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RESEARCH ARTICLE

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Liquefaction of bamboo, preparation of liquefied bamboo adhesives, and properties of the adhesives

Abstract This study investigated the liquefaction of bamboo in phenol, which involved the effects of weight ratios of phenol to bamboo, amount of catalyst, temperature, etc. The study showed that liquefaction could be accomplished with a phenol to bamboo weight ratio of 2–1: 1, a 5% catalyst of HCl or BF_3, and a temperature of 115ºC. Liquefied bamboo formaldehyde (BLF) resin adhesive for exterior use could be obtained with a phenol to formaldehyde molar ratio of 1:1.6–2.0. The curing behavior of BLF resin adhesive, studied by TG–DSC and IR analyses, showed that BLF resin adhesives had a lower curing temperature than PF adhesives but had the same characteristic trough in IR spectra as PF adhesives.

Keywords bamboo, liquefied bamboo, liquefied bamboo resin adhesive

1 Introduction

Bamboo, commonly known as “the second forest”, is a very important part of our forest resource. China is located at the center of the world’s bamboo-growing area. This area of bamboo forest is the largest in the world. It is mainly distributed in 17 provinces in southern China. With further development of bamboo processing industries, residues of various bamboo timbers increase. Hence, it is important to develop processing plants for these large reserves of residual resource material.

Most countries pay attention to the study of material energy transformation. These studies include the liquefaction of wood, bark, and crop straw. For example, Mitssunaga et al. (1995) liquefied bark and tannin in phenolic liquid using BF_3 as catalyst to prepare wood adhesives. Li (1998) used the bark of *Acacia* and Chinese fir as raw material and liquefied them in phenolic liquid to prepare liquid bark adhesives, which are used in the production of wood-based panels. However, liquefaction and adhesive preparation of bamboo have not been reported. Bamboo liquefaction is a thermochemical process that turns bamboo into liquid in an organic medium and then turns it into polymer material with many applications and great product values. It is an effective method for comprehensive utilization of bamboo. Based on the various properties of bamboo and liquefaction of wood and bark, liquefied bamboo (BL) was catalyzed in phenolic liquid to prepare liquefied bamboo formaldehyde (BLF) resin adhesive, which has potential environmental and social benefits.

2 Materials and methods

2.1Main experimental materials and equipments

Hydrochloric acid, sulphuric acid, phosphoric acid, and phenol were purchased from the Shuanglin Chemical Pharmaceutical Factory (Hangzhou, Zhejiang Province); fluorine boron (BF_3) and formaldehyde were purchased from the Sanying Chemical Pharmaceutical Factory (Lanxi, Zhejiang Province); and sodium hydroxide was purchased from the Ningbo Chemical Pharmaceutical Factory. Bamboo powder was collected from the residues of the Lin’an Baifu Bamboo Products Co., Ltd. All chemicals used were of analytical grade.

The following equipment was used in our project: an FI-IR spectrometer (IR Prestige-21, Daojin Co., Japan); a synthesis thermal analyzer (Netzsch STA409PC, Germany);

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an NDJ-79 rotary caplastometer (Tongji University, China); a QT-200 testing press from the Shanghai Jiecheng Baihe Machinery Plant; an MW-4 univeral mechnics testing machine (Jinan material testing machinery plant), and a miniature plant grinder.

2.2 Methods

2.2.1 Process of bamboo liquefaction

Crushed bamboo was ground to a powder in a plant grinder and dried in an oven at 100ºC for 1 h. An amount of phenol was poured into a three-necked flask equipped with a stirrer, condenser, and thermometer. The flask was heated to around 100ºC in an oil bath, then a catalyst was poured into the flask and we gradually added bamboo powder. Subsequently, the temperature of the liquefied bamboo powder was controlled at around 115ºC. Finally, we calculated the contents of the involatile matter, the combined phenol, and the free phenol in the liquefaction liquid. The calculations were made using the following formulas:

involatile matter (%) = weight of involatile matter/weight of test material × 100%

amount of combined phenol (%) = involatile matter (%) – initial bamboo powder matter (%)

amount of free phenol (%) = initial phenol mass part (%) – combined phenol mass part (%)

2.2.2 Preparation of BLF resin adhesive

We took some liquefied bamboo and adjusted the pH value to 8–9 using a sodium hydroxide solution. Given a specified molar ratio of phenol to formaldehyde, we added formaldehyde twice to the liquefied bamboo at 85ºC: two thirds of the total amount for the first time and the remaining one third for the second time to carry out an additional polycondensation reaction. When a specified viscosity was reached, the reaction stopped.

2.2.3 Plywood test

Samples were prepared to conform to GB/T 17657-1999 standards. All the samples for bonding strength tests were gently boiled in water for 4 h, dried in an oven for 20 h at (62±2) ºC, and then again gently boiled in water for 4 h.

2.2.4 Adhesive property indices

Appearance: brown; pH value: 10–12; solid content: 45%–55%; storage period >90 days; bonding strength >1.0 MPa.

3 Results and discussion

3.1 Effects of liquefaction conditions on liquefied bamboo

3.1.1 Effect of catalysts on liquefaction results of bamboo

With a phenol to bamboo weight ratio of 2:1, a liquefaction temperature of 115ºC, and using H_2SO_4, H_3PO_4, HCl, and BF_3 as catalysts, we obtained the liquid products BL-1, BL-2, BL-3, and BL-4 in a period of 2 h. We then tested the residue rates of the combined phenol and free phenol. The results are shown in Table 1. When H_2SO_4 was used as catalyst, the bamboo powder liquefied rapidly at the beginning; the amount of combined phenol was large, the liquid thickened rapidly, and the amount of liquefied bamboo was small. With H_3PO_4 as catalyst, the rate of liquefaction was low, the liquefaction effect was unsatisfactory, and the amount of residue was large. With HCl as catalyst, the rate of liquefaction was high, the amount of combined phenol was moderate, the mobility of the liquid was good, and the amount of residue was small. With BF_3 as catalyst, the situation was the same as for HCl.

3.1.2 Effects of the weight ratio of phenol to bamboo on liquefaction result of bamboo

Given the same conditions as mentioned in 3.1.1, but adjusting the weight ratio of phenol to bamboo to 3:1, 2:1, and 1:1, we obtained samples of BL-5, BL-3, and BL-6 and then measured the residue rates, the combined phenol, and the free phenol. The results are shown in Table 1. From the results we see that, as the amount of bamboo powder increases, the residue rate increases as well. The combined phenol increased only slightly. With an increase in the combined phenol, the proportion of polymer and the viscosity of liquid continued to increase. The mobility of the liquid and the liquefied amount of the bamboo powder were also affected. Given the degree of liquefaction, the most suitable phenol/bamboo ratio was in the range of 2:1–1:1.

3.1.3 Effects of temperature on the liquefaction result of bamboo

Under the conditions of a phenol/bamboo ratio of 2:1, HCL as catalyst, and a liquefaction time of 2 h, we adjusted the temperature of liquefaction to 100, 115, 120, and 130ºC and obtained BL-7, BL-3, BL-8, and BL-9. The results showed that there were large amounts of solid bamboo and residue at 100ºC, but with the increase of the liquefaction temperature, the amount of combined phenol increased and the residue rate began to increase again. Given our results, the liquefaction effect was optimal at 115ºC.

3.1.4 Effects of catalyst dosage on liquefaction result

Again, under the conditions of a phenol to bamboo ratio of 2:1, liquefaction time of 2 h, and a temperature of 115ºC, we adjusted the dosage of the HCL catalyst to 3%, 5%, 8%, and 15% and obtained BL-10, BL-3, BL-11, and BL-12. From the results, also shown in Table 1, we see that with the increase of the catalyst dosage, the rate of liquefaction accelerated, the residue rates decreased, and the combined phenol only increased by a small amount. The effect of increases in liquefaction was not obvious when the dosage of the catalyst was more than 8%.

Table 1 Liquefaction effects of bamboo

Samples	Liquefaction condition				Variance of BL composition			
	Catalyst type	Catalyst dosage /%	$m_p : m_b$ phenol：bamboo	Liquefaction temperature /ºC	Involatile matter /%	Residues /%	Combined phenol /%	Free phenol /%
BL-1	H_2SO_4	5	2: 1	115	70.80	5.50	37.50	29.10
BL-2	H_3PO_4	5	2：1	115	74.40	10.12	41.10	25.50
BL-3	HCl	5	2：1	115	64.30	1.95	31.00	35.60
BL-4	BF_3	5	2：1	115	65.80	1.85	32.50	34.10
BL-5	HCl	5	3：1	115	54.30	0.22	29.30	45.70
BL-6	HCl	5	1：1	115	85.40	2.47	35.40	14.60
BL-7	HCl	5	2：1	100	66.10	6.65	32.80	33.80
BL-8	HCl	5	2：1	120	78.30	5.94	45.00	21.60
BL-9	HCl	5	2：1	130	80.10	8.36	46.80	19.80
BL-10	HCl	3	2：1	115	63.20	5.95	30.00	36.60
BL-11	HCl	8	2：1	115	66.40	1.50	33.10	33.50
BL-12	HCl	15	2：1	115	68.50	1.40	35.20	31.40

3.2 Properties of BLF resin adhesive

3.2.1 Effects of the molar ratio of phenol to formaldehyde on the properties of BLF resin adhesives

By adding formaldehyde twice to BL-3 under alkaline conditions to carry out a poly-condensation reaction, we obtained BLF-1, BLF-2, BLF-3, and BLF-4 and then tested their viscosity, storage period, and bonding strength. The results are shown in Table 2. By increasing the phenol dosage, bonding strength and wood failure increased, while the storage period decreased.

3.2.2 Effects of the ratio of phenol to bamboo on the properties of BLF resin adhesives

Given the previous conditions, but with a molar ratio of phenol to formaldehyde of 1:1.6, adjustment of the weight ratio of phenol to bamboo to 3:2, 2:1, and 1:1 resulted in BLF-5, BLF-2, and BLF-6, respectively. The results of the tested samples are also shown in Table 2. The effects of the ratio on the bonding strength of BLF and the wood failure of BLF plywood were not apparent.

3.2.3 Comparison of the properties of BLF and PF resin adhesives

We carried out gluing tests of PF resin and BLF-6 with a phenol to bamboo ratio of 1:1 and phenol to formaldehyde molar ratio of 1:1.6. The results showed that both bonding strength and wood failure met the standard of GB/T and the intensities of the samples, gently and repeatedly cooked, are all more than 1 MPa (Table 2).

Table 2 Effects of reaction conditions on the properties of BLF resins

Samples	$n_p : n_f$ phenol：formaldehyde	$m_p : m_b$ phenol：bamboo	Viscosity /(MPa·s)	Storage period /day	Bonding results	
					Bonding strength /MPa	Wood failure /%
BLF-1	1：1.5	2：1	700	30	1.03	30
BLF-2	1：1.6	2：1	300	90	1.67	60
BLF-3	1：1.8	2：1	650	45	1.88	65
BLF-4	1：2.0	2：1	800	20	2.22	72
BLF-5	1：1.6	3：1	200	90	1.60	70
BLF-6	1：1.6	1：1	600	80	1.58	66
PF*	1：1.6	–	120	90	1.89	75

Bonding strength of PF resin was tested with a pressing temperature of 140ºC, and that of other samples at 110ºC

3.2.4 Effects of curing behavior on properties of resin adhesives

We compared the bonding strength and wood failure of PF, BLF-2, and BLF-6 by a pressing test. The test results, recorded at the same ratio of phenol to formaldehyde (1:1.6) and different press temperatures, are presented in Table 3.

The temperature of the press greatly affected the bonding strength and wood failure of plywood. Bonding strength and wood failure improved with an increase in press temperatures. BLF resin adhesive had a more satisfactory bonding strength and wood failure at 110ºC. However, PF could not meet this demand at the same temperature.

TG–DSC analysis of PF, BLF-2, and BLF-6 was performed with a thermal analyzer (Net2stch STA409PC, Germany). The samples were heated within a range of 25–300ºC at a heating rate of 10 ºC/min using nitrogen. The results show that all DSC curves displayed two absorption troughs and all TG curves correspondingly exhibited two big weight losses. The first displayed an extramolecular dehydrated absorption trough, and the second displayed intra-molecular dehydration at the corresponding glass transition temperature (Fig. 1). For PF, BLF-2, and BLF-6, the temperatures of the first absorption troughs were 63.2, 64.9, and 56.2ºC, respectively, and the temperatures of the second were 153.8, 114.8, and 112.5ºC. The weight losses for the first trough were 37.5%, 29.2%, and 36.4% respectively, and, for the second, the weight losses were 10.6%, 22.1%, and 14.8%, respectively. The respective glass transition curing temperatures were 153.8, 114.8, and 112.5ºC.

Table 3 Effects of pressing temperatures on properties of plywood

Samples	Pressing temperature /ºC	Pressing time /min	Bonding strength /MPa	Wood failure /%
	110	3	0	0
PF	125	3	0.70	15
	140	3	1.89	75
	110	3	1.67	60
BLF-2	125	3	1.85	78
	140	3	1.89	100
	110	3	1.58	66
BLF-6	125	3	2.22	75
	140	3	2.53	100

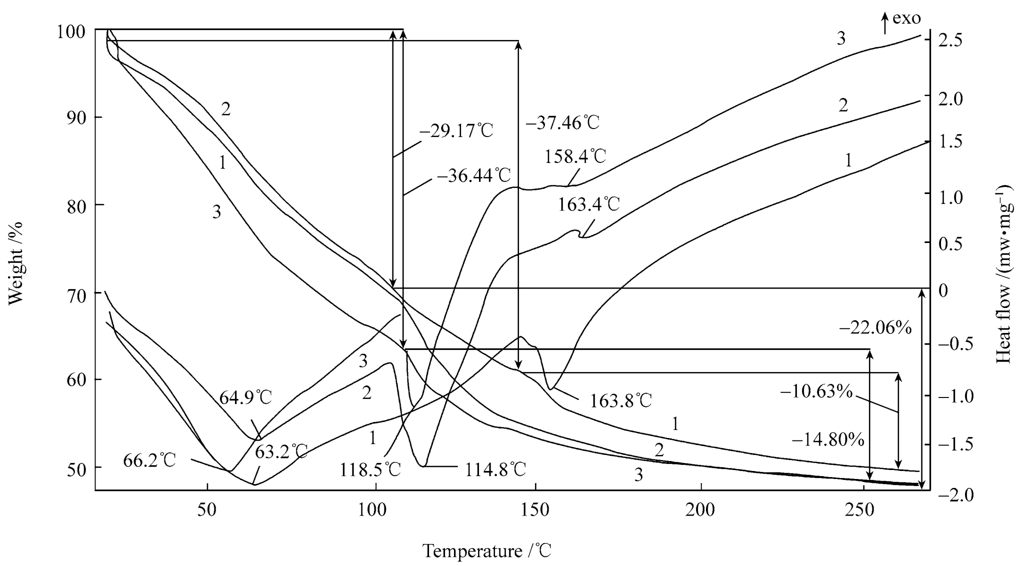


Fig. 1 TG-DSC curve of BLF and PF. 1: PF resin; 2: BLF-2 resin; 3: BLF-6 resin

At the same time, the DSC sample curves of BLF-2 and BLF-6 exhibited small dips at 163.4 and 158.4ºC, probably caused by re-crystallization of BLF resins. Small amounts of pure PF resin, which caused the re-crystallization, were formed by addition and poly-condensation reactions of liquefied phenol resin to formaldehyde, as shown in Fig. 1.

From our experiment we observed that BLF resin adhesives cured at 110ºC, i.e., plywood with BLF resin adhesive reached a good bonding strength by curing at 110ºC, while the temperature for PF curing was between

140–150ºC.

3.3 Analysis of bamboo liquefaction and gluing mechanism

Bamboo and wood have basically similar chemical components: abundant lignin and cellulose. Lignin is a component that liquefies easily with its p-hydroxy phenyl-propane, guaiacyl phenylpropane, and lilacinphenylpropane units (Hui et al., 1997). The bamboo was liquefied in phenol and its mobility, processing properties, curing behavior, and mechanical properties depend, to a large degree, on the condition and kind of liquefaction.

The FT-IR spectra were obtained from a FI-IR spectrometer (Daojin, IR prestige-21) using KBr pellets containing liquid bamboo. The results are shown in Fig. 2. Figure 2 shows two strong absorption bands at 3,440 and 1,240 cm^{-1}, which correspond to phenolic hydroxyl and aromatic ether linkage. BL exhibited strong absorption especially at 1240 cm^{-1}. It is possible that the products of the decomposition of lignin and cellulose were grafted on to the phenolic hydroxyl ring and the products of lignin, or that the aromatic ether linkage was incorporated by phenolic hydroxyl rings and the products of lignin. Pu and Shiraishi (1994) studied lignin liquefied in phenol and used GC–MC technology to analyze the guaiacyl glycerine-β-guaiacyl ether (GG) model. They suggested that homogeneous cracking of GG first occurred at the β-O-4 linkage to form free guaiacyl groups, and then phenol was incorporated into an array of phenolic compounds. Zhang et al. (2001) carried out a GC–MC analysis on bamboo vinegar, produced by cracking and destructive distillation of bamboo, which indicated that there were many methoxyphenols and consisted of more than 16% 2,6-dimethoxyphenol and 4.2% 2-methxyphenol. This also showed that these basic units of bamboo lignin were easy to separate at the fourth linkage of phenol rings.

Cellulose is also the main component of bamboo. Yamada et al. (1996) studied direct phenol liquefaction of cellulose in the presence of water and discovered that the low-molecular intermediates were 5-hydroxymethylfurfural, oligosaccharide, and glucose. The study showed that cellulose was degraded into oligosaccharide, and then 5-hydroxymethxylfurfural turned into a polymer through a poly-condensation reaction. Figure 2 confirms that BL exhibits an absorption peak of —CH_2OH at 100 cm^{-1}, which is consistent with the description provided.

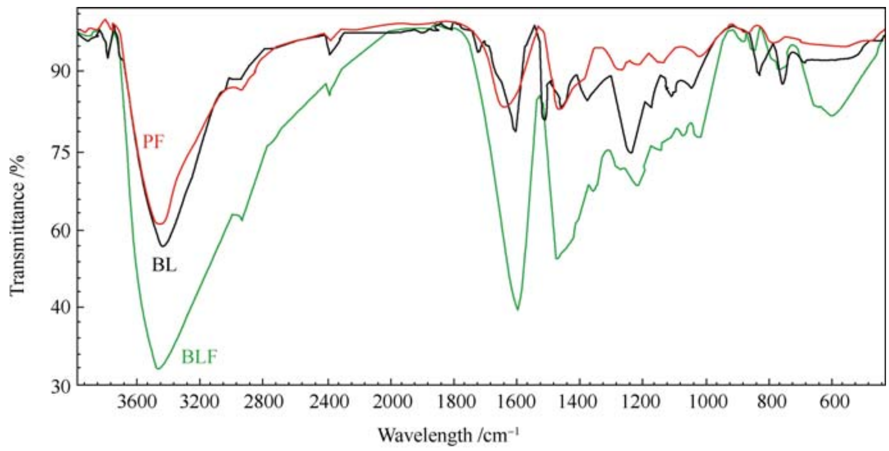


Fig. 2 IR spectra of BL, BLF, and PF

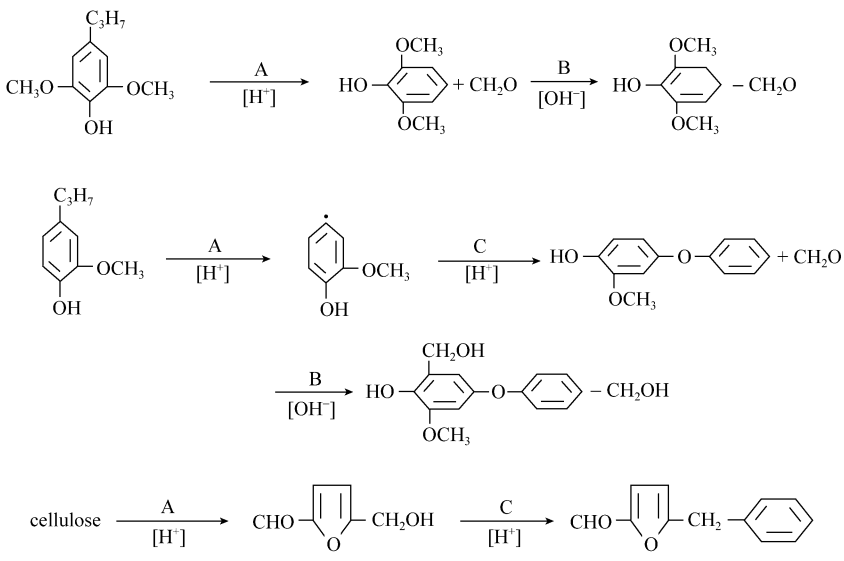
We carried out additional poly-condensation reactions with BL and formaldehyde to form BLF resins, which were compared with pure PF using Fourier transform–infrared (FT–IR) analyses.

We suggested that several characteristic troughs of BLF were consistent with those of PF. This indicated that after being liquefied in phenol, bamboo was changed into liquefied PF adhesives whose structure was better. Several possible reaction procedures of bamboo liquefaction and gluing are given below.

4 Conclusion

The liquefaction of bamboo in phenol was influenced by species and the amount of catalyst, temperature, and the weight ratio of phenol to bamboo. The study showed that the liquefaction effect was good using HCl or BF_3 as catalyst and the liquefaction could be accomplished with a dosage >5%. The study also showed that it could reach liquefaction at 115ºC with a phenol to bamboo weight ratio of 2:1–1:1 and liquefied bamboo with good mobility could be obtained.

BLF was influenced by the molar ratio of phenol to formaldehyde in resin. As the mole number of formaldehyde increased, the bonding strength and wood failure increased; in contrast, the storage period shortened. It was more suitable to control the phenol to formaldehyde molar ratio of 1:1.6. The effect of the weight ratio of phenol to bamboo did not greatly affect BLF properties.



A: cracking in phenal; B: poly-condensation; C: poly-condensation in phenol

Compared to the properties of pure PF, those of BLF were essentially close to PF in mechanical bonding properties of plywood.

TG–DSC analysis showed that the curing temperature of BLF resin was 110℃ and that of PF resin was between 140–150℃.

Analyses of BL, BLF, and PF resin were done by the IR method. The results showed that there were abundant hydroxyl and aromatic ether linkages. This was the reason that the lignin and cellulose of bamboo were cracked to bulk fragments and conjugated with phenol. Several characteristic troughs of BLF appearing in the IR spectra were basically the same as those of PF.

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