

Modification of Wood Flour/Phenolic Resin Composites with Bamboo Pulp Residue

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Abstract

The purpose of this paper is to discuss the influence of different proportions of bamboo pulp residue on the bending strength, the static bending strength, the water absorption rate, and the microstructure of wood flour/phenolic resin composites. The level of bamboo pulp residue ranged from 0 to 30 percent. According to the optimum technological parameters of the pretest, the resin content, the molding temperature, and the molding time were controlled within 51 to 54 percent, 152°C to 160°C, and 51 to 60 s/mm, respectively. Compared with the control group, there were remarkable improvements in the mechanical properties, indicating that the bending strength, the static bending strength, and the water absorption rate increased by 39, 31, and -6 percent, respectively. The greatest level of bamboo pulp residue was 20, 20, and 10 percent for the bending strength, the static bending strength, and the water absorption rate, respectively. All of the above proved that the wood flour/phenolic resin composites can be modified by adding bamboo pulp residue.

According to statistics from 2016, the forest coverage rate in China is approximately 21.93 percent, far below the world's overall forest coverage of 30 percent (Yi 2017). Also, China is one of the world's largest producers and consumers of wood materials (Yu et al. 2018). Currently, commercial timber is being cut by more than one third, and it is estimated that the supply and demand gap will reach 180 million m³ by 2020 (Bai 2008, Xu et al. 2015), which makes the disparity between supply and demand of wood more prominent. In China, about 150 million tons of forestry residues are produced every year during harvest and timber production (Huang 2018), and 100 thousand tons of bamboo sawdust need to be managed every year (Wang 2012). A large amount of waste can be used to form new products or materials through scientific processing, thus fully using resources, saving high-quality raw materials, and solving the problem of insufficient raw materials. Use of forestry waste can also ease the gap between supply and demand, reduce the costs of production, and lessen the burden on enterprises (Liu 2003). This usage is an important way to promote the development of regional economies in forest areas (Bai 2018).

There are two traditional treatment methods of pulping solid waste produced by the paper industry: landfill and incineration. These methods create serious problems for soil

and atmosphere pollution and are a great waste of resources (Cao 2009). According to statistics, each ton of paper pulp production yields about 150 kg oven-dry weight of paper sludge and 0.65 tons of white mud under the current technological conditions (Tuomas et al. 2014). The main components of paper sludge are fiber fines, lignin, polysaccharides, and several kinds of inorganic salts (Zhang and Liu 2015). At present, there is much research regarding the efficient use of paper sludge in the world, which mainly focuses on the use of mixed sludge to make bricks, composite materials, compost, fuel incineration, and so on. After modifying the methods by using a coupling agent, the

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sludge can be filled in thermoplastic materials such as polypropylene, polyethylene, polyvinyl chloride, etc. (Rujnićsokele et al. 2005). The white mud can be used to prepare polymer matrix composites, cement-based composite materials, and nanocomposite materials (Wang 2011).

Bamboo pulp residue, a currently hot topic for researchers, was also studied. In the process of bamboo pulping and paper making, the main solid residues are bamboo sawdust and white mud. The treatment methods of white mud were stacking and landfill, and the main treatment of bamboo sawdust was incineration, which causes serious pollution and destruction to the environment (Ren 2014). Results from the research on how best to use bamboo pulp sludge state that it can be used to manufacture plates and improve soil, and it has agriculture applications (Liu et al. 2009). According to other researchers who have conducted experiments, high-performance bamboo-plastic composite materials can be prepared by using the bamboo pulp residue, which saves resources, turns waste into consumable goods, creates more raw material sources for the manufacture of bamboo-plastic composites, and decreases energy consumption in the treatment of bamboo pulp residue (Chen et al. 2012). Also, it greatly reduces the production and processing costs of products and effectively balances the contradiction between environmental protection and economic benefits (He et al. 2014).

Therefore, this article explains how bamboo pulp residue was selected to replace part of the wood flour used to prepare wood flour/phenolic resin composites. We studied the effect of different ratios of bamboo pulp residue on phenolic resin composites performance based on the optimal parameters from the pretest. By modifying the phenolic resin composites with bamboo pulp residue, we can effectively improve the performance of wood flour/phenolic resin composites and expand the application of bamboo pulp residue.

Materials and Methods

Materials

Poplar powder was 80 mesh, prepared from wood products processing residue sawdust through smashing and grinding (purchased from Tang County, Hebei, China). Thermosetting phenolic resin (PF) was 60 to 100 cps viscosity (25°C), 1.195 to 1.205 g/cm³ specific gravity, 42.5 to 44.5 percent solid content, pH 12 to 14, alkalinity 7.2 to 7.7 percent, red transparent liquid, product name 14L962 (Beijing Taier Chemical Co., Ltd., Beijing, China). Phosphorus pentoxide (P₂O₅) was analytically pure. For bamboo pulp paper residue, bamboo outer skin was the main compound (Guizhou Chitianhua Paper Co., Ltd., Guizhou, China).

Material preparation

In the laboratory, bamboo pulp residue/wood flour-reinforced phenolic resin composites were prepared by a wet process. First, the wood flour and bamboo pulp residue were mixed in proportion (Table 1). Next, the mixture was evenly mixed with the liquid phenolic resin (Table 1). Then, water was removed by the DZF-6020 vacuum dryer, and, finally, semifinished molded plastic products were obtained.

Owing to the uneven nature of mixing through manual operation, it was necessary to manually stir the phenolic resin into the container first, dividing the mixture into small

Table 1.—The ratio of materials in composites.

Wood flour ratio (%)	Bamboo pulp residue ratio (%)	Phenolic resin ratio (%)		
		The first group	The second group	The third group
90	10	54	54	51
80	20			
70	30			

parts. Then, the LD-Y500A high-speed universal grinder was used with a variable pressure plug to stir, which is suitable for mixing small batches of materials in the laboratory. During this process, material particles were mixed, causing collision and friction, making the materials evenly mixed within a short molding time (Zhao 2012). Owing to the fast rotation speed in the universal grinder and the material colliding with the impeller, a large amount of heat was generated. To avoid the material curing too early, the EA-T1625X-YELLOW stepless voltage regulator was equipped to adjust the speed. The transformer was divided into 10 files, the voltage regulator was adjusted for four to five gears, and the materials were mixed for 5 minutes according to their amount. The mixed materials had a high moisture content at this time, which lengthened the molding powder's production cycle. This issue may cause the product to blister and penetrate, resulting in defective products. Then it was dried. Through the experimental analysis, the moisture content must be less than 10 percent. Because the molding temperature can affect the curing of the thermosetting phenolic resin, a DZF-6020 vacuum oven was used for drying, and an appropriate amount of P₂O₅ solid powder was placed in the vacuum oven to remove moisture quickly. The materials were dried in the vacuum drying oven for 24 hours at room temperature until moisture content was below 10 percent.

After drying, some molding powder formed in bulk. The DQM-2L variable frequency single planetary ball mill was used to crush and mix materials, using the impact of the falling, grinding body, and the grinding effect of the grinding body with the grinding ball's inner wall. The ball milling speed was 100 r/min, and the powder was milled for 10 hours.

The molding powder was obtained, then composite materials were prepared through a molding process, with a molding pressure of 15 MPa and a molding dimension of 160 mm by 15 mm by 10 mm.

Performance testing

Bending strength was determined according to the GB/T1936.1-2009 Wood bending strength test method. Static bending strength was determined according to the GB/T1449-2005 fiber reinforced plastic bending performance test method. Water absorption rate was determined according to the provisions of GB/T11718.3-2009. Before and after immersion, the mass ratio and weight difference of composite specimens were determined and calculated with a balance. Five test pieces were selected for each group, and their arithmetic mean values were taken as the results.

The SU8010 scanning electron microscope was used to characterize the microstructure of the cross section of the composites.

Results and Discussion

Effect of different ratio residue on the bending strength

According to the pretest, the resin content was 54.23 percent, the molding temperature was 156.82°C, the molding time was 60 s/mm, and the prediction value of the bending strength was 45.35 MPa. The verification test yielded similar conditions, in which the resin content was 54 percent, the molding temperature was 157°C, the molding time was 60 s/mm, and the bending strength was 43.783 MPa. According to the pretest and the filler ratio in composites, this research reports the latter conditions. The ratio of bamboo pulp residue to total filler was 10, 20, and 30 percent. The test results of bending strength are shown in Figure 1.

Figure 1 shows that the bending strength was 43.783 MPa when the ratio of bamboo pulp residue was 0 percent, which means the filler was pure wood flour. When the bamboo pulp residue accounted for 10, 20, and 30 percent of the filler, the bending strength was 52.54, 60.85, and 54.73 MPa, respectively. Compared with the filler that was pure wood flour, adding the bamboo pulp residue increased the bending strength of composites by 20.00, 38.98, and 25.00 percent. The greatest bamboo pulp residue level was 20 percent. The reason may be that the bamboo fibers' strength, toughness, and stiffness were better than wood flour (Wang et al. 2016). With the increase of bamboo sawdust, the number of hydroxyl groups in bamboo/wood fibers increased. Phenolic resin can effectively wrap the mixed filler by the dehydration condensation reaction. With the hydroxyl groups in bamboo pulp residue and wood flour, strong hydrogen bonding occurred between the molecular chains of cellulose, thus increasing the strength of the composites (Ren et al. 2014). However, when the amount of bamboo sawdust was increased too much, it could not be effectively wrapped with phenolic resin, so the strength began to decrease.

Effect of different ratio residue on the static bending strength

According to the pretest, when the resin content was 54.29 percent, the molding temperature was 160.11°C, the molding time was 51.88 s/mm, and the predicted value of the static bending strength was 26.5167 MPa. The verification test predicted similar conditions, in which the resin content was 54 percent, the mold temperature was 160°C, and the molding time was 51 s/mm. Five sets of parallel tests were performed, and the average value was 25.231 MPa. This research reports the latter conditions; the ratio of bamboo pulp residue to total filler was selected as 10, 20, and 30 percent. The test results of static strength are shown in Figure 2.

Figure 2 shows that when the filler was pure wood flour, the static bending strength was 25.231 MPa, and when the ratio of bamboo pulp residue was 10, 20, and 30 percent, the static bending strength was 30.59, 32.81, and 31.54 MPa, respectively. The static strength of the composites' materials increased by 21.24, 30.03, and 25.00 percent by the bamboo pulp residue proportion of 10, 20, and 30 percent, respectively. The composites were strongest when the addition ratio was 20 percent. This is related to the increase of bamboo sawdust, leading to greater numbers of hydroxyl groups in the mixture. With the dehydration condensation

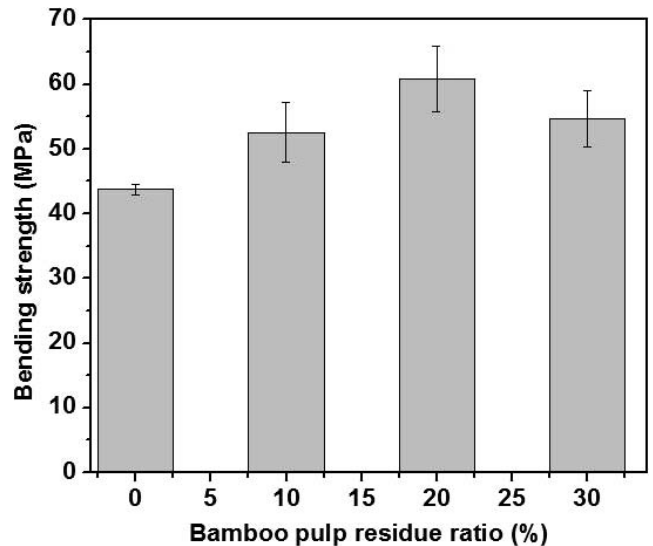


Figure 1.—Effect of bamboo pulp residue filler ratio on the bending strength.

reaction, phenolic resin can effectively wrap mixed filler with hydroxyl groups in bamboo/wood flour. Also, strong hydrogen bonding occurred between the molecular chains of cellulose, increasing the strength of the composites. When the amount of bamboo sawdust increased, it could not be effectively wrapped with phenolic resin, and the static bending strength started to decrease (Zhang et al. 2006).

Effect of different ratio residue on the water absorption rate

According to the pretest, when the resin content was 50.61 percent, the molding temperature was 152.35°C, the molding time was 60 s/mm, and the water absorption rate prediction value was 5.33 percent. The verification test predicted similar conditions, in which the resin content was 51 percent, the mold temperature was 152°C, and the

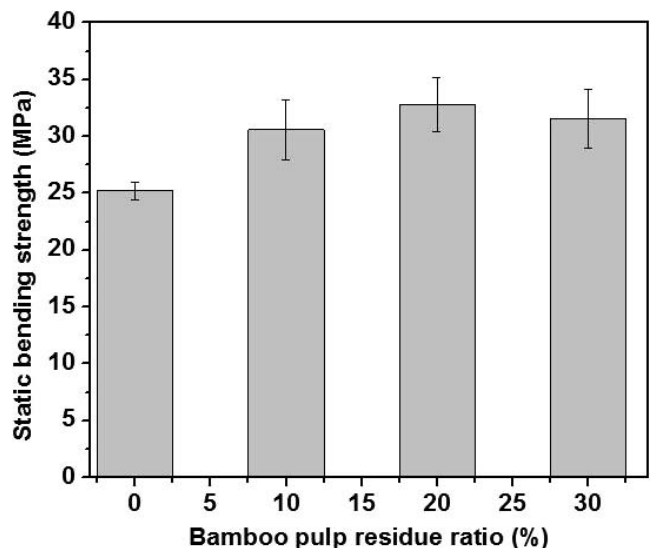


Figure 2.—Effect of bamboo pulp residue filler ratio on the static bending strength.

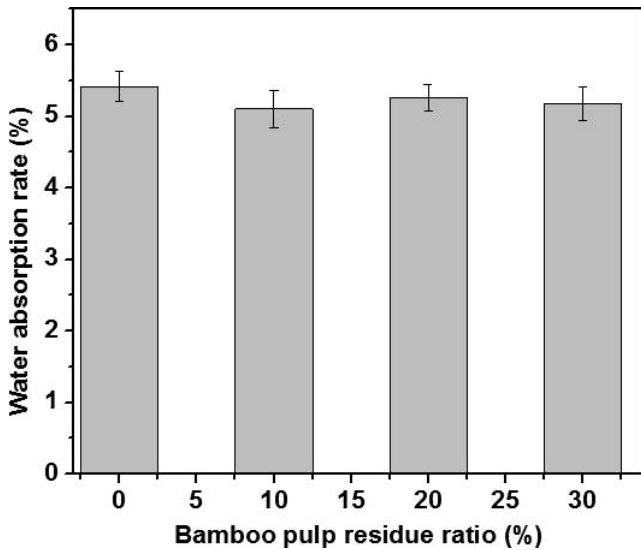


Figure 3.—Effect of bamboo pulp residue filler ratio on the water absorption rate.

molding time was 60 s/mm. Five sets of parallel tests were performed, and the average value obtained was 5.42 MPa. Testing with the water absorption rate as the dependent variable, this research reports the latter conditions. The results are shown in Figure 3.

The effect of bamboo pulp residue on the water absorption rate is shown in Figure 3. It shows that the water absorption rate of pure wood flour was 5.42 percent, the ratio of bamboo pulp residue to filler was 10, 20, and 30 percent, and the water absorption rate was 5.11, 5.26, and 5.18 percent, respectively. Compared with the pure wood flour group, the water absorption rate was not much different, and the trend in the figure was not obvious. Therefore, the addition of bamboo pulp residue had little effect on the water absorption rate of phenolic resin composite materials, only a certain degree of reduction by 5.72, 2.95, and 4.43 percent, respectively. The reason may be that there were a large number of hydroxyl groups in the

bamboo sawdust and wood flour fiber molecules, and the surface had strong chemical polarity and strong water absorption. However, the phenolic resin is nonpolar and hydrophobic. With the increase of bamboo pulp residue, the phenolic resin cannot wrap it, thus excessive hydrophilic hydroxyl groups were exposed, which increased the water absorption (Lei 2015).

Microstructure analysis of composite materials

Figure 4 shows the microstructure of pure composites with wood flour as fillers, and Figure 5 shows the microstructure of composites with bamboo pulp and wood flour as fillers. Figure 4 shows that the microstructure of the composite materials without bamboo pulp residue was lamellar, and the structure was relatively smooth where the fiber was covered more uniformly by the adhesive. The structure of the composite materials with bamboo residue added in Figure 5 presents a loose three-dimensional network. From a mechanical perspective, the three-dimensional network structure had two effects: interweaving forces and chemical bonds (Tang 2016), which also explained that the mechanical properties of the composite materials with bamboo pulp residue were better than those of composite materials with pure wood flour. The reason for forming a three-dimensional mesh structure was that, through the same process conditions, bamboo pulp residue became harder, and wood flour became softer. Therefore, the destruction of bamboo pulp fiber structure was less than wood flour fiber, making it easy to form a three-dimensional mesh structure. Thus, bamboo pulp residue can be added to enhance the mechanical properties of composites.

Conclusions

In this study, we found that it was feasible to modify wood flour/phenolic resin composites by adding bamboo pulping residue. There was a significant enhancement effect on composites when the proportion of bamboo pulp residue ranged from 10 to 30 percent. The bending strength increased by 20.00, 38.98, and 25.00 percent, and the static bending strength increased by 21.24, 30.03, and 25.00

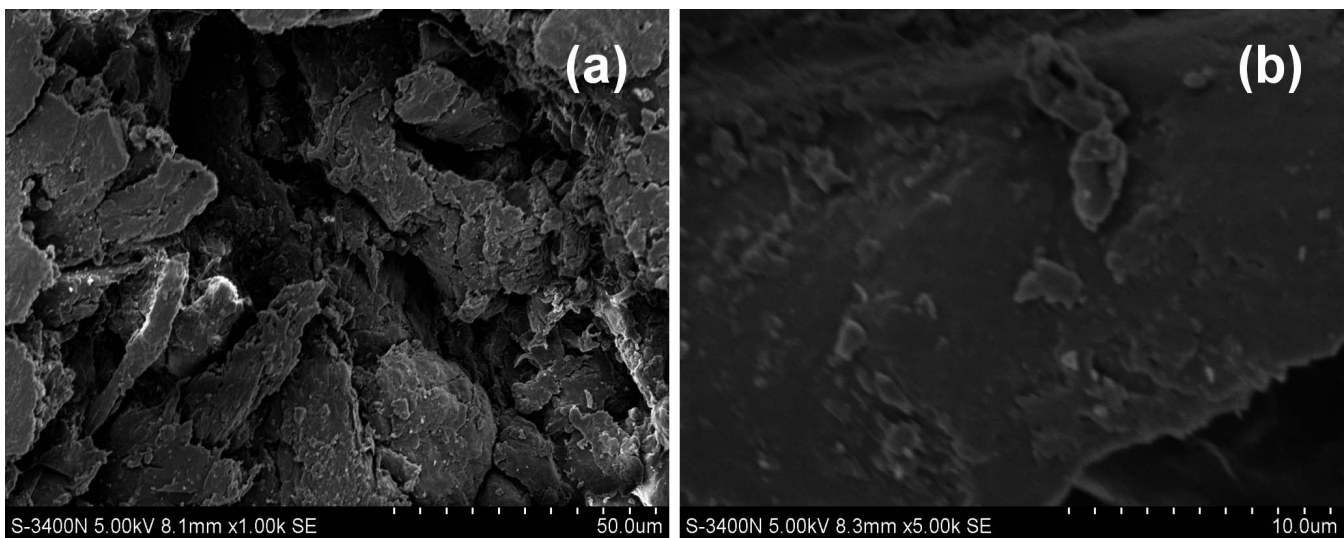


Figure 4.—Microstructure of composites without added bamboo pulp residue. (a) $\times 1,000$. (b) $\times 5,000$.

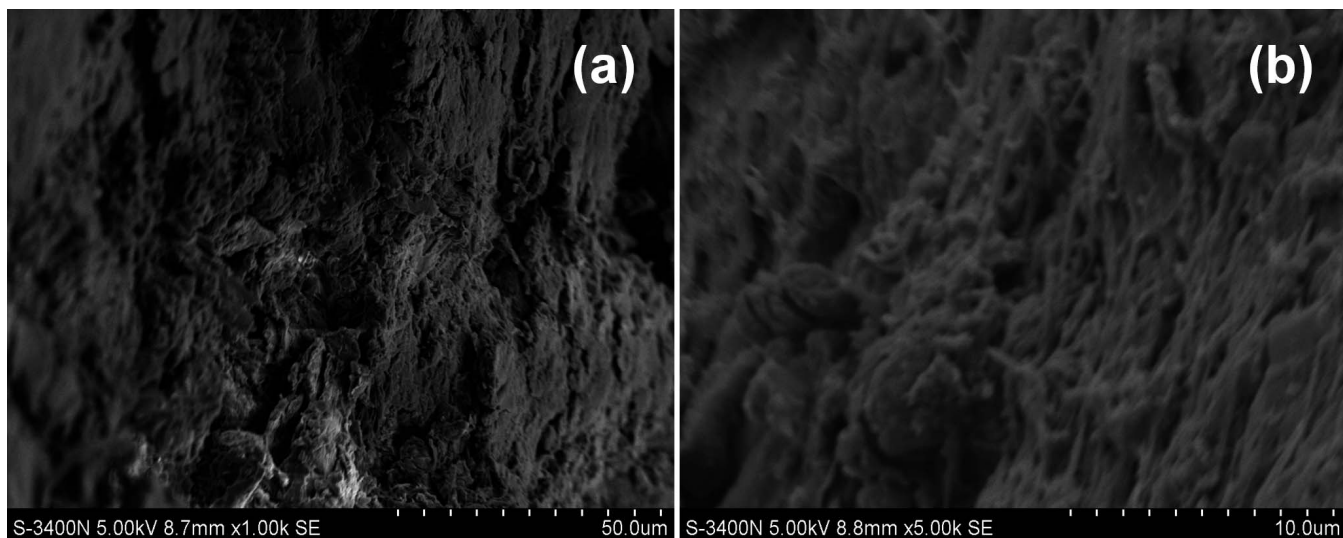


Figure 5.—Microstructure of composites with bamboo pulp residue. (a) $\times 1,000$. (b) $\times 5,000$.

percent with the bamboo pulp residue proportion of 10, 20, and 30 percent, respectively. There was no obvious effect on the waterproof performance, which decreased by 5.72, 2.95, and 4.43 percent, respectively. However, there was a slight improvement when the proportion of the bamboo pulp residue came to 10 percent.

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