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Urea formaldehyde resin with low formaldehyde content modified by phenol formaldehyde intermediates and properties of its bamboo particleboards

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ABSTRACT: Phenol formaldehyde reaction solution (PFS) was used to synthesize urea–formaldehyde resins (PFSUF resins) with low formaldehyde content. In addition, the prepared PFSUF resins were used as adhesives to bond bamboo particleboards. Mechanical properties, fracture morphology, water absorption ratio, and dimensional stability of bamboo particleboards have been studied by tensile tests, SEM tests, water absorption analysis, and swelling ratio analysis, respectively. The results demonstrate that the main ingredient of PFS is phenol formaldehyde intermediate 2,4,6-trimethylolphenate and proper amount of PFS can be used to reduce the formaldehyde content of UF resins effectively. The results also show that bamboo particleboards bonded with PFSUF resins exhibit better mechanical properties, water resistance, and dimensional stability than that bonded with pure UF resin. However, the results of TG and mechanical properties analysis exhibit that alternative curing agents to ammonium chloride should be studied to improve the curing properties of the PFSUF resins with low formaldehyde content. Taken together, this work provides a method of preparing environment-friendly PFSUF resins with low phenol and low formaldehyde content and the prepared resins have potential application in wood industry. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42280.

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INTRODUCTION

In the past several decades, urea–formaldehyde resins (UF) have been widely used as adhesives for interior-grade wood-based panels because of their excellent properties, including low cost, fast curing, colorless, and excellent adhesion to wood.[1–6] Nevertheless, their main drawbacks are low water resistance and emission of formaldehyde from the wood panels.[2,7–9] Nowadays, companies are compelled to manufacture low formaldehyde emission panels because of the increasingly stringent environmental requirements in the world.[10,11]

Until now, many different strategies have been attempted to improve the comprehensive properties of UF resins. For example, reducing the F/U mole ratio is one of effective and practical methods to decrease formaldehyde emission at the expense of deteriorated mechanical properties of particleboard panels.[12–14] Addition of formaldehyde-scavenging agents such as melamine,[15–17] tannin,[18,19] and phenol[20–22] is another way that is commonly used to reduce formaldehyde emission or improve water resistance of UF resins. Recently, phenol formaldehyde resins and urea formaldehyde resins have been commonly combined to complement each other with their own advantages.[23–26] Urea was often used to accelerate the curing process of PF resins and reduce the cost of PF resins, and phenol was used to improve water resistance of UF resins and reduce the formaldehyde emission of UF resins because of the hydrophobic property of benzene ring and the higher reaction equilibrium constants of reaction between phenol and formaldehyde. However, incomplete reaction of phenol and formaldehyde happened in PF resins and phenol-modified UF resins system causes free phenol and formaldehyde residue. Both free phenol and formaldehyde are highly toxic and considered environmental hazards.[27] It is interesting to use phenol formaldehyde intermediates such as polymethylols phenol partly instead of phenol and formaldehyde. What's more, some earlier references report the synthesis of the polymethylols phenol with high yield by mean of direct reaction of phenol and formaldehyde under strong alkali condition.[28–30] Nevertheless, almost all the

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methods mentioned to synthesize polymethylols phenol require large quantities of organic solvents (acetone and isopropyl alcohol).[28–30] From the angles of environmental protection and complexity of UF preparation process, it's a good idea to adopt phenol-formaldehyde reaction solution (PFS) instead of pure polymethols phenol to prepare phenol modified UF resins. Tomita and Hse[31] have studied the reaction of 2,4,6-trimethylols phenol and urea under acid conditions and reported that PFS can be used directly to react with urea after acidification. However, the study on modification of UF resins with PFS under traditional alkali–acid–alkali process has not been reported in the literature. Here, we tried to synthesize UF resins with low formaldehyde content by reacting UF resins with certain amount of PFS under traditional alkali-acid-alkali process.

Wood has been profoundly used in various forms of building and decorative materials with the development of wood adhesives.[32] Nowadays, high demand for wood products and poor reproducibility of wood have caused the short supply and increased cost of wood.[33] In search of low cost building and decorative materials, bamboo has been selected as an alternative to wood products because it can be renewed much more rapidly than wood. The time needed for bamboo harvest is 3–5 years while the time needed for most woods harvest is several decades.[34] However, the low mechanical strength caused by strong hydrophilic characteristics of cellulose limits the application of bamboo products and stimulates efforts to develop new bamboo composite.[35] Therefore, another purpose of this study is to adopt the prepared low formaldehyde content PFSUF resins as adhesives to bond bamboo fiber to prepare bamboo particleboards and to enhance the mechanical strength and water resistance of bamboo particleboards.

In this work, phenol formaldehyde reaction solution (PFS) under strong alkali condition was directly applied to prepare PFSUF resin with low formaldehyde content under alkali–acid–alkali process and the prepared PFSUF resin was used as adhesive for bamboo powder adhesion. Mechanical properties, fracture morphology, water absorption ratio, and swelling ratio of bamboo particleboards were investigated by tensile tests, SEM tests, water absorption analysis, and swelling ratio analysis, respectively.

MATERIALS AND EXPERIMENTAL PROCEDURE

Materials

Analytical grade urea (≥99%) and formalin (37%) were used for the synthesis of UF resins. Formalin was titrated by sodium sulfite method before use. Analytical grade phenol (≥99%) was used directly without further purification. Aqueous solutions of both formic acid (20 wt %) and sodium hydroxide (20 wt %) were used to adjust the pH level during the UF resin synthesis. Aqueous solution (20 wt %) of ammonium chloride (NH_4Cl) as hardener was used. Paraffin wax (mp 60–62°C) was used to improve the water resistance of all bamboo particleboards. The bamboo powder (about 100 mesh) used in this study was obtained from Jiangmen, Guangdong, China.

Methods

Preparation of PFS

PFS was prepared according to the method developed by Freeman.[30] Sodium hydroxide (20.00 g, 0.50 mol) was dissolved in 50.0 mL of water and added to 47.00 g (0.50 mol) of phenol. After cooling to below 25°C, the calculated amount of 37% (wt %) formalin (F/P = 3.0 (mole ratio)) was added dropwise to the solution with stirring and cooling by ice. The reaction mixture was gradually turned yellow and was allowed to stand at room temperature for 3 days and PFS was obtained.

Preparation of Urea–Formaldehyde Resins Modified by Phenol Formaldehyde Intermediates

All PFS-modified UF resins (PFSUF) and pure UF resins were prepared following traditional alkaline–acid–alkaline three-step reaction according to reference with a slight modification.[1] One hundred twenty grams of formalin (F) was placed in the 250 mL three-neck flask with a stirring rate (200 ± 10 rpm) and then adjusted pH to 8.0 with aqueous NaOH (20 wt %) and then heated up to 70°C. Subsequently, 35 g urea (U_1) was introduced into the flask (mole ratio of F/U is 2.00). After the urea was dissolved, PFS was added (mole ratio of benzene ring in PFS solution to total urea (P/U) is 0, 1/80, 1/40, and 1/20, respectively) and the pH was regulated to 8.0 with formic acid (20 wt %). Then the mixture was heated to up to 90°C under reflux for 1 h to allow for methylolation reactions. The second stage of UF resin synthesis consisted of the condensation of the methylolureas. The acidic reaction was brought by adding formic acid (20 wt %) to obtain a pH value of about 4.5, and the condensation reactions were performed until it reached cloud point, indicating that high molecular weight UF resin was formed. Then, the second urea was placed in the flask ($F/(U_1+U_2)=1.45$) and the pH was simultaneously adjusted to 6.5. The reaction was maintained for 30 min at 90°C. Finally, aqueous NaOH (20 wt %) was added to adjust the pH value of the final UF resin to 8.0 and the third urea was added ($F/(U_1+U_2+U_3)=1.20$) and the temperature was cooled to 75°C and held for another 30 min. Then, water of the prepared resin is removed by vacuum distillation to give the adhesive with solid content (about 60%). The obtained resin was cooled to room temperature.

Manufacturing of Bamboo Particleboard

Bamboo particleboards were manufactured according to Shen *et al.*[35] The dimensions and density of bamboo particleboard panels were selected as 10 cm × 10 cm × 3 mm and 900 ± 10 kg/m^3, respectively. Bamboo powder was blended with PFSUF resins or UF resins, paraffin, and ammonium chloride. The mass ratio of the solid resin to bamboo powder (over dried) was 25/75. The amount of paraffin and ammonium chloride were 0.5% and 1% (based in solid resin), respectively. Each batch of sample was pressed under a temperature of 165°C and the pressure of 8.0 MPa for 10 min. Four panels were manufactured for each PFSUF resin and neat UF resin. The tensile strength, elongation at break, flexural strength, fracture morphology, water absorption and swelling ratio of bamboo particleboards were characterized.

Characterization

The viscosity of the neat UF resin or not was measured with Brookfield DV-III programmable rheometer.[36] Free formaldehyde in the prepared adhesives was determined by sodium sulfite method.[1] The measurements were done with three

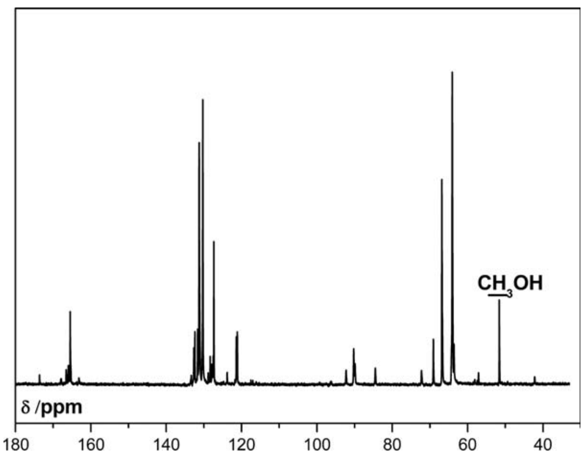

Figure 1. ^{13}C-NMR spectrum of PFS (non-acidification and non-freeze-dried).

replications for each sample. The gel time and pot life of the adhesives were measured by adding NH_4Cl hardener at the 1% level of solid resins at 100°C and room temperature, respectively.[1] The measurements were done with three replications for each adhesive prepared;

^{13}C-NMR spectra were taken on a DRX-400 MHz (Bruker) superconducting-magnet NMR spectrometer with D_2O or DMSO-d_6 as solvent and TMS as an internal standard. Both the PFS and neat UF resin or not were characterized by ^{13}C-NMR directly.

A FT-IR spectrophotometer (Bruker, TENSOR 27, Germany) was used. KBr tabletting method was taken to characterize the neat UF resin or not. The resin samples for KBr tabletting were obtained by freeze-drying. Finally, samples were mixed with KBr powder and pressed into pellets.

Thermogravimetric analysis was made with NETZSCH TG 209F3 at a heating rate of 10°C/min under N_2 atmosphere and over a temperature range from 35 to 700°C. The cured neat UF resin or not sample for TGA test was obtained by mixing resin with NH_4Cl hardener at the 1% level of solid resins and curing at 100°C.

Tensile tests and three point bending tests of bamboo particleboards were conducted using a universal testing machine (SANS-CMT4104, Meitesi Industry System (China) Co.) All mechanical tests were performed according to ASTM D638 for tensile tests and ASTM D790 for flexural tests.[35] Each value of the studied sample is the median value of six specimens.

The fracture surface morphology of the bamboo particleboards were studied by SEM (Hitachi, Japan). The fracture surfaces of bamboo particleboards were sputtered with gold and then photographed.

Water absorption was measured according to Shen *et al.*[35] The bamboo particleboards prepared were directly used for the test and bamboo particleboards (40 mm × 40 mm × 3 mm) were immersed in de-ionized water at room temperature, calculating the relative weight change for 24 h. The bamboo particle boards were withdrawn from water and weighed after shaking off any free water at different time. Swelling ratio of bamboo particleboards was measured by the volume increase ratio of the bamboo particleboards immersed in water for 24 h. The sample size was measured by Vernier caliper with the accuracy of 0.02 mm. Each value is the average of three replications.

RESULTS AND DISCUSSION

Characterization of PFS by ^{13}C-NMR

PFS was obtained according to the method of Freeman and PFS (non-acidification and non-freeze-dried) was directly used for ^{13}C-NMR characterization. Figure 1 shows the ^{13}C-NMR spectrum of the PFS. Two large signals at 63.5 and 66.3 ppm were assigned to carbons of the o- and p- methylol groups of 2,4,6-trimethylolphenate, respectively, showing that the major ingredient of PFS is 2,4,6-trimethylolphenate, which is in agreement with previous reports.[31]

Properties of PFSUF Resins with Different P/U Mole Ratios

Properties of PFSUF resins with different amount PFS (calculated by P/U mole ratios) are shown in Table I. As the P/U mole ratio increases, the viscosity of the PFSUF resins exhibits a slight increase, which is controlled by the condensation time under acid condition and the mole ratio of P/U. As the P/U mole ratio increases from 0 to 1/40, the free formaldehyde in the resin decreases sharply from 1.426% to less than 0.001%. We maintained that adding PFS can raise the reaction extent of urea and formaldehyde, causing the decreasing of free formaldehyde in PFSUF resin. In addition, a decrease in the free formaldehyde reduces the reactivity of the PFSUF resins, which makes the curing condition less acidic and increases the gel time as shown in Table I. The pot life of PFSUF resins (mixed with curing agent) extends with the decrease of free formaldehyde accordingly.

IR Analysis of Neat UF Resin or not

IR spectra of PFS modified UF resins or not samples are shown in Figure 2 and the spectra were normalized using the I_{1660} band intensity as the reference. All FTIR spectra exhibit the characteristic peaks of UF resin: Stretching vibration peaks of O–H and N–H between 3700 and 3100 cm^{-1}, stretching peaks

Table I. Properties of PFSUF Resins with Different P/U Mole Ratio

No.	P/U mole ratio	Viscosity (mPa·s)	Free formaldehyde concentration (%)	Gel time (s)	Pot life (h)
UF	0	62.7	1.426	73	24<t<28
PFSUF-1	1/80	87.6	0.515	83	28<t<32
PFSUF-2	1/40	90.3	<0.001	96	32<t<40
PFSUF-3	1/20	91.8	<0.001	117	40<t<48

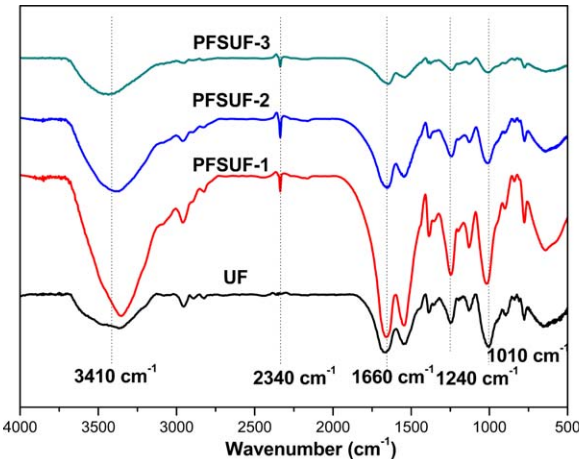

Figure 2. FTIR spectrum of neat UF resins or not. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

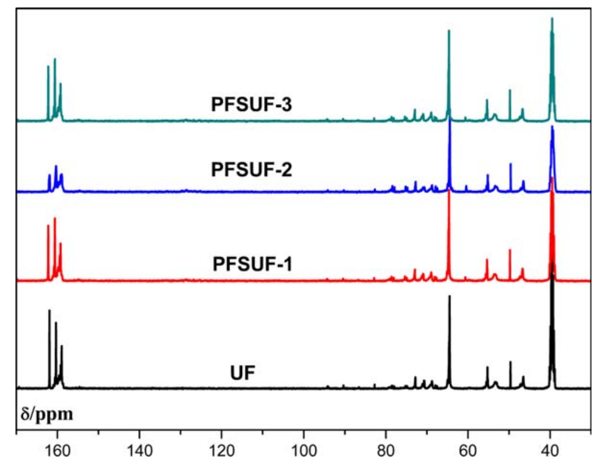

Figure 4. ^{13}C-NMR of neat UF resins or not (non-freeze-dried). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of C-H between 2889 and 2955 cm^{-1}, stretching vibration of C=O at 1660 cm^{-1}, stretching vibration of C-N at 1240 cm^{-1} and stretching vibration of C–O at 1010 cm^{-1}.[37,38] No clear evidence of reaction between PFS and UF resins exists in the IR spectra.

^{13}C-NMR Analysis of PFSUF Resins

The ^{13}C NMR spectra of PFS modified UF resins or not shown in Figures 3 and 4 can be split up into four main areas according to the Refs. 39 and 40: (1) phenolic carbon, the substituted and un-substituted urea carbonyl groups with signals from 160 to 165 ppm; (2) methylene groups with signals from 40 to 60 ppm; (3) methylol groups with signals from 65 to 72 ppm; and (4) methylene ether groups with signals from 69 to 90 ppm. The resonances in the chemical shift range of 49.0–50.0 ppm represent methanol that exist in formaldehyde solution as a stabilizer. We can observe from Figure 3 that freeze-drying might have removed most of methanol, but it could not remove them completely. The spectra of PFSUF resins with different mole ratio of P/U are shown in Figure 4. It can be seen from Figure 4 that most of the peaks for the UF remained unchanged for the PFSUF resins. What's more, due to low P/U mole ratio in the experiment, the resonance peak of methylene bridges (p-Ph-CH_2-NHCO-) that related to the reaction between hydroxymethyl phenol and urea was not found in the Figure 4.

pH Variation of neat UF resin or not (mixed with NH_4Cl)

To illustrate the effect of PFS on the free formaldehyde of UF resins, pH variation of the neat UF resin or not (mixed with NH_4Cl) with time was tracked and the results are shown in Figure 5. It can be seen from Figure 5 that pH decreases as time goes on after the resins mixed with NH_4Cl. This was caused by the reaction between the free formaldehyde and ammonium chloride which makes the resins acidic.[5] It can also be observed from Figure 5 that as the P/U mole ratio increases, the pH value of PFSUF resins increases when the time was the same. In addition, the decrease of pH becomes slow when the P/U mole ratio increases, indicating that the resins with higher P/U mole ratio have longer pot life. The result is in agreement with the result shown in Table I.

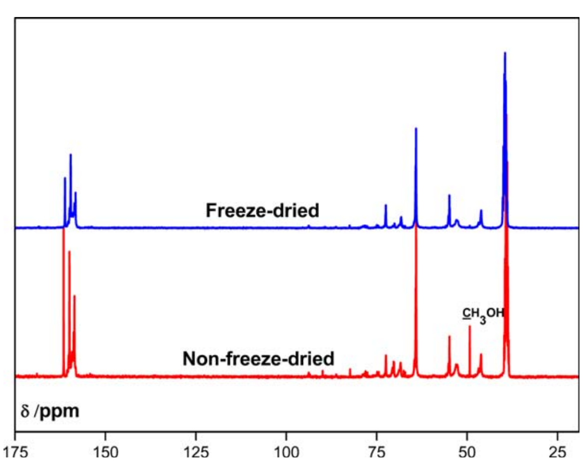

Figure 3. ^{13}C-NMR of PFSUF resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

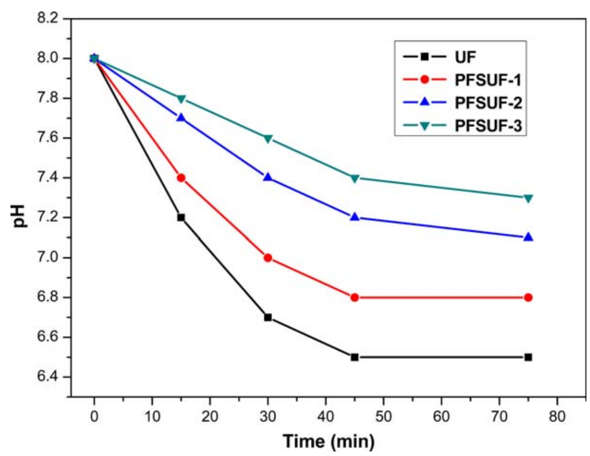

Figure 5. pH variation of neat UF resins or not (mixed with NH_4Cl). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. TGA Data of the Cured Neat UF Resin or not

No.	$T_{5\%}$ (°C)	T_{max-1} (°C)	T_{max-2} (°C)	$T_{50\%}$ (°C)
UF	180.3	165.0	249.3	281.2
PFSUF-1	179.9	168.7	260.3	295.3
PFSUF-2	182.1	172.6	259.5	285.2
PFSUF-3	173.6	178.8	252.9	282.0

TGA of the Cured Neat UF Resin or not

Thermal stability of the cured neat UF resins or not was evaluated by TGA at a heating rate of 10°C/min under a nitrogen atmosphere and the results are listed in Table II. From Table II, we can observe that the cured resins exhibit a slight increase in the degradation temperature (T_{max}, $T_{50\%}$) when the mole ratio of P/U increases from 0 to 1/20. However, the degradation temperature (T_{max-2}, $T_{50\%}$) of the cured PFSUF-2 and PFSUF-3 is lower than that of the cured PFSUF-1. This phenomenon might be explained by the fact that the commonly used NH_4Cl was not an idea curing agent for UF resins with low formaldehyde emission like PFSUF-2 and PFSUF-3. According to these results, it can be concluded that there is a demand for finding new curing system to improve the curing properties of the PFSUF resins with low formaldehyde content.

Mechanical Properties of Bamboo Particleboards

The results for the tensile strength, elongation at break obtained by tensile test and flexural strength of bamboo particleboards bonded with neat UF resin or not are shown Figure 6. From Figure 6, it is observed that both tensile strength and flexural strength of bamboo particleboards increases firstly and then exhibits a decreasing when the mole ratio of P/U rises from 0 to 1/20. This can be explained by the incomplete curing of PFSUF resins in bamboo particleboards when the formaldehyde concentration is low. Because less free formaldehyde makes the curing condition less acidic. Therefore, to improve the curing properties of PFSUF resins with low formaldehyde content, it is necessary to find alternatives to traditional curing agent (ammonium chloride). From Figure 6, it can be found that elongation at break of bamboo particleboards obtained by tensile test decreases with the increasing of amount of PFS. It is known that cured UF resin has the disadvantages of fragileness. Here, incorporation of 2,4,6-trimethylolphenate (main ingredients of PFS) can make the cured UF resins more fragile. Therefore, new methods such as introduction of soft segment like PVA should be taken to overcome the fragileness of UF resins.

Fracture Morphology Analysis of Bamboo Particleboards

The morphology of tensile fracture surface of bamboo particleboards was characterized by SEM and the micrographs are

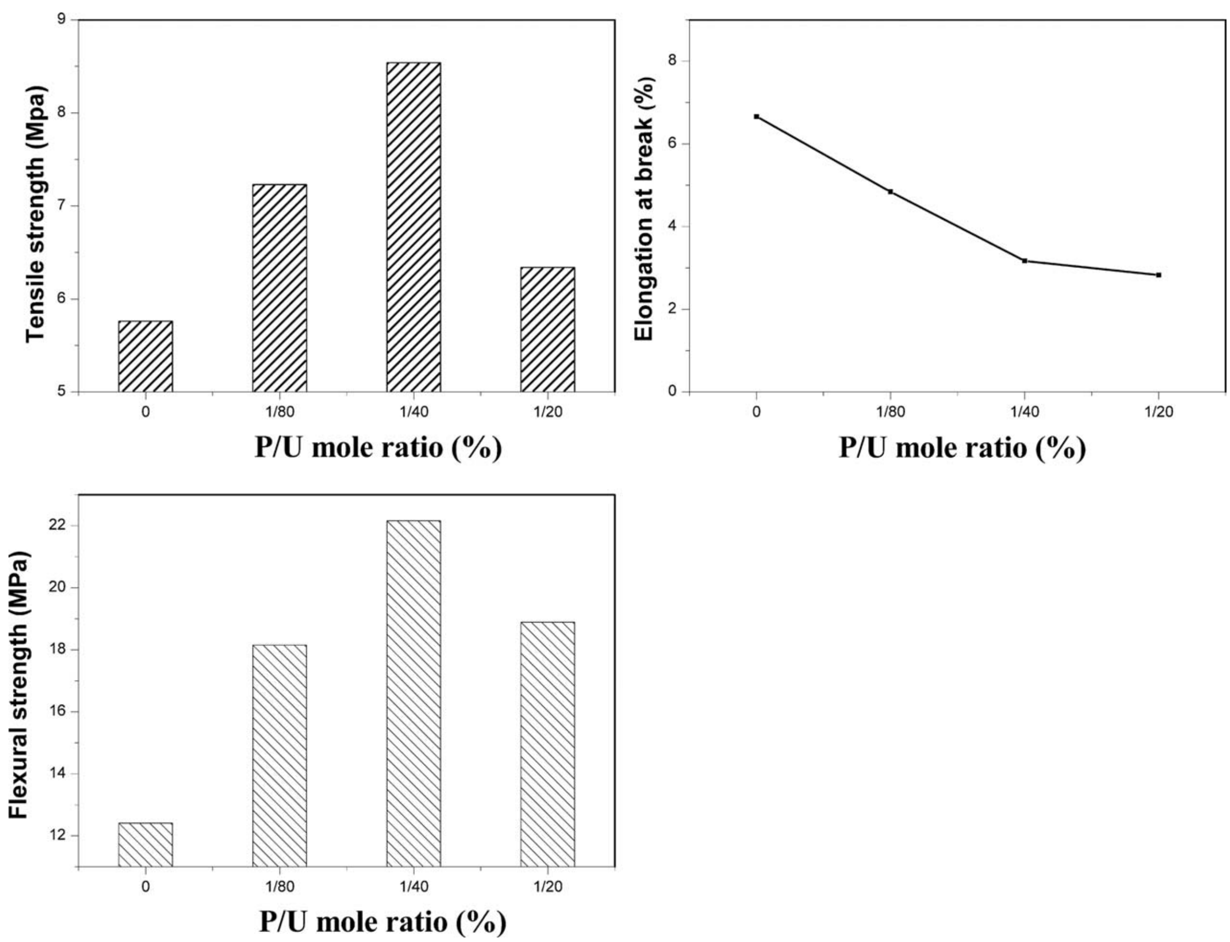

Figure 6. Mechanical properties of bamboo particleboards bonded with neat UF resin or not.

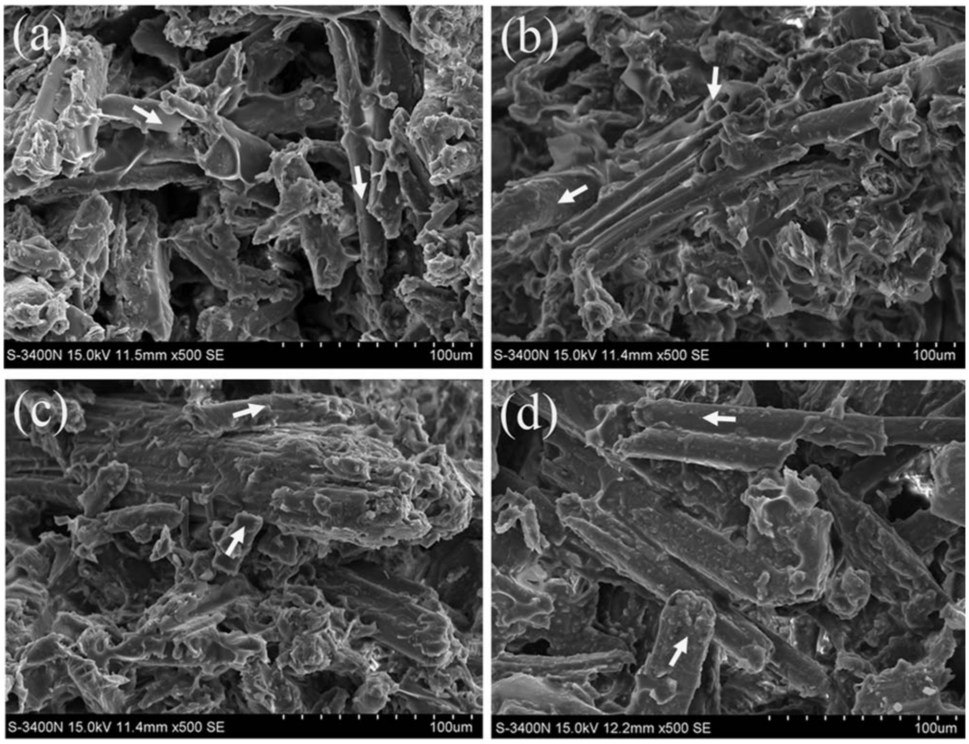

Figure 7. Morphology of the fracture surface of bamboo particleboards (BP) bonded with neat UF resin or not: (a) BP bonded with UF resin; (b) BP bonded with PFSUF-1; (c) BP bonded with PFSUF-2; (d) BP bonded with PFSUF-3.

magnified 500 times as shown in Figure 7. From Figure 7, we can see that some tubular structures (marked by white arrow) exist in bamboo particleboards. In addition, Figure 7 demonstrates that rough morphology and many cavities exit in the rupture surface of bamboo particleboards bonded with pure UF resins, while the rupture surface of bamboo particleboards bonded with PFSUF resins exhibits a relative smooth morphology and little cavities, which means that those bamboo particleboards bonded with PFSUF resins have higher interfacial adhesion than those bamboo particleboards bonded with neat UF resins. This might be explained by the fact that the hydrophobic property of PFSUF resins is higher than that of pure UF resins because of the incorporation of 2,4,6-trimethylolphenate, which might reduce the penetration of PFSUF resins into the cavity of tubular structures and increased the contact area between PFSUF resins and bamboo fiber. Therefore, the rupture surface of bamboo particleboards bonded with PFSUF resins [Figure 7 (b,c) and (d)] is more compact than the rupture surface of bamboo particleboards bonded with neat UF resins.

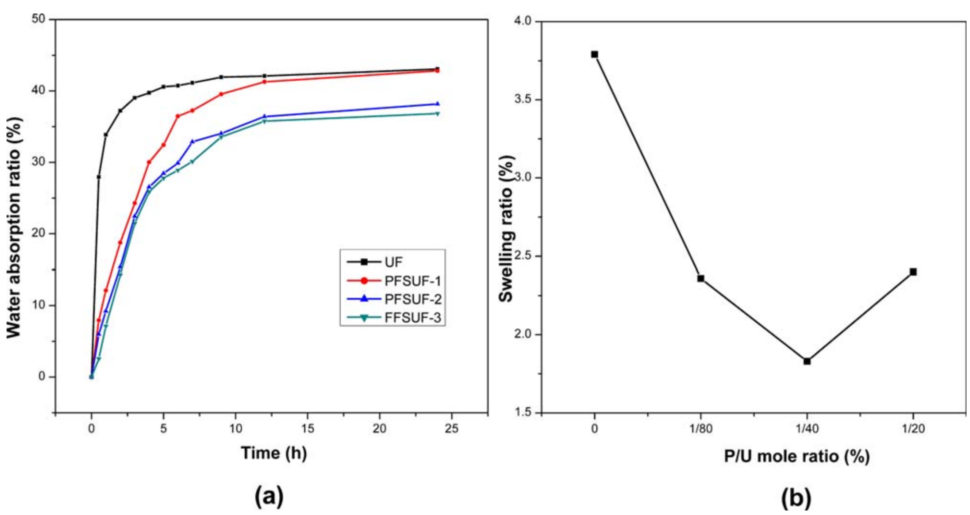

Figure 8. Water absorption ratio and swelling ratio of bamboo particleboards bonded with neat UF resin or not. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Water Absorption and Swelling Ratio of Bamboo Particleboards

Cellulose is hydrophilic because it contains numerous hydroxyl groups, which generally leads to the reduction of mechanical properties. Generally, the water absorption ratio of the bamboo fiber is above 50%.[35] Here, the water absorption of the bamboo particleboards can be enhanced by PFSUF resins, and the effects of PFSUF resins on the water absorption ratio and swelling ratio of bamboo particleboards at 27°C are shown in Figure 8. It can be seen from Figure 8 that the water absorption of bamboo particleboard bonded with pure UF resins is increased quickly during the first 4 hours and then it is almost leveled-off. In addition, the water absorption rate of the bamboo particleboards is decreased with the increased mole ratio of P/U, indicating that the water resistance of bamboo particleboards is improved by the incorporation of phenol ring. What's more, as the mole ratio of P/U increases, the water absorption ratio of bamboo particleboards (24 h) decreases from 43.1 to 36.8%. From Figure 8, we can note that the swelling ratio of bamboo particleboards (2 h) is decreased firstly and then exhibits a slight increase when the mole ratio of P/U is 1/20. We attribute it to the incomplete curing of PFSUF-3 (P/U = 1/20) with low formaldehyde content. According to these results, it can be concluded that PFSUF resins can be used to improve water resistance and dimensional stability of bamboo particleboards. Combined the analysis of mechanical properties with the analysis of water absorption, we conclude that more suitable curing condition needs to be studied to overcome the incomplete curing of PFSUF resins with low formaldehyde content.

CONCLUSIONS

PFS was obtained by reacting phenol with formaldehyde under strong alkali condition and the main ingredient of PFS was 2,4,6-trimethylolphenate which was confirmed by ^{13}C-NMR. PFS has been directly used to synthesize urea–formaldehyde resins (PFSUF resins) with low formaldehyde content under traditional alkali–acid–alkali method. As the amount of PFS (calculated by P/U) increases, the free formaldehyde concentration of the PFSUF resins was decreased. Accordingly, the gel time and pot life were increased. In addition, the prepared PFSUF resins have been successfully used as adhesives to prepare bamboo particleboard and mechanical properties, water absorption and dimensional stability of bamboo particleboards were improved by introducing certain amount of PFS. However, the results of TG and mechanical properties analysis exhibit that alternative curing agents to ammonium chloride should be studied to improve the curing properties of the PFSUF resins with low formaldehyde content. Taken together, this work provides a method of preparing environment-friendly PFSUF resins with low phenol and low formaldehyde content and the prepared resins have potential application in wood industry.

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