Preparation and Characterization of Bio-Oil Modified Urea-Formaldehyde Wood Adhesives

Ben Li, Ji-zong Zhang, Xue-yong Ren, Jian-min Chang,* and Jin-sheng Gou

Wood-derived bio-oil was used to decrease formaldehyde emissions from urea-formaldehyde (UF) resin during the process of making three-layered plywood. The obtained bio-oil urea formaldehyde (BUF) resins were characterized by their physical, chemical, and mechanical properties (*e.g.*, viscosity, solid content, pH value, shelf life, formaldehyde emissions, and bonding strength), analyzed for their specifications, and characterized with Fourier transform infrared spectroscopy and thermogravimetric analysis. The synthesized resins were further employed to prepare the plywood with the veneers glued. The resulting BUF plywood displayed much lower formaldehyde emissions and comparable bonding strength. For the modification on formaldehyde emission of the plywood, it was concluded that the bio-oil can be used to effectively reduce formaldehyde emissions from UF wood adhesive.

Keywords: Adhesives; Bio-oil; UF; Formaldehyde emission content

*Contact information: College of Materials Science and Technology, Beijing Forestry University, Beijing, 100083, China; *Corresponding author: cjianmin@bjfu.edu.cn*

INTRODUCTION

Urea-formaldehyde (UF) resins are widely used in the wood industry due to their high reactivity and cost efficiency, accounting for approximately 60% of the wood adhesive market (Huang *et al*. 2011). However, the use of UF adhesives has a drawback, in that carcinogenic formaldehyde is emitted during the use of UF-bonded panels, which limits their interior application (Dunky 1998; Roffael 2012). This study explores an effective modification to reduce the formaldehyde emission content while still maintaining the cost advantage.

Numerous efforts have been made to develop an effective method to decrease formaldehyde emissions from UF-bonded wood composites. Modifiers such as melamine, phenol, and polyvinyl acetate have been used to synthesize low-emittable formaldehyde UF adhesives (Tomita *et al*. 1994; Tohmura *et al*. 2001; Kim and Kim 2005; Young *et al*. 2004; Hse 2009). However, considering the high price of the above-mentioned modifiers, application of renewable natural compounds such as casein, vanillin, and plant waste with multifunctional structures (*e.g.*, almond shell and sugarcane bagasse) has been a focus of research in recent years (Uchiyama *et al*. 2007; Wang *et al*. 2007; Navarrete *et al*. 2013; Ye *et al*. 2013).

Biomass, which is abundantly available, represents an alternative source of valuable chemical compounds. Bio-oil derived from biomass by fast pyrolysis can be used to produce biomass-derived chemicals such as phenolic compounds, which are further used to synthesize resins (Cheng *et al*. 2012). Extensive inquiries have been conducted into the use of bio-oils as a phenol substitute in the synthesis of phenol-formaldehyde resins. This analysis indicates that bio-oil can be useful for the production of phenol-formaldehyde resins (Mourant *et al*. 2007; Fan *et al*. 2010; Chaouch *et al*. 2014). Bio-oils have also been employed as potential sources of bio-phenols in modifying UF resin (Tian *et al*. 2012). However, previous work has focused on producing bio-oil urea-formaldehyde (BUF) resin with phenolic fractions separated from bio-oil by solvent extraction. This extraction process is complicated and time-consuming, and it negatively affects the process economics.

The objective of this study was to develop a modified UF adhesive with improved properties while maintaining a cost advantage by using whole bio-oil. The bonding strength and formaldehyde emissions of BUF resins were examined to confirm the positive effect of adding bio-oil to the UF adhesive system. The adhesive structure was analyzed to show interactions between the UF resin and bio-oil.

EXPERIMENTAL

Materials

The bio-oil used in this study was derived from fast pyrolysis of larch sawdust and was made at the Institute of Wood Based Material, Beijing Forestry University, China. The bio-oil had a pH value of 3.5 obtained with a PHS-3B pH meter (Shanghai Precision and Scientific Instrument Co. Ltd.; Shanghai, China), and was composed of 34% phenolic compounds, 30% water, 15% organic acids, and 21% other compounds, including sugars, esters, and ketones (Fan *et al*. 2010).

Other raw materials used in the resin synthesis include the following: urea, 50% sodium hydroxide, and formic acid (90% reagent-grade products supplied by Beijing Chemical Industries, Beijing, China); formaldehyde aqueous solution (37% industrial-grade product supplied by Xilong Chemical Industries, Guangdong, China); flour (food-grade product supplied by Guchuan Flour Products Mill, Beijing, China); and poplar veneers from Beijing Woodworking Factory Co., Ltd.

Methods

Preparation of the BUF resins

After removing approximately 10 wt.% water through vacuum distillation, the moisture content of the obtained bio-oil was approximately 18 wt.%.

Bio-oil urea-formaldehyde resins with various amounts of bio-oil were synthesized using a traditional procedure including an alkaline methylolation followed by a mild acid condensation step. All of the resins had a final formaldehyde-to-urea (F/U) molar ratio of 1.12.

In a typical run, with the synthesis of 10% BUF resin used as an example, 45.0 g of urea and 4.8 g of bio-oil were added to 91.0 g of formaldehyde in a 250-mL four-necked flask equipped with a mechanical stirrer, a water cooled condenser, a pressure-equalizing addition funnel, and a thermometer. The pH value of the mixture was adjusted to 7.8 to 8.5 using a 50% sodium hydroxide aqueous solution, and the mixture was heated to 85 °C. After remaining for 40 to 60 min at the previous pH value, the mixture was adjusted to a pH of 4.8 to 5.2 using a 90% formic acid solution. The flask was then held at 90 °C for 40 to 60 min. Subsequently, 12.0 g of urea was added to the reaction system at a constant temperature for 30 min. After this, the pH value of the mixture was finally adjusted to 8.0 using the 50% sodium hydroxide solution. Then, 3.0 g of urea and 1.2 g of bio-oil were added to the flask. The reaction temperature was decreased to 75 °C and kept for 30 min. The obtained resin was cooled down to room temperature.

A series of BUFs were prepared using bio-oil amounts of 0, 5, 10, and 15 wt.% (wt.% of urea). The as-synthesized BUF resins were designated UF, BUF-5%, BUF-10%, and BUF-15% for the sake of convenience.

Preparation of three-layered plywood panel

A three-layer laboratory plywood panel, with dimensions of 400 mm × 400 mm × 4.5 mm, was prepared using *poplar* veneer and the as-synthesized BUF resins for the water resistance and formaldehyde emission tests. Each resin was mixed with wheat flour (20 wt.% of the resin) and NH_4Cl (2 wt.% of the resin), and smeared on the double surfaces of the middle layer of veneers with a brush at a spread rate of 280 to 320 g/m^2. After the spreading, the adhesive-coated veneer was stacked between two uncoated veneers with the wood grain directions of two adjacent veneers perpendicular to each other. Finally, the plywood was hot pressed at 125 °C with a pressure of 1.1MPa for 5 min.

Characterization of bonding strength of plywood

The plywood bonding strength was measured according to the Chinese standard GB/T 9846 (2004). The three-layer plywood produced using each BUF adhesive was cut into specimens of 25 mm × 100 mm with a 20 mm × 25 mm notch in each piece. Twenty specimens for each sample were submerged into water at 63 ± 3 °C for 3 h. After conditioning, wet strength was measured to evaluate the water resistance of the resins using a MWD-10 universal material testing equipment (Jinan Huaxin Testing Instrument Co. Ltd., Jinan, China) with a test loading speed of 10 mm/min, and the results were averaged.

Characterization of formaldehyde emission content of plywood

The formaldehyde emissions of plywood formed using the as-prepared BUF adhesives were tested according to the Chinese standard GB/T 17657 (1999). The three-layer plywood was cut to a size of 50 mm × 150 mm. The specimens were then placed in a 10-L desiccator with a crystal dish filled with 300 mL of deionized water for 2 h. The formaldehyde emission content was obtained from the concentration of formaldehyde absorbed in the water using a UV-3150 SHIMZDZU UV-vis-NIR spectrometer.

Fourier transform infrared (FTIR) spectroscopy analysis

Fourier transform infrared spectroscopy, in absorbance mode, was used to characterize the functional group of the resins. Potassium bromide (KBr) pellets with 1 mass % of the powdered resin were produced. A Bruker Vertex 70 Fourier transform IR spectrometer (Germany) was used to determine spectra. The spectra obtained ranged between 4000 and 400 cm^{-1}, with a resolution of 4 cm^{-1} and 32 scans.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out with a PerkinElmer TGA-4000. All the samples were cured at 60 °C for 3 h in a convective drying oven obtained powder adhesives. Specimens were placed in alumina crucibles, with an empty alumina crucible used as a reference. Specimens were heated to 600 °C at a heating rate of 10 °C/min in a N_2 atmosphere.

RESULTS AND DISCUSSIOIN

Physical Properties of BUF Resins

All of the BUF resins had a dark color with the odor of bio-oil. The viscosity, solids content, and shelf life of all the resins were measured according to Chinese standards (GB/T 14074 2006). The pH value was measured with a PHS-3B pH meter (Shanghai Precision and Scientific Instrument Co. Ltd.; Shanghai, China) at 25 ^{o}C. Three replicates were made for each resin type under both tests, and the results are presented in Table 1. All of the BUF resins had a solids content similar to that of the pure UF resin (49 to 53 wt.%), regardless of formulation. All of the BUF resins exhibited higher viscosities (determined at room temperature, *i.e.*, 23 ^{o}C) than the UF resin, and the viscosity values of the BUF resins increased with increasing amounts of bio-oil. This phenomenon may be explained by the highly complex compounds in bio-oil, such as aldehydes, phenolic compounds, long-chain ketones, and esters, which may participate in the methylolation or condensation reactions with urea and formaldehyde to form large complicated molecules, which increased the viscosity of the final products (Cheng *et al*. 2011). Meanwhile, the increased amount of bio-oil caused a reduced shelf life for the BUF resins. The BUF - 10% had a similar shelf life to the UF resin; after 40 days of storage at 4 °C, the resin was still in a fluid form. The BUF-15%, however, precipitated in about a month. The shorter shelf life may result from the precipitation effects and the lower solubility of bio-oil products in water at low temperatures. The BUF resins can potentially become a uniform liquid again when they are heated up. Therefore, the documented shorter shelf life for the BUF resins would not affect the applications of the BUF resins.

Table 1. Physical Properties of BUF Resins

Type	Solid content (wt.%)	Viscosity (mPa·s)	pH	Shelf life (d)
UF	49.50±0.50	324±30	8.80±0.15	42±2
BUF-5%	51.79±0.50	337±30	8.75±0.15	41±2
BUF-10%	52.38±0.50	372±30	8.62±0.15	40±2
BUF-15%	52.54±0.50	392±30	8.83±0.15	33±2

Properties of Plywood Bonding by BUF Resins

Bonding strength and formaldehyde emission content

Plywood was prepared using various synthesized BUF resins as adhesives. The influences of the bio-oil addition on the bonding strength and formaldehyde emission content of the prepared plywood are compared in Figs. 1 and 2, respectively.

As shown in Fig. 1, all of the BUF resin adhesives surpassed the minimum wet tensile strength requirement of 0.7 MPa for interior application according to the Chinese standard (GB/T 9846 2004). The plywood specimens with the BUF adhesives had similar tensile strengths when compared to those with the pure UF resin (≤ 10% bio-oil). However, for addition amounts up to 15%, the bonding strength of plywood obviously decreased. These results reveal that the BUF adhesives were more sensitive to water than the UF adhesives. They could be used as adhesives for the production of interior wood products. Although we found that an increase in the addition amount of bio-oil caused a decrease in the mechanical properties of the panels tested under wet conditions, the wet bonding strength of specimens were not significantly affected by an increase in bio-oil from 5 to 10%.

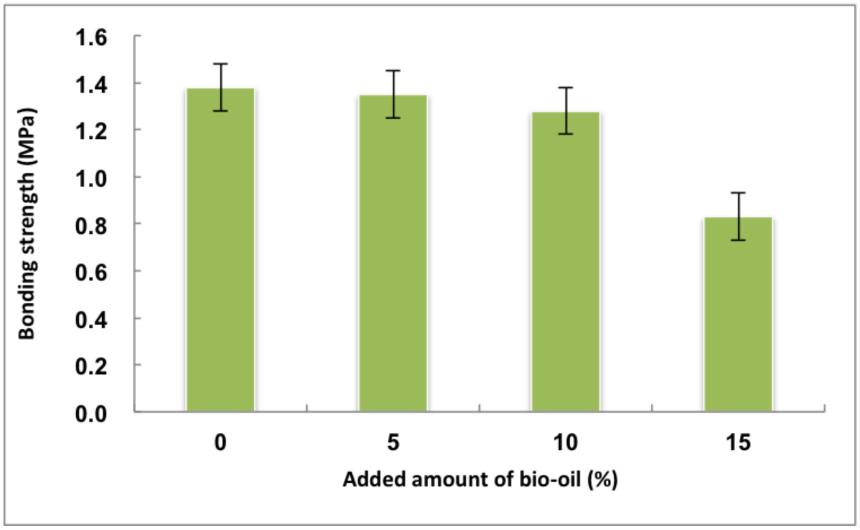


Fig. 1. Average bonding strength of plywood specimens prepared with BUF adhesives

This observation may be due to the fact that the plywood was hot pressed via a traditional process (at 125 °C with a pressure of 1.1MPa for 5 min). However, the cure characteristics of BUF resin may be different from pure UF resin, and the parameters of curing process may not suitable for BUF resins, which finally caused the hydrolysis sensitivity of the specimens.

Formaldehyde emission is an important parameter for the practical application of plywood bonded by UF adhesives. In many studies, it has been shown that formaldehyde is primarily emitted from residual formaldehyde in the resin, generated by condensation reactions between hydroxymethyl groups, or released by hydrolytic degradation of weakly bonded structures in cured resin (Conner 1996; Samaržija-Jovanović *et al*. 2010). As indicated in Fig. 2, the amount of formaldehyde emission of plywood made from blank UF resin was 2.24 mg/L, while the amount of formaldehyde emission for BUF was about half that under the same conditions and could be further reduced with increasing amounts of bio-oil.

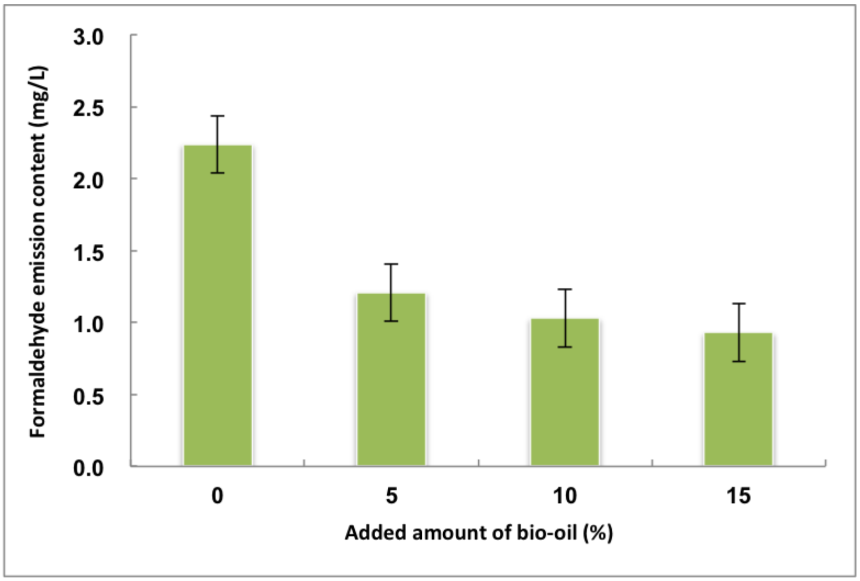


Fig. 2. Formaldehyde emissions from plywood specimens prepared with BUF adhesive

Because bio-oil addition can effectively reduce the formaldehyde emissions, all the plywood specimens made by the BUF resin met the requirements for interior-grade plywood products (*i.e.*, ≤ 1.5 mg/L) in accordance with the Chinese standard (GB/T 9846 2004). The result indicated that a possible reaction between bio-oil and formaldehyde might take place, and the multifunctional structures in bio-oil, such as hydroxyalkyls and phenolics, can effectively reduce formaldehyde emissions (Cheng *et al*. 2012). These results suggest that it is practically feasible to produce BUF as an interior plywood adhesive to decrease formaldehyde emissions without compromising the bond strength of panels made from UF resins.

FTIR Analysis

FTIR spectroscopy was used to confirm the modification of UF resin and examine the effect of bio-oil on the structure of UF wood adhesive (Fig. 3). The spectra of the conventional and modified resins were almost identical. As shown in Fig. 3, the absorption peak at 3345 cm^{-1} was assigned to the OH stretching modes. BUF resins showed sharper characteristic absorption peaks in this region. The sharpness of these bands indicated a reduction in the extent of hydrogen bonding interaction, which was expected because the structure was more cross-linked (Samaržija-Jovanović *et al.* 2010). The bands at 2960 cm^{-1} corresponded to the asymmetric and symmetric stretching vibration of CH_2 groups. The absorption peaks at 1055 cm^{-1} and 1000 cm^{-1} were attributed to the C-OH stretching vibration. The absorption bands observed at 1396 cm^{-1} and 1250 cm^{-1} corresponded to C=O groups. The observed bands at 2290 cm^{-1}, 1138 cm^{-1}, 812 cm^{-1}, and 619 cm^{-1} were due to the C-O-C groups. Compared with pure UF resin, each BUF resin showed the characteristic C=C peaks of a benzene ring at 1600 cm^{-1} and 1450 cm^{-1}, confirming that the phenolic compounds of bio-oil were successfully introduced into the UF resin.

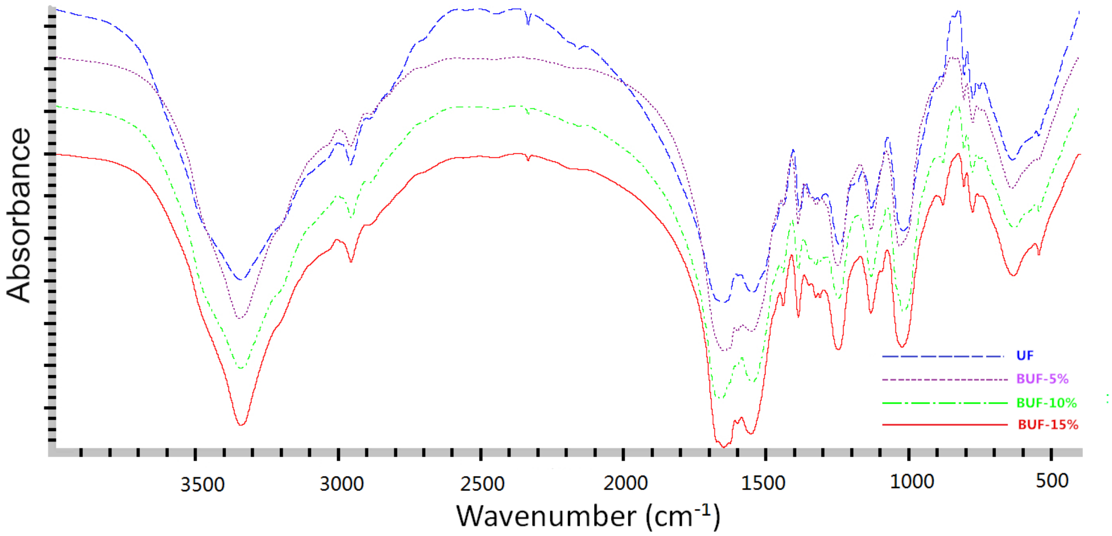


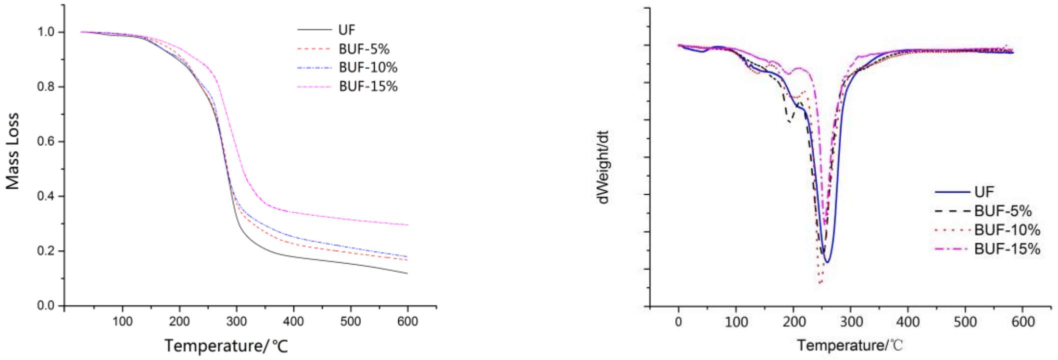
Fig. 3. FTIR spectra of UF and BUF resins

TGA Analysis

The TGA curves of the synthesized UF and BUF resins are simultaneously displayed in Fig. 4. It was obvious that all the curves present with three separate stages due to the typical degradation of UF resins.

The first step corresponds to a loss of weight of 20%. This loss of weight consists of the loss of water and partial volatilization, the water is present either because of the quantity added during the synthesis of the resin or results from the condensation reactions. The second stage was partly due to the release of formaldehyde accompanied with water. The crosslinking reaction and the degradation of unstable hydroxyl-methyl and methylene ether groups contribute to the formaldehyde emission, while the polymer undergoes modification to give progressively more stable structures. The third stage corresponded to the main chain scissions.

Figure 4 presents the dependence of mass loss on temperature. The rate of water evaporation during condensation reactions almost overlapped in all cases. However, differences were found in the second stage. The modification by bio-oil can effectively reduce the weight loss of UF resins during the second stage, which corresponded to the slow release of free formaldehyde. The decreased weight loss of bio-oil-modified resins can be attributed to the formation of higher crosslinking structures, which were more stable and could notably reduce formaldehyde emissions. Apparently, the added bio-oil improved the thermal stability of the UF resin. The enhanced thermal stability contributed to the decreased formaldehyde emissions from plywood. Additionally, higher thermal stability suggested that the BUF can be used in a wider temperature range.



(a) (b)

Fig. 4. Thermogravimetric curves of cured BUF resins (a); Corresponding derivative curves (b)

CONCLUSIONS

1. Bio-oil was introduced into the preparation of urea-formaldehyde resin and was shown to be highly effective in reducing formaldehyde emissions.
2. As the bio-oil percentage increased, the wet strength of plywood decreased, but it still met the Chinese standard requirements (GB/T 9846 2004). However, the formaldehyde emission content of plywood was markedly reduced, from 2.24 to 0.93 mg/L. The modified UF resins displayed improved thermal stability, and the benzene structure of bio-oil was successfully introduced into urea formaldehyde resin. This indicates that a condensation reaction occurred among the bio-oil, urea, and formaldehyde.
3. Considering that bio-oil is effective for reducing formaldehyde emissions while maintaining the cost advantage without compromising the bond strength of plywood, it can be used for fabricating UF resin panels with high performance.

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