Front. For. China 2008, 3(4): 493–498
DOI 10.1007/s11461-008-0076-x

RESEARCH ARTICLE

Fengwen SUN, Xiaoke LI, Qian ZHANG

Technologies of liquefaction of bamboo and preparation of adhesive

Abstract The technology of liquefying processed-waste bamboo with phenol is investigated by single factor trials and an orthogonal design. We studied the preparation technology and properties of adhesives from this phenol-liquefied bamboo with formaldehyde (BPF). The results show that temperature has a significant effect on liquefaction. The effect of the mass ratio of phenol to bamboo comes second and the catalyst dosage within the range of 2%–4% is the least effective. The optimum conditions of liquefaction are as follows: a mass ratio of phenol to bamboo 3.5, a catalyst dosage of 4%, liquefying temperature 145°C and liquefying time 60 min. The liquefaction rate of bamboo reached 99.1%. For the preparation of the adhesive, a mass ratio of liquefied bamboo products to formaldehyde (37%) is 100 to 164.8–199.5, while the ratio 100 to 108.2 is the best. This adhesive has a lower curing temperature than that of normal PF resin. At a hot-press temperature of 130 or 140°C, this new adhesive provides excellent bonding strength of plywood. The most favorable temperature for hot-pressing is 140°C.

Keywords bamboo utilization, liquefaction, adhesive

1 Introduction

China has abundant bamboo resources. In the last 20 years, industrial utilization of bamboo has played an important role in alleviating the pressure on wood supplies and promoting national economic development. But because bamboo has thin walls, a hollow structure and a highly tapered culm, its processing methods are considerably different from those of timber. The outer and inner parts of bamboo are difficult to bond with traditional wood adhesives and as a result, the immediate consumption ratio of bamboo was only 20%–50% in industrial utilization, causing an enormous amount of bamboo wasted (Luo and Wen, 2004; Zheng et al., 2005). Processed-waste bamboo is mainly used as fuel and a small amount as edible fungus culture medium. In recent years, chemical utilization of bamboo has attracted worldwide attention (Zhang, 2001). One method is the technology to produce bamboo carbon rods and bamboo activated carbon using bamboo particles (Liu et al., 2003; Wang et al., 2004). Another method of using bamboo at an industrial level involves a liquefaction mechanism, the alternation of solvent and catalyst, liquefaction technology and the utilization of liquefaction products (Fu et al., 2004; Li et al., 2005). Our project systematically investigated the liquefaction of processed waste bamboo in an acid catalytic and phenol solvent and we further studied the preparation technologies and properties of adhesives for outdoor use, made from liquefaction products instead of phenol.

2 Materials and methods

2.1 Materials

Bamboo: The processed-waste bamboo for our trials was obtained from floor processed bamboo waste. We put the samples into a plant grinder to process it into bamboo powder of sizes between 0.18–0.9 mm in diameter. The powder was dried for 12 h at 103°C and then placed into the desiccator where it remained as material for liquefaction and analysis.

Reagents: First-grade phenol from the Beijing Yan Shan Petrochemical Lt. Co.; Concentrated sulfuric acid, chemically pure, mass fraction: 98%; Formaldehyde: industrial grade, first-rate, mass fraction: 37%; caustic soda: mass fraction: 40%.

2.2 Methods

2.2.1 Process of bamboo liquefaction

We put the bamboo powder and phenol into a 500 mL three mouth flask with a condenser in accordance with a

Translated from *Chemistry and Industry of Forest Products*, 2007, 27(6): 65–70 [译自: 林产化学与工业]

Fengwen SUN (✉), Xiaoke LI, Qian ZHANG
Bamboo Engineering Research Center, Nanjing Forestry University, Nanjing 210037, China
E-mail: sunfw2188@sohu.com

given mass ratio, heated the oil bath and stirred the reactants synchronously. Sulfuric acid of a given mass ratio was put into the flask when the inner temperature reached 30°C below the set temperature. We began timing while the temperature reached a set temperature and cooled the reactants quickly to room temperature at a predetermined time.

2.2.2 Test method of liquefaction technology

We first used single factor trials to determine the region where significant effects might be expected from the action of the various factors. We then used a $L_9(3^4)$ orthogonal design to investigate the interaction of the factors on liquefaction products in order to determine the best liquefaction technology.

2.2.3 Measurement of bamboo liquefaction rate of liquefaction products

We used methanol to dissolve the liquefaction products and then filtered them through a Buchner filter by using filter papers (medium speed quantitative filter paper) and then used methanol to wash the filter residue until it became colorless. We dried the filter residue at 103 ± 2°C to constant quality and then put it into the desiccator and weighed the filter residue after it cooled down to room temperature. We used the following formula to calculate the liquefaction proportion.

$$y_R = (m_r/m_0) \times 100\%;\ y_L = 1 - y_R$$

where m_r is the amount of oven-dry bamboo powder residue (g), m_0 is the amount of oven-dry bamboo powder before liquefying (g), y_R is the proportion of residue (%) and y_L is the proportion of liquefaction (%).

2.2.4 Preparation of adhesive from the liquefaction product with formaldehyde (BPF)

The phenol-liquefied bamboo product, 40% caustic soda and a certain amount of H_2O were put into the 500 mL three mouth flask in a 40–45°C water bath and stirred for 10 min. We then slowly added the formaldehyde solution into the flask, heated the water bath to the set temperature at a rate of about 2°C/min, and maintained it for 20 min as the temperature slowly increased to 70°C. Then, the temperature was increased quickly to 85–92°C and kept at this temperature for a certain amount of time. We determined the viscosity of the adhesive continuously in the process of chemical reaction, cooled the reaction below 40°C quickly with cold water when the viscosity met our standard of qualification and stopped stirring, discharging the reaction products.

2.2.5 Preparation of phenol formaldehyde adhesive (PF)

We placed the melting phenol in the reaction vessel, stirred and heated to 40–45°C, added water and liquid caustic soda and stirred for 15 min. We added the first batch of formaldehyde (80% of the total amount of formaldehyde), heated to 85–90°C and let the mixture react for 60 min at this temperature. Then, the rest of the formaldehyde was added, we determined the viscosity after reacting for 30 min at a temperature of 90 ± 2°C and cooled the reaction products below 40°C and discharged them. The molar ratios of phenol to formaldehyde to caustic soda are 1:1.98:0.4 in the formulation.

3 Results and discussion

3.1 Effects of various factors on bamboo liquefaction

Given previous studies on wood liquefaction, we selected the mass ratios of phenol to bamboo, catalyst dosage, liquefying temperature and liquefying time as the main factors affecting our experiment. We fixed the parameter values of three of the factors and studied the effect of the variation in the other factor on bamboo liquefaction.

3.1.1 Effect of liquefying time on bamboo liquefaction

Liquefying time is the most important factor that affects the reaction of bamboo liquefaction. For the mass ratio of phenol to bamboo of 3:1, a catalyst dosage of 3% and a liquefying temperature of 130°C, the effects of liquefying time on bamboo liquefaction are shown in Fig. 1.

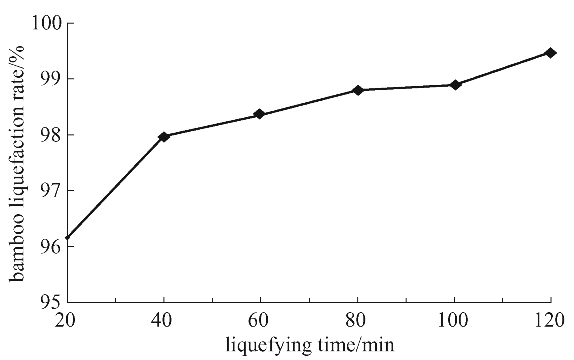

Fig. 1 Effect of time on bamboo liquefaction

Figure 1 shows that in the first 40 min of reaction, the liquefaction speed was relatively fast. The proportion of bamboo liquefaction was 96.16% after reacting for 20 min. When the reaction time was 40 min, the proportion of bamboo liquefaction was 97.98%, after which the speed slowed. When the reaction time reached 100 min, the proportion of bamboo liquefaction was 98.89%, an improvement of only 0.91%. This experimental result shows that the effect of bamboo liquefaction is very clear in the first 20–40 min. The liquefaction reaction approached equilibrium over time. In our case the proportion of liquefaction did not improve very much over time after 40 min. Lin et al. (2001) used sulfuric acid in wood phenol liquefaction and found that the liquefaction time had an obvious effect on liquefaction, which is the same as our experiment.

3.1.2 Effect of liquefying temperature on bamboo liquefaction

Liquefaction temperature has the same effect on bamboo liquefaction as liquefaction time. For a mass ratio of phenol to bamboo of 3:1, a catalyst dosage of 3% and liquefying time of 40 min, the effect of liquefying temperature on bamboo liquefaction is shown in Fig. 2.

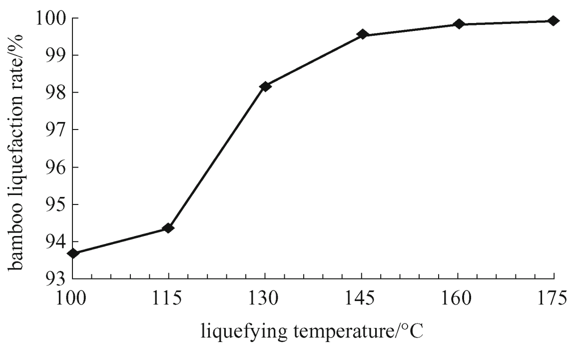

Fig. 2 Effect of temperature on bamboo liquefaction

Figure 2 shows that, given the increase in reaction temperature, the general trend in the proportion of liquefaction is improved. The increasing amplitudes are different within the different temperature ranges, which can be divided into three stages, where the temperatures of 115°C and 145°C are important inflection points. At the initial stage of rising temperature, i.e., from 110–115°C, the speed of bamboo liquefaction was very slow and the proportion of liquefaction only improved by 0.75%. In the middle stage of the rising temperature, i.e., from 115–145°C, the proportion of liquefaction increased quickly and reached 99.52% at a temperature of 145°C. At temperatures higher than 145°C, the liquefaction rate became flat and the liquefaction efficiency tended to become stable. Alma et al. (1996) used sulfuric acid as a catalyst in wood phenol liquefaction and found that liquefaction temperature has a clear effect on the liquefaction rate.

3.1.3 Effect of mass ratio of phenol to bamboo on bamboo liquefaction

Phenol plays the role of catalyst in decomposition and as an inhibitor in the recondensation of intermediate products, which make the mass ratio of phenol to bamboo be an important factor in the effect on bamboo liquefaction. For a liquefying temperature of 130°C, a liquefying time of 40 min and a catalyst dosage of 3%, the effect of the mass ratio of phenol to bamboo on bamboo liquefaction is shown in Fig. 3.

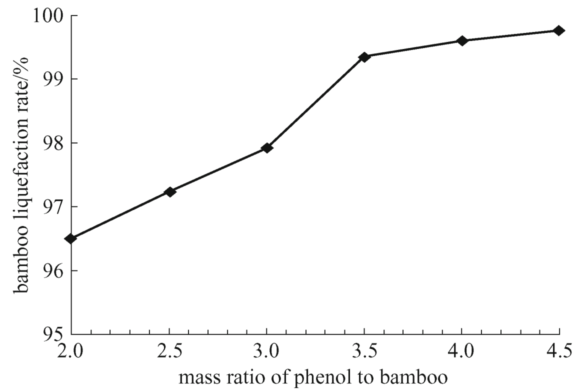

Fig. 3 Effect of mass ratio of phenol to bamboo on bamboo liquefaction

From Fig. 3 we can see that the mass ratio of phenol to bamboo has an obvious effect on bamboo liquefaction. With an increase in the mass ratio of phenol to bamboo, the general trend of liquefaction rate is one of improvement. With the increases of mass ratio of phenol to bamboo, the numerical changes can be divided into two stages: in the first stage, where the mass ratio of phenol to bamboo increased from 2 to 3.5, the proportion of bamboo liquefaction increased quickly from 96.5% to 99.36%; at the second stage, when the mass ratio of phenol to bamboo increased from 3.5 to 4.5, the increase had little discernable effect on bamboo liquefaction, which shows that the liquefaction reaction approached equilibrium. Alma et al. (1996) used sulfuric acid as a catalyst in wood phenol liquefaction and found that the mass ratio of phenol to wood had an obvious effect on the proportion of residue. When the mass ratio of phenol to wood increased from 1 to 5, the proportion of residue of liquefaction products reduced by 33%. With a further improvement in the mass ratio of phenol to wood, the amount of residue of liquefaction products reduced to about 1%.

3.1.4 Effect of catalyst dosage on bamboo liquefaction

Catalysts promote bamboo degradation reactions. A strong acid catalyst affects both the rate and the form of the liquefaction reaction. For a liquefying temperature of 130°C, a liquefying time of 40 min and a mass ratio of phenol to bamboo of 3:1, the effect of the catalyst dosage on bamboo liquefaction is shown in Fig. 4.

From Fig. 4 we can see that the catalyst dosage has the same effect on bamboo liquefaction as the mass ratio of phenol to bamboo. Along with the increase in the catalyst dosage, the liquefaction rate also increased. It also has two stages: in the first stage, when the catalyst dosage was

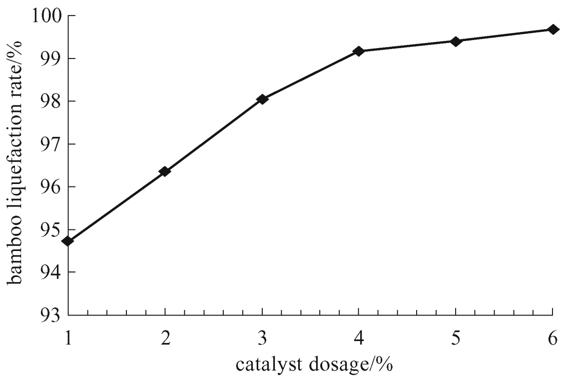

Fig. 4 Effect of catalyst dosage on bamboo liquefaction

between 1% to 4%, it had an obvious effect on the liquefaction rate; When the catalyst dosage was 1%, the proportion of liquefaction was 94.71%; When the catalyst dosage increased to 4%, the proportion of liquefaction was 99.17%. During the second stage, when catalyst dosage increased from 4% to 6%, the increase had no significant effect on the bamboo liquefaction rate. Alma et al. (1996) used sulfuric acid as a catalyst in wood phenol liquefaction and found that when the catalyst dosage increased from 0.5% to 3%, the proportion of residue of liquefaction products reduced by 24%.

3.2 Optimum conditions of bamboo liquefaction

We need to consider the combined effects of various factors on bamboo liquefaction to determine the optimum technological parameters. We selected an incomplete $L_9(3^4)$ orthogonal design (Table 1) and according to the rules of the effect of a single factor, determined the test level of every factor. The test scheme and range analysis results are listed in Table 2 and significant test results of liquefaction are listed in Table 3.

Table 1 Factors and levels graph

level	A time/min	B temperature/°C	C mass ratio of phenol to bamboo	D catalyst dosage/%
1	20	115	2.5	4
2	40	130	3.0	3
3	60	145	3.5	2

The test results and the analysis in Tables 2 and 3 show that the order of the effect of the four factors we selected in our experiment is as follows: temperature (B) > mass ratio of phenol to bamboo (C) > time (A) > catalyst dosage (D). Within the test ranges, the effect of temperature and mass ratio of materials on liquefaction rate are very clear, as is the effect of time on liquefaction rate. The effect of the catalyst dosage has no statistically significant effect on the liquefaction rate; a favorite horizontal combination is $A_3B_3C_3D_1$. On the condition of optimum liquefaction technology we conducted a replicate test, for which the conditions were as follows: a liquefaction time of 60 min, liquefaction temperature of 145°C, mass ratio of phenol to bamboo of 3.5 and a catalyst dosage of 4%. We obtained a proportion of bamboo liquefaction products of 99.1%.

3.3 Preparation of BPF adhesives

We used the liquefaction products obtained under optimum liquefaction technology and added formaldehyde with different weight proportions (Table 3) into the reaction vessel with the same control process to make the adhesive.

The reaction process shows that the greater the formaldehyde dose, the shorter the time that the adhesive reached the viscosity level set at a high temperature. In the holding process at a temperature of 92°C, after BPF_1, BPF_2 and BPF_3 reached our set viscosity, the viscosity increased very quickly, gel occurred in 2–5 min after many repetitive experiments. When the formaldehyde dose is larger, the holding temperature will be 85°C, and the BPF_4 and BPF_5 reaction temperature at 90 ± 2°C. The rational holding times are listed in Table 4.

We determined each performance index of the adhesive according to the standard GB/T 14074–2006 *Testing methods for wood adhesives and their resins*. The results are listed in Table 5.

3.4 Adhesion properties of BPF adhesives

At first, we employed differential scanning calorimetry to analyze the hot-curing characteristics of several adhesive samples, under the following test conditions: nitrogen flow rate 50 mL/min, heating rate 10°C/min, temperature range 25–300°C, sample mass 10 mg (Zhu, 2004). The results are listed in Table 6.

Compared to PF, the first absorption peak of BPF, temperature difference is $\pm$ 12°C. The first absorption peak of BPF_3 is the nearest to that of PF, which shows that they have similar hot-curing characteristics. The degree of difference of the first absorption peak between BPF_5 and PF is the greatest, in second place are BPF_4, BPF_1 and BPF_2, the differences are 11.1, 10.5 and 2.6°C, respectively. The curing temperature of BPF is lower than that of PF. The curing temperature of PF is 150.1°C, and the highest and lowest curing temperatures of BPF are 146.2 and 130.9°C, respectively, which shows that BPF cures more fully under lower heating temperatures.

Secondly, we used these adhesives to make three layers of poplar plywood and tested their bonding strength. The thickness of the veneer was 1.7 mm and the moisture content 8%–12%. We mixed the adhesives with flour according to a certain proscribed ratio and stirred uniformly. The viscosity was 2200 mPa·s. The amount of glue spread was 270–280 g/m^2 and the curing time was 1 h. Hot pressing parameters were as follows: temperature 130 and

Table 2 Design and result of orthogonal trial

test No.	A time/min	B temperature/°C	C mass ratio of phenol to bamboo	D catalyst dosage/%	bamboo liquefied ratio/%
1	20	115	2.5	4	94.89
2	20	130	3.0	3	96.00
3	20	145	3.5	2	99.27
4	40	145	2.5	3	98.62
5	40	115	3.0	2	94.71
6	40	130	3.5	4	99.37
7	60	130	2.5	2	98.78
8	60	145	3.0	4	98.95
9	60	115	3.5	3	97.43
k_1	96.72	95.68	97.43	97.74	
k_2	97.57	98.05	96.55	97.35	
k_3	98.39	98.95	98.69	97.59	
range	1.67	3.27	2.14	0.39	

Table 3 Analysis of variance of bamboo liquefaction ratio

factors	mean square errors	degrees of freedom	*F* values	critical value of *F*
A	4.167	2	18.276	$F_{0.10} = 9.00$
B	17.130	2	75.132	
C	6.921	2	30.355	
D	0.228	2	1.000	
error	0.23	2		

Table 4 Mass ratios of tested raw material

resins	phenol-liquefied product: formaldehyde solution (m:m)	heating time
BPF_1	100:216.8	20
BPF_2	100:199.5	22
BPF_3	100:182.1	30
BPF_4	100:164.8	32
BPF_5	100:147.4	35

140°C, specific pressure 1.3 MPa, time 1 min/mm. We tested its strength according to the standard GB/T 17657–1999 *Test methods of evaluating the properties of wood – based panels and surface decorated wood-based panels* after laying the plywood for 24 h. The results of the specimens tested are listed in Table 6.

The data from Table 6 shows that for each adhesive, under the two heating temperature, the bonding strength of the plywood is better at 140°C. For the five BPF adhesives, the bonding strength of BPF_3 was best, even better than PF at 130°C. All of these adhesives can meet the standards of class I plywood at 140°C.

4 Conclusions

1) When sulfuric acid is used as a catalyst, the bamboo has good liquefaction in phenol. In the process of

Table 5 Physical properties of several adhesives

resins	appearances	viscosity/mPa·s (by rotational viscometer)	solid mass part/%	storage time/d
BPF_1	fuscous non-transparent viscous liquid	605	39.64	3–5
BPF_2	fuscous non-transparent viscous liquid	630	38.34	10–15
BPF_3	fuscous non-transparent viscous liquid	670	40.30	⩾60
BPF_4	fuscous non-transparent viscous liquid	596	39.52	⩾60
BPF_5	fuscous non-transparent viscous liquid	625	41.58	⩾60
PF	rufous semitransparent viscous liquid	800	48.39	⩾60

Table 6 Hot-curing characteristics and bonding strength of several resins

	hot-curing characteristics		bonding strength/MPa	
	temperature of the first endothermic peak/°C	curing temperature/°C	hot-pressing at 130°C	hot-pressing at 140°C
BPF_1	78.0	134.8	1.25	1.40
BPF_2	91.1	138.0	1.30	1.48
BPF_3	89.8	139.6	1.48	1.65
BPF_4	77.4	130.9	1.35	1.52
BPF_5	76.5	146.2	0.80	1.11
PF	88.5	150.1	1.32	1.72

bamboo liquefaction, the effect of temperature on the liquefaction rate is most obvious. In second place, is the mass ratio of phenol to bamboo, time and catalyst dosage. In the test ranges, the higher the temperature, the greater the phenol dosage, the longer the time and the greater the catalyst dosage, the better the effect of liquefaction.

2) The results of the single factor trial and orthogonal trials show that the optimum liquefaction technology of liquefying processed-waste bamboo with phenol occurs under the following conditions: mass ratio of phenol to bamboo 3.5, catalyst dosage 4%, liquefying temperature 145°C and liquefying time 60 min. The proportion of liquefaction of bamboo reached 99.1%.

3) We can use the liquefaction products of processed-waste bamboo with phenol to prepare plywood for outdoor use with excellent properties. For good results, the following specifications apply: mass ratio of liquefied bamboo products to formaldehyde (37%) is100 to 164.8–199.5, while the ratio 100 to 108.2 is the best. This adhesive has a lower curing temperature than that of normal PF resins. At a hot-press temperature of 130 or 140°C, this new adhesive can provide excellent bonding strength of plywood which meets the national standard requirements. The most favorable temperature is 140°C.

References

Alma M H, Yoshioka M, Shiraishi N (1996). Preparation of sulfuric acid-catalyzed phenolated wood resin. Wood Sci Tech, 32: 297–308

Fu S Y, Ma L F, Li W S (2004). Studies on liquefaction of bamboo and properties of liquefied-bamboo adhesives. Chem Ind For Prod, 24(3): 42–46 (in Chinese)

Li G Y, Qin T F, Huang L H (2005). Preparation and characterization of liquefied wood in presence of phenol under acid catalysis. China Wood Ind, 19(2): 28–31 (in Chinese)

Lin L, Yao Y, Shiraishi N (2001). Liquefaction mechanism of β-O-4lignin model compound lignin in the presence of phenol under acid catalysts. Part II Reaction behavior and pathways. Holzforschung, 55: 624–630

Liu Z K, Shao Q J, Yu Y L, Ye D H (2003). Study on comprehensive of utilization of bamboo surplus material of processing (II). J Bamboo Res, 22(3): 44–48, 61 (in Chinese)

Luo X X, Wen R M (2004). Research and commentary of the developing and utilization of the remainders of bamboo material processed. J Hunan City Univ (Nat Sci), 13(3): 62–64 (in Chinese)

Wang S D, Zheng X F, Bai R H, Song D Y (2004). A study on producing active carbon by the surplusages of bamboo timber. J Bamboo Res, 23(2): 39–41 (in Chinese)

Zhang Q S (2001). Paying great attention on bamboo chemical processing and exploiting bamboo charcoal applying technique. J Bamboo Res, 20(3): 34–36 (in Chinese)

Zheng D D, Liu Y Y, Lin X Y, Bai S, Ruan R S (2005). Approaching the bamboo waste development and utilization. J Fujian For Sci Tech, 32(2): 153–157 (in Chinese)

Zhu C S (2004). Polymer Structure Analysis. Beijing: Science Press, 158–196 (in Chinese)