of the final liquefaction), so it did not need to be filtered and can be used to synthesize directly.



Figure 1. Liquefaction reactor.

Preparation of Chinese fir-based adhesives

For preparing Chinese fir-based adhesives, the Chinese fir liquid was used to prepare resins in the reaction flask. The three weight ratios of Chinese fir (CF) liquid to phenol-formaldehyde (PF) (60/40, 55/45 and 50/50), three molar ratio of formaldehyde to phenol (the values are 2:1, 2,5:1 and 3:1) were chosen respectively as the variables. The typical synthesis procedure was described as below in which the PF/CF was 60/40 with molar ratio of 2:1. The preparation conditions of all adhesives are summarized in table 1.

Table 1. Preparation conditions of Chinese fir-based adhesives and control PF adhesives.

Adhesive ID	Chinese fir liquid (g)	Phenol (g)	37% Formaldehyde (g)	50% NaOH solution (g)	CF/PF	F/P
60/40-2:1	160,50	47,00	60,00	/	60/40	2:1
55/45-2:1	130,78	47,00	60,00	/	55/45	2:1
50/50-2:1	107,00	47,00	60,00	/	50/50	2:1
60/40-2,5:1	183,00	47,00	75,00	/	60/40	2,5:1
55/45-2,5:1	149,11	47,00	75,00	/	55/45	2,5:1
50/50-2,5:1	122,00	47,00	75,00	/	50/50	2,5:1
60/40-3:1	205,50	47,00	90,00	/	60/40	3:1
55/45-3:1	167,44	47,00	90,00	/	55/45	3:1
50/50-3:1	137,00	47,00	90,00	/	50/50	3:1
2:1	/	47,00	60,00	21,40	/	2:1
2,5:1	/	47,00	75,00	24,40	/	2,5:1
3:1	/	47,00	90,00	27,40	/	3:1

47g of phenol and 60g of formalin (the F/P molar ratio was 2) were charged into a three-necked, 500mL flask equipped with a condenser, a thermometer, a teflon stirrer and the reaction temperature was maintained at 45-50°C for 30min. Then the temperature was gradually raised to around 80°C, and 160g of Chinese fir liquid was then added during a period of 50min. After all of the Chinese fir liquid had been infused, the reaction temperature was set at 92±2°C immediately and maintained until the Gardner-Holdt viscosity reached 500±20mPas(20±2°C). The viscosity measurements were carried out at 5-min intervals. The finished adhesive was cooled to room temperature and kept in the refrigerator for use. About 250g of each adhesive sample was prepared. The PF resin was prepared as control sample. The solid content, free formaldehyde content and free phenol content of prepared adhesives were determined according to the China Industry Standard (GB/T 14074-2006).

Resin solid content

The percent of resin solid content is calculated by the following equation.

$$S(\%) = \frac{S_1}{S_0} \times 100$$

where “S” was the percent of resin solid content and “S₀” and “S₁” were the weight of the resin before and after dried, respectively.

Free formaldehyde content

The free formaldehyde content of the prepared resins was determined by the hydroxylamine hydrochloride method. Accurately weighed about 0,003 or 0,005g of resin sample was transferred into 250mL beaker and dissolved in 50mL methyl alcohol or 50ml 75% isopropyl alcohol. Simultaneously, the pH value of the solution was adjusted to 3,5 by adding 1N hydrochloric acid solution. 25mL of 10% hydroxylamine hydrochloride solution was added and stirred for 10min. Finally, the mixture solution was titrated with 0,1N or 1N sodium hydroxide solution. Free formaldehyde content was calculated by using following formula.

$$\% \text{Free formaldehyde content} = \frac{3c(V_1 - V_0)}{m}$$

where “ V_1 ” and “ V_0 ” are volumes of sodium hydroxide solution required in the titration for sample and blank, respectively. “ c ” is the exact normality of sodium hydroxide solution. “ m ” is weight of sample in g.

Free phenol content

The percentage of free phenol was evaluated according to bromometry method. Accurately weighed about 0,002g of resin sample was taken in 1000mL round-bottomed flask. To that 100mL distilled water was added and the pH value of the solution was adjusted to 4 by 20% hydrochloric acid solution. Then steam distilled until the negative test for phenol with bromine water. The distillate was diluted to 1000mL with double distilled water. An aliquot of 50mL was taken in Erlenmeyer flask and 25mL of 0,1N bromate-bromide solution and 5mL concentrated HCl was added. The flask was then closed and kept in dark for 15min. After that 0,0018g potassium iodide was added and kept in dark for another 10min. Finally, the mixed solution was titrated with 0,1N sodium thiosulphate solution using starch as indicator. The free phenol was calculated by following formula

$$\text{Phenol content (by weight)} = \frac{(V_1 - V_2) \times c \times 0.01568 \times 1000}{m \times 50} \times 100\%$$

where “ V_1 ” and “ V_2 ” are the volumes of 0,1N sodium thiosulphate solution required for blank and sample, respectively. “ m ” is the weight of sample in g and “ c ” is the exact normality of sodium thiosulphate solution.

Viscosity measurements

The viscosity of the Chinese fir-based adhesives and PF resins were measured using a Brookfield rotary viscometer with spindle at $20 \pm 2^\circ\text{C}$. An average value of three replicate measurements was reported.

Evaluation of plywood

Eucalyptus veneers with dimensions of $320\text{mm} \times 320\text{mm} \times 2,1\text{mm}$ were used to prepare 3-layer plywood panels. Chinese fir-based adhesive was applied to both sides of a veneer at a spread rate of $350\text{g}/\text{m}^2$ (for double bondlines). The adhesive-coated veneer was then stacked between two uncoated veneers with the grain directions of two adjacent veneers perpendicular to each other. Thereafter, the assembled veneers were pre-pressed (pressure, 1MPa) at room temperature for 1h. After that, the pre-pressed veneers were hot-pressed at 120°C for 6min at the same pressure of 1MPa. Each resin obtained was used to prepare 3 piece of plywood. The specimens were maintained at $20 \pm 2^\circ\text{C}$ and $45 \pm 5\%$ relative humidity for 24 hours, sawn to get samples for the test of bonding strength and formaldehyde emission. A total of 48 specimens of $100 \times 25\text{mm}$ (4 cycles' test, 12 specimens were prepared for each cycle) were cut from each panel for bond strength tests, according to JIS K6806-2003 standard. Ten specimens of $150 \times 50\text{mm}$ were cut from panel to determine the formaldehyde emission according to JIS A1460-2003 standard. The formaldehyde emission was tested by a 120-mm-diameter, 60-mm-high crystallizing dish containing 300mL of distilled water was placed in the bottom of a 240-mm-diameter desiccator with a

capacity of 10 ± 1 L. Ten pieces of test specimens (with dimensions of $150\times 50\times 6$ mm) were clamped in a metal support, with no contact between specimens and allowed to stand on the perforate plate located over crystallizing dish in the desiccators at $20\pm 2^\circ\text{C}$ for 24h. Formaldehyde emissions from the specimens were absorbed by the distilled water, which was subsequently used as the sample solution.

Fourier Transform Infrared (FT-IR) Spectroscopy test

The adhesive sample was placed in an oven at $160\pm 2^\circ\text{C}$ until a constant weight was obtained. FT-IR spectra of both samples were performed in a Perkin Elmer model Spectrum V10 instrument. Each spectrum was recorded in a frequency range of $400\text{--}4000\text{cm}^{-1}$ using potassium bromide (KBr) disc. The KBr was previously oven-dried at 300°C to reduce the interference of water.

Differential Scanning Calorimetry (DSC) test

DSC measurements were conducted on a NETZSCH 204 F1 differential scanning calorimeter. Dynamic scans were conducted in a temperature range of $30\text{--}250^\circ\text{C}$, at constant heating rate of $10^\circ\text{C}/\text{min}$, under nitrogen atmosphere at a flux rate of $50\text{mL}/\text{min}$. For sample preparation, the sample was placed in an oven at $40\pm 2^\circ\text{C}$ until a constant weight was obtained. About $0,006\text{g}$ of the resin was used in an aluminum crucible of $40\mu\text{L}$ with a perforated lid.

RESULTS AND DISCUSSION

Technical properties analysis

All of the Chinese fir-based adhesives had the dark color with the specific smell. The resin solid content, free formaldehyde content and free phenol content were measured and the results are presented in table 2.

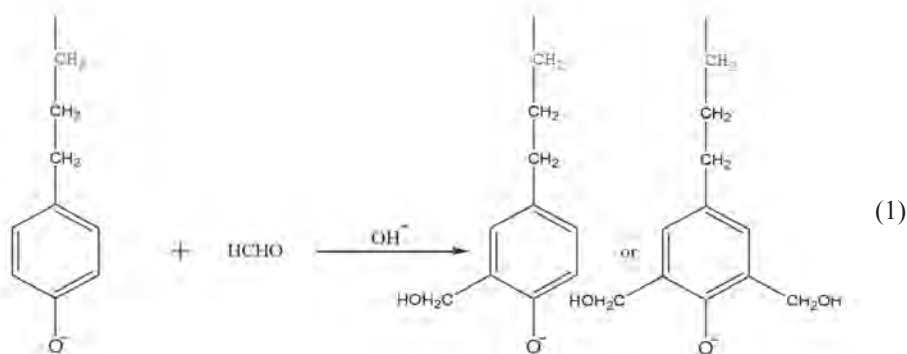
Table 2. Resin solid content, free formaldehyde content and free phenol content.

Adhesive ID	Solid content (%)	Free formaldehyde content (%)	Free phenol content (%)
60/40-2:1	46,16±0,06	0,185±0,007	0,048±0,0013
55/45-2:1	47,08±0,03	0,258±0,003	0,066±0,0019
50/50-2:1	48,71±0,11	0,276±0,002	0,081±0,0007
60/40-2,5:1	42,27±0,11	0,368±0,002	0,031±0,0011
55/45-2,5:1	44,17±0,03	0,498±0,002	0,062±0,0007
50/50-2,5:1	46,74±0,07	0,693±0,003	0,085±0,0010
60/40-3:1	40,78±0,16	1,021±0,003	0,018±0,0002
55/45-3:1	42,89±0,17	1,724±0,001	0,056±0,0005
50/50-3:1	45,41±0,03	1,921±0,003	0,070±0,0006
2:1	54,99±0,16	0,355±0,002	0,126±0,0006
2,5:1	49,48±0,12	1,284±0,019	0,098±0,0003
3:1	47,93±0,03	4,241±0,015	0,074±0,0006

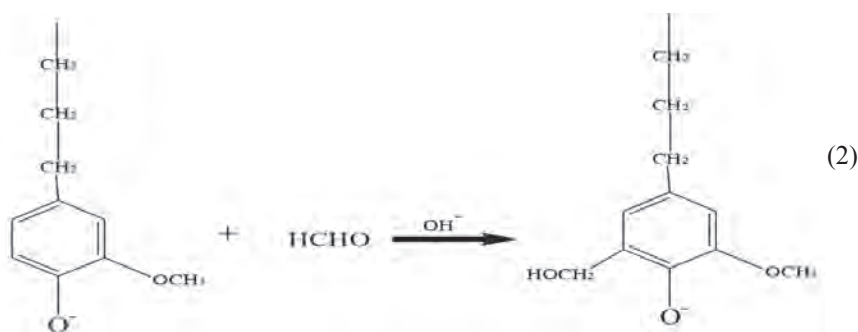
Resin solid content is an important property for phenolic resin. Low solid content adhesive will eject out more water during the hot pressing, which could reduce the bonding strength of the plywood. As expected, the control PF resin adhesives have higher solid content than the Chinese fir-based adhesives at the same F/P molar ratio. The solid content of Chinese fir-based adhesives ranges from 40,78% to 48,71%, which exceeded the minimum requirements of 35% in phenolic resin adhesive (Jin *et al.* 2010). With increasing the CF/PF mass ratio and F/P molar ratio, a decreasing solid content in Chinese fir-based adhesives was observed.

Free formaldehyde and free phenol are the components of toxicity in phenolic or aldehydic synthetic resin. In general, low toxic PF resin follows with poor bond strength, while great bonding strength is often accompanied with high toxicity. Results in table 1 showed that the free formaldehyde and free phenol of the synthetic Chinese fir-based adhesives would decrease along with the increasing addition of Chinese fir liquid. With the CF/PF rising from 50/50 to 60/40, the free formaldehyde content and free phenol content of the Chinese fir-based adhesives (F/P=2:1) decreased from 0,276% to 0,185% and 0,081% to 0,048%, respectively, which were far less than those of control PF resin. The free formaldehyde and free phenol were similar to those of the Chinese fir-based adhesives with higher F/P molar ratios (Hassan *et al.* 2009). As known, the alkaline liquefaction of Chinese fir breaks down lignin, cellulose and hemicellulose. The lignin was further hydrolyzed to three main structural units of benzyl propane: guaiacyl (G), hydroxyl phenyl (H) and syringyl (S) (Moze 1999). H-type units have 2 reactive sites at C3 and C5 position in the ring, susceptible of reacting with formaldehyde, while in S-type units both C3 and C5 positions are linked to a methoxy group, resulting in low reactivity with formaldehyde. From this point of view, lignin

with H groups as the principal structural units must be a priori more suitable for PF formulations, and the G groups take the second place. The units of H and G react with formaldehyde in alkaline medium producing H-hydroxymethyl and G-hydroxymethyl, the reaction formula is illustrated in equation (1) and equation (2). Then the H-hydroxymethyl and G-hydroxymethyl occurred the dehydrolytic condensation and form the cross-linked structure. When exposed at high temperature ($200^{\circ}\text{C}\sim 220^{\circ}\text{C}$), cellulose and hemicellulose were firstly degraded through hydrolysis path to oligosaccharide and then converted in alkaline pathway to glucose (Yin *et al.* 2011). And the glucose then degraded in alkaline conditions to generate carboxylic acid so that reduce the pH value of the solution. As soon as the pH value less than 7,0 the glucose transformed to hydroxymethyl furfural (HMF) through diverse elimination reactions. Due to the similar chemical property to formaldehyde, the phenol was consumed by the condensation reaction of the HMF, which occurred at three reactive sites. Hence, the use of an optimum amount of formaldehyde and phenol can form and improve the chance of Chinese fir liquid's incorporation into the PF resin structures.



P-hydroxy group reaction with formaldehyde



G-hydroxymethyl group reaction with formaldehyde

Bonding properties analysis

Table 3. Boiling bond strength of plywood on different test conditions.

Adhesive ID	28-h ^a boiling test (wood failure)	52-h ^b boiling test (wood failure)	76-h ^c boiling test (wood failure)	100-h ^d boiling test (wood failure)
60/40-2:1	1,14±0,03 ^e (60 ^f)	1,01±0,03(50)	0,89±0,05(30)	0,41±0,05(10)
55/45-2:1	1,32±0,08(80)	1,22±0,08(75)	1,02±0,03(55)	0,85±0,04(25)
50/50-2:1	1,51±0,06(90)	1,35±0,03(70)	1,23±0,05(60)	1,08±0,03(50)
60/40-2,5:1	0,96±0,06(60)	0,72±0,03(20)	0,33±0,04(0)	failure
55/45-2,5:1	1,42±0,04(90)	1,11±0,05(60)	0,93±0,04(45)	0,71±0,03(30)
50/50-2,5:1	1,38±0,05(85)	1,14±0,05(70)	0,95±0,04(50)	0,77±0,05(30)
60/40-3:1	0,56±0,04(30)	failure	failure	failure
55/45-3:1	0,84±0,04(50)	0,46±0,04(10)	failure	failure
50/50-3:1	1,00±0,07(60)	0,82±0,04(50)	0,71±0,03(30)	failure
2:1	1,54±0,05(90)	1,28±0,05(75)	1,12±0,05(70)	0,91±0,05(60)
2,5:1	1,48±0,05(90)	1,11±0,04(80)	0,98±0,05(60)	0,78±0,05(40)
3:1	1,34±0,05(80)	1,01±0,06(60)	0,89±0,04(30)	failure

^a 4h in boiling water, 20 h in 63±3°C oven, 4h in boiling water;

^b 4h in boiling water, 20 h in 63±3°C oven, 4h in boiling water, 20 h in 63±3°C oven, 4h in boiling water;

^c 4h in boiling water, 20 h in 63±3°C oven, 4h in boiling water, 20 h in 63±3°C oven, 4h in boiling water, 20 h in 63±3°C oven, 4h in boiling water;

^d 4h in boiling water, 20 h in 63±3°C oven, 4h in boiling water, 20 h in 63±3°C oven, 4h in boiling water, 20 h in 63±3°C oven, 4h in boiling water, 20 h in 63±3°C oven, 4h in boiling water, 20 h in 63±3°C oven, 4h in boiling water;

^e unit: MPa; ^f unit: %.

In order to enhance the bonding strength and boiling water resistance, formaldehyde and phenol were used to co-polymerize with alkaline Chinese fir liquid. The boiling bonding strength and wood failure were evaluated for plywood panels bonded with various Chinese fir-based adhesives and control PF resin adhesives. The test results are presented in table 3. To verify the boiling water resistance and durability, the test specimens were measured on more rigor conditions after the plywood specimens had been subjected to a 54-h, 76-h and 100-h cycle. The results showed that all the 28-h boiling-drying-boiling tests for panels prepared with Chinese fir-based adhesives with F/P=2 exceeded 1,1MPa without evaluating the wood failure. This means that the Chinese fir-based adhesives formulation with F/P=2 exceed the requirement set by JIS K6806-2003 for application in exterior use. The results in the 52-h boiling cycle test were also outstanding because the values were greater than 1.0MPa as before. Moreover, the 76-h boiling tests for panels prepared with the formulation of 50/50-2:1 and the 55/45-2:1 were $1,23\pm 0,05$ MPa and $1,02\pm 0,03$ MPa, which still met the JIS K6806-2003 standard 0,98MPa. In the 100-h boiling cycle procedure, nothing but the evaluated value of the adhesive 50/50-2:1 exceeded the minimum requirement of JIS K6806-2003 standard. All the results above indicated that the Chinese fir-based adhesive had wonderful water resistance and durability, especially the adhesive 50/50-2:1.

The boiling bonding strength and wood failure of adhesive 50/50-2:1 for the 52-h cycle test, 76-h cycle test, and 100-h cycle test were $1,35\pm 0,03$ MPa (70%), $1,23\pm 0,05$ MPa (60%), and $1,08\pm 0,03$ MPa (50%) apparently, while the results for the control PF were $1,28\pm 0,05$ MPa (65%), $1,12\pm 0,05$ MPa (50%), and $0,91\pm 0,05$ MPa (40%) under the same test conditions. This could be attributed to the higher reactivity of the liquefaction, or more active sites on the liquefaction using a catalyst of NaOH. More active sites could react with more formaldehyde and phenol, thereby resulting in a higher crosslinking density of the adhesive after curing. That is why the adhesive 50/50-2:1 had better boiling water resistance and durability than the control PF resin. And it is important that the Chinese fir liquid is not used as filler but raw material reacted with formaldehyde and phenol.

Formaldehyde emission

Formaldehyde emission of specimens was measured by 24-h desiccator method. figure 2 shows the formaldehyde emission results for the various specimens. Each specimen was tested twice and good repeatability of results was obtained with a maximum relative standard deviation of less than 2%. The formaldehyde emission of all the panels approached to the value of E_0 specified in the JIS A1460-2003 standard (the value is less than 0,5mg/L) except the panel bonded with the control PF resin with the F/P ratio of 3:1. The quantity of formaldehyde emission of plywood bonded with Chinese fir-based adhesives decreased with the increasing CF/PF ratio as shown in figure 2. It can be seen that the sample in the group of F/P=3:1, with a CF/PF ratio of 60/40, achieving the lowest formaldehyde emission value of 0,102mg/L, which was only 1/5 of the E_0 specified value. Panels bonded with the Chinese fir-based adhesives emitted less formaldehyde than panels bonded with the control PF resin adhesive by 50–80%. This may be due to the depolymerization products of lignin maintaining their aromatic character and high reactivity, which act as radical scavengers and can therefore readily react with free formaldehyde in the mixture, during crosslinking process (Kunaver *et al.* 2010).

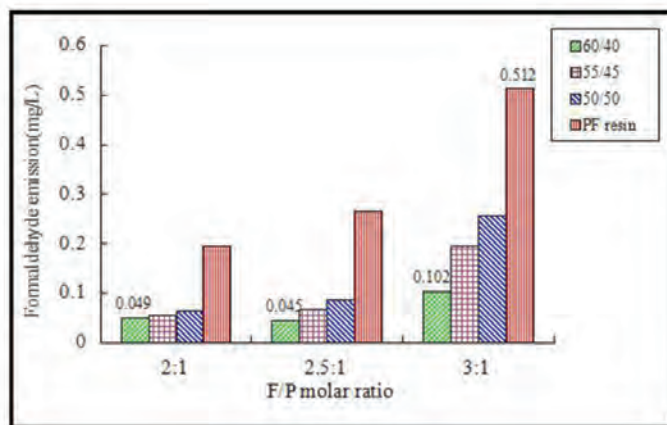


Figure 2. Formaldehyde emission of plywood.

FT-IR analysis

The spectra of the Chinese fir-based adhesive and control PF resin adhesive are presented in figure 3, figure 4 and figure 5. (Hirokazu *et al.* 2011, Kadla *et al.* 2002, Poljanšek and Krajnc 2005).

As shown in figure 3, the Chinese fir-based adhesive showed a similar FT-IR absorbance to that of the control PF resin adhesive. The band at 3420cm^{-1} in Chinese fir-based adhesive and the band at 3416cm^{-1} in control PF resin are assigned to aromatic and aliphatic OH groups while the bands at 2948 , 2850 and 1460cm^{-1} in Chinese fir-based adhesive and the bands at 2946 , 2845 and 1458cm^{-1} in control PF resin are related to the C–H vibration of CH_2 and CH_3 groups. They are typical vibrations of methoxyl groups. However, with the incorporation of wood components, the FT-IR spectra of the Chinese fir-based adhesive contained some different bands compared with that of the control PF resin. The major difference in the spectra between the Chinese fir-based adhesive and control resin adhesive is the absorbance in the carbonyl region. As shown in figure 4, the peaks at 1733 , 1698 , and 1652cm^{-1} in Chinese fir-based adhesive are ascribed to the ester carbonyl stretch, aryl ketone or aldehyde carbonyl stretch, and the di-substituted alkene $\text{C}=\text{CH}_2$, respectively. However, the control PF resin showed no absorbance in this region as expected. Furthermore, the spectra of the Chinese fir-based adhesive also showed two weak bands at 1473 and 879cm^{-1} caused by tetra substituted (1, 2, 4, and 6) ring which did not occur in the spectra of control resin. It implies that the existence of some lignin fragments, most of which are tetra substituted aromatic rings in the Chinese fir-based adhesive. The other difference in the spectra between the Chinese fir-based adhesive and control resin occurred at 1077cm^{-1} (figure 5), with the band attributed to the ether linkage on the furan ring and the band at 1048cm^{-1} attributed to the single bond C–O–C stretch with $-\text{CH}_2\text{OH}$ vibrations. Based on the above discussion, the bands at 1077 , 1048cm^{-1} are associated with the 5-HMF that reacted with phenol during the polycondensation reaction.

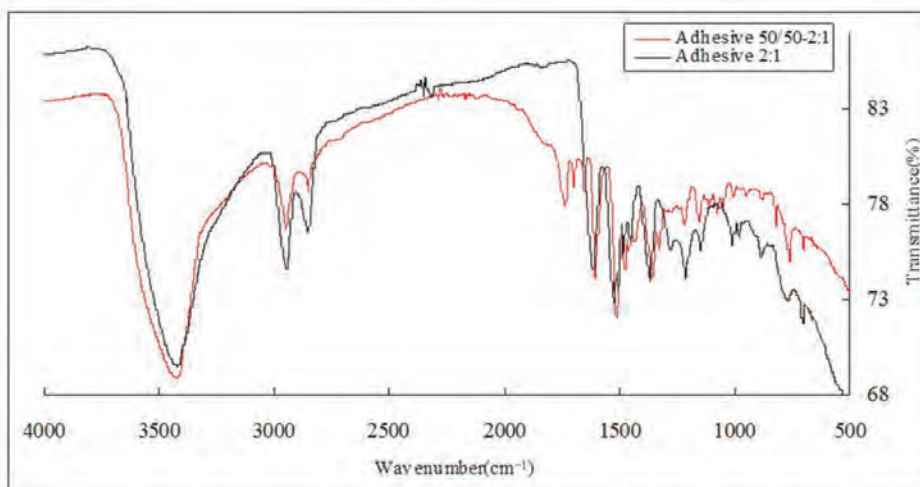


Figure 3. FT-IR spectra of adhesive 50/50-2:1 and adhesive 2:1.

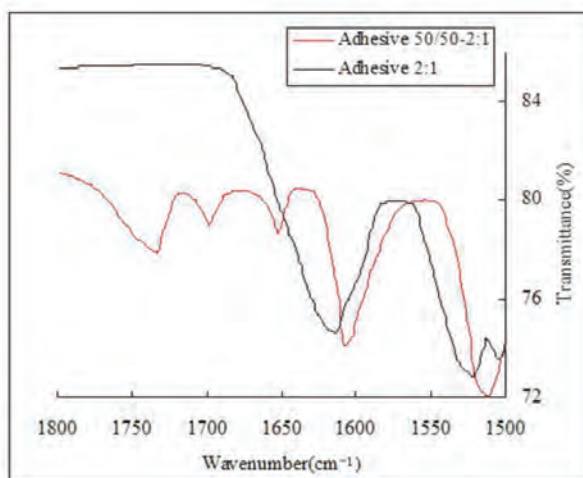


Figure 4. FT-IR spectra of adhesive 50/50-2:1 and adhesive 2:1.

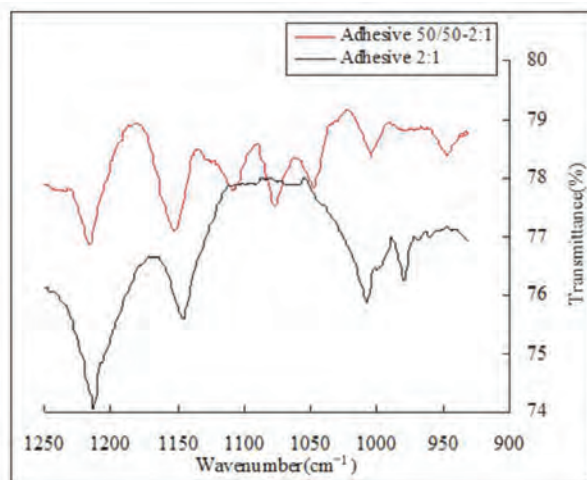


Figure 5. FT-IR spectra of adhesive 50/50-2:1 and adhesive 2:1.

DSC analysis

The isothermal DSC curves at a heating rate of 10°C/min of Chinese fir-based adhesives and control PF resin adhesives are shown in figure 6 and figure 7. The results obtained are summarized in table 4 containing onset temperature, peak temperature and ΔH .

Table 4. The onset temperature, peak temperature and ΔH of the adhesives.

Adhesive ID	Onset temperature (°C)	Peak 1 temperature (°C)	Peak 2 Temperature (°C)	ΔH (mJ/mg)
1:2	114,7	/	141,8	96,4
(70/30)-1:2	116,4	/	149,3	68,7
(60/40)-1:2	115,6	/	147,5	72,9
(50/50)-1:2	114,6	/	146,1	78,3
(50/50)-1:2,5	112,5	142,1	155,0	89,2
(50/50)-1:3	111,4	144,8	159,5	101,5

Figure 6 and figure 7 show that the resin samples gave a single or two exothermic peaks in the range of 141,4–157,5°C. Both of the exotherms obtained in the resin systems were attributable to the curing reaction. According to the previous research (Christiansen and Gollob 1985), the lower exothermic peak in the range of 141,4–144,8°C has been attributed to the addition reaction of free formaldehyde to phenolic ring, and the upper exothermic peak in the range of 143,8–157,5°C was associated with the chain-building condensation reactions, involving hydroxymethyl groups attached to various phenolic species. The appearance of single exothermic peak is mainly due to the F/P molar ratio below 2,3 that resulted in the overlapping of exothermic signals, two well-separated exothermic peaks are revealed when the F/P molar ratio was larger than 2,3 (Holopainen *et al.* 1997).

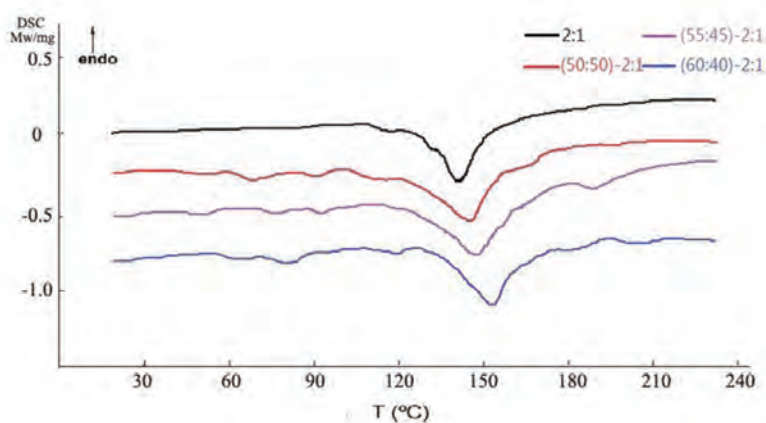


Figure 6. DSC curves of adhesive at F/P=2.

Figure 6 shows the DSC curves of the Chinese fir-based adhesives (F/P=2) with a CF/PF ratio of 50/50, 55/45 and 60/40, respectively. As the data listed in table 4, the extrapolated onset temperatures for the Chinese fir-based adhesives at F/P=2 were found to be 114,6°C, 115,6°C and 116,4°C, respectively. It was close to the control PF resin adhesive of the same molar ratio, but slightly higher than the Chinese fir-based adhesive with larger F/P molar ratio. This indicated that with larger F/P molar ratio Chinese fir-based adhesives were more reactive at the low temperatures. As far as the effect of CF-to-PF ratio is concerned, it can be seen from figure 6 that the onset temperature and peak temperature of the Chinese fir-based adhesives shifted to higher temperatures with an increase of CF/PF mass ratio. However, the ΔH s of cure were significantly reduced. Compared with the control PF resin at the same molar ratio, the Chinese fir-based adhesives had higher peak temperature and lower ΔH . This is probably because lignin has less free ring positions than phenol and more steric impediments that delays the hardening of Chinese fir-based adhesives. Furthermore, lignin introduces an extra amount of methylol groups similar to those produced by formaldehyde during curing, what will act in the opposite way.

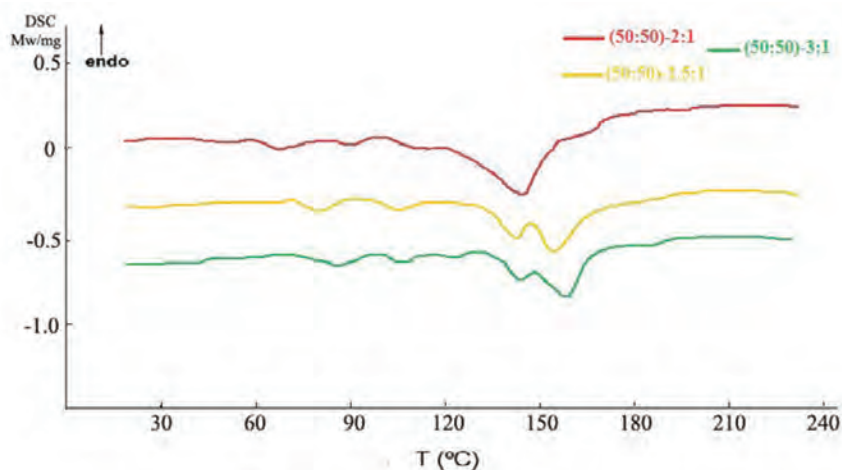


Figure 7. DSC curves of Chinese fir-based adhesive with CF/PF=50/50.

Figure 7 shows the DSC curves of the Chinese fir-based adhesives (CF/PF=50) with F/P molar ratios of 2:1, 2,5:1 and 3:1. Due to the F/P molar ratio lower than 2,3, the DSC curve of the Chinese fir-based adhesive (F/P=2:1) reveals only a single exothermic at the peak temperature of 146,1°C. The DSC curves of the Chinese fir-based adhesives (CF/PF=50) with a F/P molar ratio of 2,5:1 and 3:1 manifested that the curing behavior is completed in two steps which are signified by two exothermic curves. The peak temperature for the Chinese fir-based adhesive with a molar ratio of 2,5:1 was 142,1°C and 155°C, respectively. And they were 144,8°C and 157,2°C for the Chinese fir-based adhesive with a molar ratio of 3:1. This implies that the Chinese fir-based resins with larger F/P molar ratio needed a higher temperature for completely curing. The ΔH in table 4 suggested that the Chinese fir-based adhesive (CF/PF=50/50 and F/P=3:1) reacted more strongly than the other resins due to the larger ΔH released during curing.

CONCLUSIONS

The alkaline Chinese fir (*Cunninghamia lanceolata*) liquid is proved to be useful raw material for plywood adhesives. The process of liquefaction is easy to carry out which make it possible for industrial production. The synthetic Chinese fir-based adhesives exhibit excellent improvements in free formaldehyde content and free phenol content. More important, the properties of plywood glued with the Chinese fir-based adhesives (CF/PF=50/50, F/P=2:1) after 100-h boiling drying cycle still meet the requirement of the JIS K6806-2003 standard in exterior application and the formaldehyde emission is only 0,074mg/L which is much less than that of the E_0 specified in the JIS A1460-2003 standard (the value is less than 0,5mg/L). In addition, the cost of this adhesive appears much lower than that of the synthetic phenolic resins traditional used for wood adhesives. Hence, we can predicate that the Chinese fir-based adhesive will not only help reduce the polymer industry's dependence on petro-chemical industry but also be applied for industrial production.

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