Characterization and Application of Urea-Formaldehyde-Furfural Co-condensed Resins as Wood Adhesives

Jizhi Zhang,[a,b] Hui Chen,[a] Antonio Pizzi,[b] Yonghua Li,[a] Qiang Gao,[a]* and Jianzhang Li [a]*

Furfural, as an organic compound derived from biomass materials, was used to partially substitute for formaldehyde in the synthesis of UF resin. Urea-formaldehyde-furfural co-condensed (UFFR) resins with different substitute ratios of furfural to formaldehyde (FR/F) were prepared. The effects of the FR/F substitute ratio on the performances of UFFR resins were investigated. Matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF-MS) and Fourier transform infrared spectroscopy (FT-IR) were applied to characterize the chemical structures of UFFR resins. Plywood bonded by these resins was manufactured, and its bond strength and formaldehyde emission were measured. The results showed that the substitution of furfural in place of formaldehyde could reduce the free formaldehyde content effectively at the expense of prolongation of the curing time. The spectra of MALDI-TOF and FTIR confirmed the co-condensation of urea-formaldehyde-furfural both in uncured and cured resins. Plywood prepared under optimized parameters could yield high bond strength and low formaldehyde emission, which were 0.84 MPa and 0.23 ppm, respectively. The optimized parameters were as follows: a FR/F substitute ratio of 1/3; 1% $(NH_4)_2S_2O_8$ as the curing agent; and a hot pressing temperature of 130 °C. Hence, it is feasible to substitute partially formaldehyde by furfural to prepare UFFR resins as wood adhesives for plywood.

Keywords: Furfural; Urea-formaldehyde resin; Co-condensation; Wood adhesives; Plywood

Contact information: a: MOE Key Laboratory of Wooden Material Science and Application, Beijing Forestry University, 100083 Beijing, People's Republic of China; b: ENSTIB-LERMAB, University of Lorraine, 27 rue Philippe Seguin, BP 1041, 88051, Epinal, France;
** Corresponding author: gao200482@163.com, lijianzhang126@126.com*

INTRODUCTION

Urea-formaldehyde (UF) resins are currently the predominant wood adhesives in the manufacture of interior grade plywood, medium density fiberboard (MDF), particleboard, and other non-structural wood products due to their high reactivity, fast curing, water solubility, and low price (Pizzi and Mittal 2003; Rowell 2012). However, they have poor water resistance and emit formaldehyde, which limits their range of application (Myers 1982, 1984, 1990; Dunky 1998). These issues have stimulated efforts to develop improved and/or new adhesives based on UF resins. One of the most effective ways is by introducing components such as melamine to modify it. In recent years, researchers have devoted more attention to use biomass materials as modifiers in place of petrochemicals.

Furfural is an important renewable, non-petroleum-based chemical feedstock, which is derived from a variety of biomass materials, including corncobs, oat, wheat bran, and sawdust. It is considered as an excellent solvent for many organic materials, such as resins and polymers. It can also be used in the fields of oil refining, plastics, pharmaceutical, and agrochemical industries (Dias *et al.* 2005). Due to the fossil fuel crisis, the furfural demand will continue to grow as the price of petroleum-based feedstock rises in the future. Chemically, furfural undergoes the same kinds of reactions as other aldehydes and other aromatic compounds. Therefore, furfural appears to be a suitable candidate in the synthesis of wood adhesives, especially phenol-formaldehyde (PF) resins (Baxter and Redfern 1958; Kim *et al.* 1994) and phenol-resorcinol-furfural cold-setting adhesives (Pizzi *et al.* 1984). However, studies on the application of furfural in UF resins have been limited. Even though the reactivity of furfural toward urea is lower than that of furfural toward phenol, furfural still has a potential of participating in the synthesis of UF resins as an aldehydic copolymer component. Moreover, there are a few advantages in the use of UFFR resins. For example, furfural can be obtained from waste biomass, and the use of furfural can reduce the amount of total formaldehyde in the adhesives and its bonded products.

In this study, furfural was used as a partial substitute for formaldehyde in the preparation of UF resins to synthesize urea-formaldehyde-furfural co-condensed (UFFR) resin. The effects of the substitution ratio of furfural to formaldehyde (FR/F) on the performances of UFFR resins were investigated. Matrix-assisted laser desorption/ ionization-time of flight mass spectrometry (MALDI-TOF-MS) and Fourier transform infrared spectroscopy (FT-IR) were applied to investigate the chemical structures of UFFR resins. Three-ply plywood bonded with UFFR resins was manufactured under different hot-pressing parameters. The performances of UFFR resins were investigated by measuring the bond strength and formaldehyde emission of the resulted plywood and the hot-pressing parameters were optimized.

EXPERIMENTAL

Materials

Formaldehyde (HCHO, 37 wt% aqueous, AR), furfural ($C_5H_4O_2$, 99%, AR), and formic acid (HCOOH, AR) were purchased from Xilong Co., China. Solid urea (CON_2H_4) was an industrial reagent obtained from Lanyi Chemical Co., China. Sodium hydroxide (NaOH), ammonium chloride (NH_4Cl), ammonium persulfate [$(NH_4)_2S_2O_8$], and all other chemicals used were of AR grade from Beijing Chemical Works, China. For convenience, hereafter when referring to molar ratios, the letters F, U, and FR may be used as abbreviations for formaldehyde, urea, and furfural, respectively.

UFFR Resins Synthesis and Measurement

UFFR resins with a final (F+FR)/U mole ratio of 1.2 were synthesized in the laboratory based on a typical three-step procedure (alkaline-acidic-alkaline). Considering the steric hindrance of the furan ring and the differences in reactivity of formaldehyde and furfural, furfural was added in the late stage of the reaction (with the second portion of urea). First, formaldehyde and urea underwent two different reaction stages, methylolation and condensation, resulting in a large number of methylene and methylene-ether linked oligomers. Second, furfural was added with the second urea. The aldehyde group of furfural reacted with the amino group of urea or unreacted methylolureas, forming numerous oligomers containing furan ring. Cross-linked networking structures were obtained during curing.

In the first stage, formaldehyde was poured into a three-necked flask, followed by the first urea portion at an F/U ratio of 2.0. The reaction mixture was blended using a stirrer. The pH value was adjusted to 8.5 to 9.0 with sodium hydroxide (30 wt%). Within 50 to 60 min, the temperature was gradually increased to 90 °C and maintained at this temperature for 1 h. During the second stage, the pH value was adjusted to the range 4.8 to 5.0 with formic acid (30 wt%) for condensation. The temperature was maintained at 90 °C until the end point was reached. The end point was determined by the cloudy appearance when dropping the solution mixture into a beaker of water at 20 °C. After the end point, the pH value was adjusted to 7.5 to 8.0 with sodium hydroxide (30 wt%). Furfural and the second urea portion were added, attaining a (F+FR)/U ratio of 1.6. The temperature was decreased to 70 to 80 °C and maintained for 40 min. After that, the temperature was decreased to 60 to 70 °C, and the third portion of urea was added. The reaction mixture was maintained for 30 min; then the pH value was adjusted to 7.5 to 8.0, and the mixture was cooled to ambient temperature and stored.

Characteristics of the resins were determined. The free formaldehyde content of the resins was measured using the ammonium chloride method. 5.0 g of resin was dissolved in 50 mL of distilled water in a 250 mL Erlenmeyer flask. Eight drops of bromocresol green-methyl red mix indicator were added, and the mixture was carefully neutralized by titration with hydrochloric acid. Then 10 mL of 10% ammonium chloride solution and 10 mL of 1 mol/L sodium hydroxide solution were added to the mixture quickly. The mixture was sealed and stirred and then kept at 20 to 25 °C for 30 min. The resulting mixture was slowly titrated with the 1 N hydrochloric acid. The non-volatile content was determined by evaporation of volatiles in 2 g of resin for 3 h at 120 °C. The curing time was determined at 100 °C after the addition of a curing agent. Different amounts of NH_4Cl or $(NH_4)_2S_2O_8$ were used as curing agents.

Preparation and Performance Measurement of Plywood

Three-ply plywood was manufactured from poplar veneers with dimensions of 410 mm × 410 mm × 1.5 mm on a laboratory hot press under the following conditions: the adhesive formulation was 100 parts resin, 1 to 2 parts curing agent (NH_4Cl or $(NH_4)_2S_2O_8$), and 15 parts wheat flour. The glue spread amount was approximately 240 g/m^2 (double glue line), the hot press temperature was 120 to 140 °C, the hot press pressure was 1.5 MPa, and the hot press time was 5 min. The formaldehyde emission of plywood was determined by Formaldemeter 400 (PPM Technology Ltd., UK). Testing samples (150 mm × 50 mm) were placed in a 1 L sealed bottle and kept at 20 ± 2 °C for 24 h. The air inside the bottle was analyzed for formaldehyde content. The results were expressed as ppm. The bond strength of plywood was tested according to Chinese National Standard GB/T 17657-2013. The plywood was cut into 8 shear specimens, soaked in water at 63 ± 2 °C for 3 h, and then dried at room temperature for 10 min before the test. The maximum force (N) that damaged the bonded wood specimen was determined by a tensile machine at a speed of 10 mm/min. Bond strength was calculated by the following equation, and the average value was obtained from 8 test specimens per panel.

$$\text{Bond strength (MPa)} = \frac{\text{Maximum Force (N)}}{\text{Effective Gluing Area (m}^2\text{)}} \tag{1}$$

MALDI-TOF-MS Analysis

The spectra were recorded on a MALDI-TOF instrument (AXIMA Performance, Shimadzu). The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The duration of a single laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity-positive, flight path-linear, mass-high (20 kV acceleration voltage), and 100 to 150 pulses per spectrum. The delayed extraction technique was used by applying delay times of 200 to 800 ns. The samples were dissolved in acetone (5 mg/mL). As the matrix, 2, 5-dihydroxy benzoic acid (DHB) was used. For the enhancement of ion formation, 0.1 M NaCl was added to the matrix. The solutions of the sample and matrix were mixed in equal amounts, and 1.5 μL of the resulting solution was placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer.

FTIR Analysis

FTIR spectroscopy (JASCO FTIR-6100E spectrometer, Japan), in transmittance mode, was used for the characterization of the functional groups of the cured UFFR resin. All samples were heated at 120 °C for 3 h and then ground to powder. KBr pellets with 1 mass% of the powdered material were produced. The spectra were obtained in the spectral area 4000 to 400 cm^{-1}, with a resolution of 2 cm^{-1} and 32 scans.

RESULTS AND DISCUSSION

Effects of the FR/F substitute ratio on the performances of UFFR resins

UFFR resins with different FR/F substitute ratios were prepared in the laboratory. These UFFR resins mixed with 1% NH_4Cl as a curing agent were applied as adhesives in the preparation of plywood, which was manufactured at a hot press temperature of 120 °C. Some technical characteristics of these UFFR resins are presented in Table 1.

Table 1. Characteristics of UFFR Resins with Different FR/F Substitution Ratios

FR/F substitute ratio	Non-volatile content [%]	Free formaldehyde content [%]	Curing time [s]	Bond strength [MPa]	Formaldehyde emission [ppm]
1/5 (1.0:0.2)	48.6	0.20	176	0.56	0.90
1/3 (0.9:0.3)	47.5	0.05	>360	0.71	0.80
1/2 (0.8:0.4)	46.9	0.01	>480	0.27	0.22

It is clear that the non-volatile content declined slightly with the increase of the FR/F substitution ratio. The free formaldehyde content of UFFR resins decreased significantly with the increase of the FR/F substitution ratio, which is consistent with the formaldehyde emission of plywood. These results are in accordance with expectations, which is, a higher FR/F substitute ratio signifies lower formaldehyde usage and higher furfural substitution. Moreover, furfural was added with the second urea portion. In this stage, a higher FR/F substitution ratio means that a relative excess of urea will react with free formaldehyde more adequately. However, the curing time was extended dramatically with the increment of the FR/F substitution ratio, indicating that the curing reactivity was decreased due to the steric hindrance and the lower reactivity of furfural. In addition, the slower curing rate caused by the lower free formaldehyde content is another important reason for the prolongation of the curing time of UFFR resins. The curing mechanism of ammonium salts is their capacity to release acid, which decreases the pH of the resin and thereby accelerates curing. This can be expressed as: $4NH_4^+ + 6CH_2O \leftrightarrow (CH_2)_6N_4 + 4H^+ + 6H_2O$. The plunge of free formaldehyde content caused by the increment of the FR/F substitute ratio led to the inability to release sufficient acid, and thus the retarding of the curing rate and the extension of curing time. In terms of the performances of plywood, the UFFR resin with an FR/F substitute ratio of 1/3 yielded the highest bond strength, 0.71 MPa. The formaldehyde emission of plywood trended downward with the increase of the FR/F substitute ratio, and the lowest value was 0.22 ppm obtained in the case of the plywood bonded by UFFR resin with an FR/F substitute ratio of 1/2.

Structure of UFFR Resin

The UFFR resin with an FR/F substitution ratio of 1/3 was chosen as an example for the chemical structure investigation. Figure 1 shows the MALDI-TOF spectrum of the UFFR resin. As described in our previous work (Zhang *et al.* 2014), the MALDI-TOF mass spectrum showed clear repetitive patterns of peaks that allow for the identification of specific oligomer series. The main peak-to-peak mass increment observed was 72 Da, which is representative of the following repeating unit I: $-NH-CO-NH-CH_2-$.

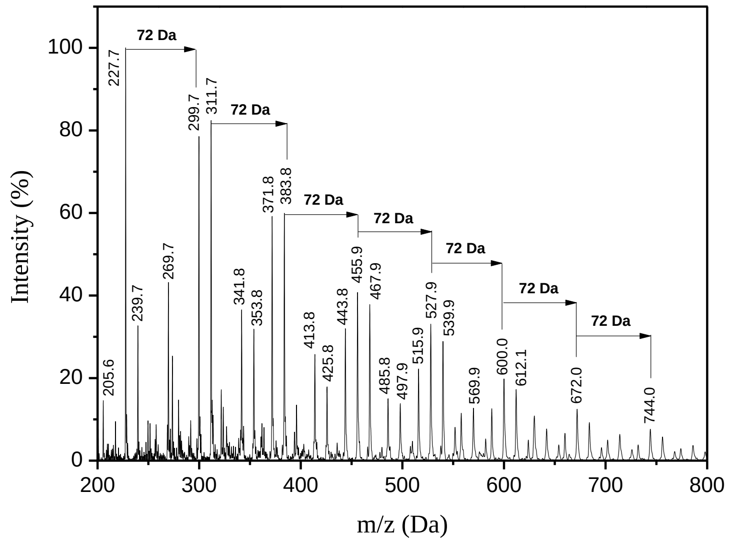
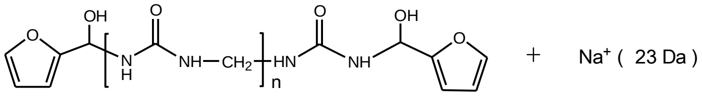


Fig. 1. The MALDI-TOF spectrum of the UFFR resin

Figure 2 shows the comparison of the MALDI-TOF spectra between UF resin and UFFR resin at a range of 250 to 650 Da. It indicated that the structures of UFFR resin were very similar to those of the UF resin, which was composed of a large number of oligomers mainly bonded by methylene and methylene-ether bond, methylolureas, unreacted urea, and free formaldehyde. The main assignments of the MALDI-TOF spectra can be referred to our previous article (Zhang *et al.* 2014). Furthermore, it is worth noticing that some remarkable peaks of 353 Da, 425 Da, 497 Da, and 569 Da appeared in the MALDI-TOF spectrum of the UFFR resin, which are attributed to the urea-formaldehyde-furfural co-condensation reactions. For these peaks, the general formula is:



Thus, for the peaks of 353 Da, 425 Da, 497 Da, and 569 Da, the number n is equivalent to 1, 2, 3, and 4, respectively. This implies that furfural can react with urea and then continue to participate in further condensation and cure reaction. Such reactions are consistent with the previous study (Novotny and Johnson 1931). In that study it was found that furfural and urea will readily condense under certain conditions of temperature and catalysts. The reaction of furfural and urea is more energetic in the presence of alkaline catalysts than the case at the same temperature in the presence of acid catalysts, which means that it is suitable to add furfural with the second portion of urea under an alkaline pH in our study. In addition, it has been found that formaldehyde has a desirable effect in producing a strong and tough final resin. The active methylene groups generated from the reaction of formaldehyde and urea have a marked accelerating effect on the final reaction. Above all, these evidences verify the feasibility of the co-condensation of urea, formaldehyde, and furfural. However, the cross-link degree of urea-formaldehyde-furfural co-polymers is lower than that of UF resin due to the steric hindrance of the furan ring and the differences in reactivity of formaldehyde and furfural.

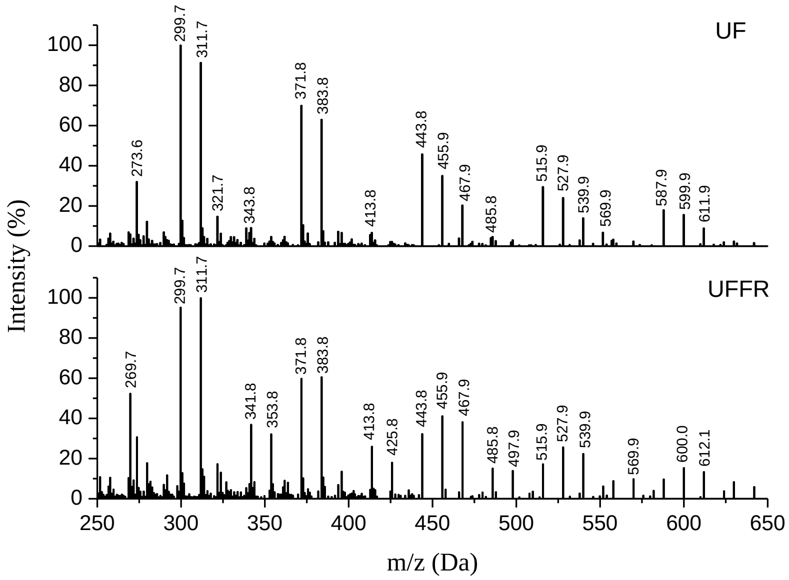


Fig. 2. Comparison of the MALDI-TOF spectra between UF resin and UFFR resin (250-650 Da)

The structure of the cured UFFR resin was investigated by FTIR spectrometry (Fig. 3). The UFFR resin was initially cured, then soaked in deionized water for 24 h while refreshing the water periodically. This was followed by complete drying before investigation. The soaking and refreshing was done to remove unreacted micromolecules and oligomers from the cross-linked network structure of the cured UFFR resin. In this way, it could be determined whether or not furfural was linked permanently into the network. In the FTIR spectrum, the extended broad bands from 3200 to 3600 cm^{-1} indicate the presence of free NH groups. The band at 2965 cm^{-1} is attributed to prominent C-H stretching. The C=O stretching frequency is inferred by the bands around 1650 cm^{-1}, and the C-N stretching of amides is revealed by the vibration at 1554 cm^{-1}. The peak at

1387 cm^{-1} is a characteristic of the C-H stretching in $-CH_2-$ and $-CH_3$. The band at 1243 cm^{-1} characterizes the in-plane ring breath and C-O stretching of furan ring, while the appearance of band at 883 cm^{-1} signifies the furan ring of furfural. This is powerful evidence that furfural was effectively incorporated into the network structure of UF resin, which matches well with the insertion of furfural in the uncured UFFR resin according to the MALDI-TOF data. Likewise, peaks at 1135 cm^{-1} and 1034 cm^{-1} are assigned to C–O stretching of aliphatic ether and C–N or NCN stretching of methylene linkages (NCH_2N), which confirmed that the cured UFFR resin was mainly linked by methylene and methylene-ether bonds. The band at 775 cm^{-1} belongs to the C=O deformation of the NCON skeleton. In brief, the data of MALDI-TOF and FTIR strongly suggest the successful co-condensation of urea, formaldehyde, and furfural. Therefore, a proposed scheme for UFFR resins is represented in Figure 4, based on the above analyses.

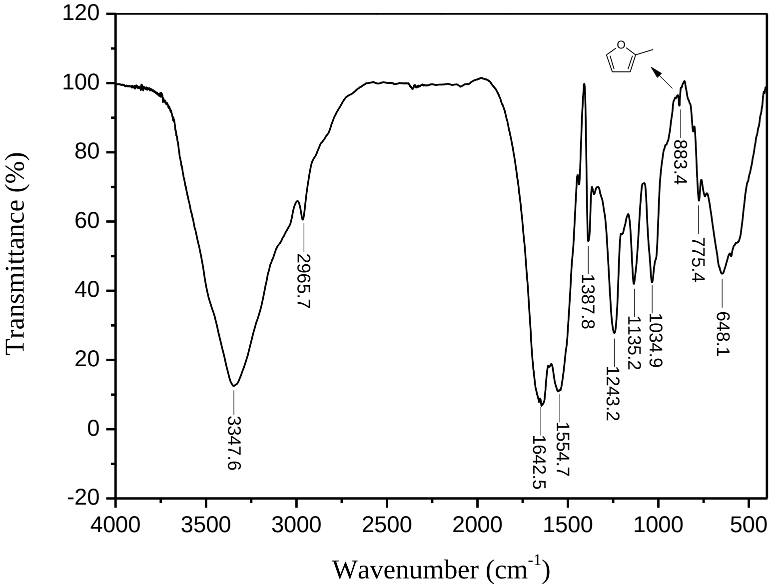


Fig. 3. The FTIR spectrum of the cured UFFR resin

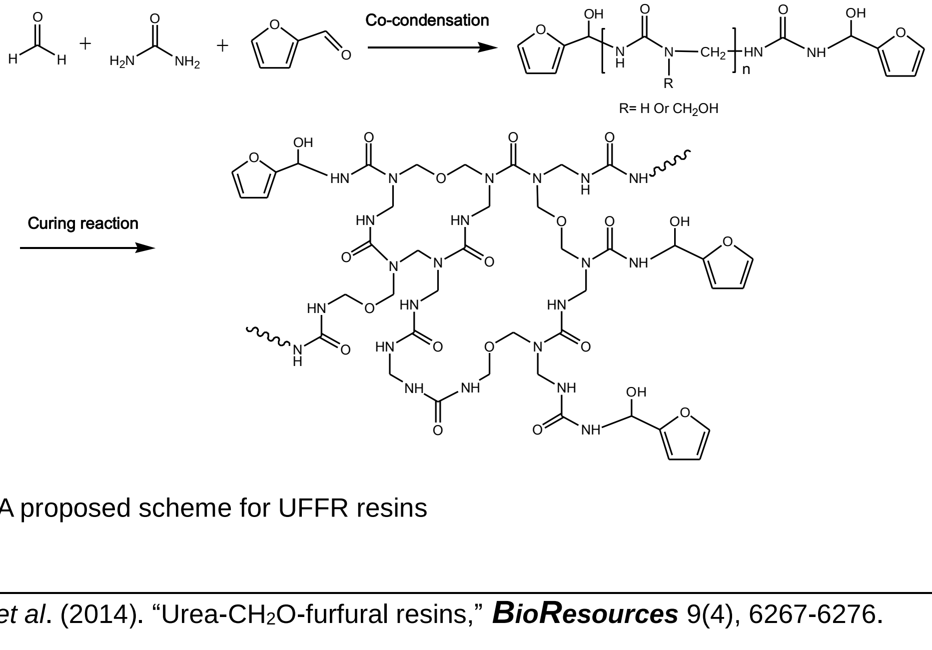


Fig. 4. A proposed scheme for UFFR resins

Application of UFFR Resins in Fabrication of Plywood as Wood Adhesives

Curing time, which signifies the resin reactivity, was determined for predicting the properties of plywood bonded with UFFR resins. Longer curing time also means that a higher temperature or a longer time will be needed to cure these resins. Table 2 presents the curing time of UFFR resins with different curing agents.

Table 2. Curing Time of UFFR Resins with Different Curing Agents

Curing agent		Curing time [s]		
		FR/F=1/5	FR/F=1/3	FR/F=1/2
NH_4Cl	1%	176	>360	>480
	2%	144	>300	>360
$(NH_4)_2S_2O_8$	1%	138	160	240
	2%	106	122	130

Apparently, the curing times were reduced by adding more curing agents due to the enhanced capacity for releasing acid. In addition, $(NH_4)_2S_2O_8$ was more effective than NH_4Cl as a curing agent. The reason is that the $S_2O_8^{2-}$ ion has a strong oxidizing ability, which might generate H_2SO_4 and HCOOH in addition to the acid generated by the reaction of ammonium ion and formaldehyde. In other words, $(NH_4)_2S_2O_8$ could release more acid than NH_4Cl during the curing process of the adhesive. Therefore, the pH of UFFR resins catalyzed by $(NH_4)_2S_2O_8$ decreased faster and thus the curing of UFFR resins were promoted. Furthermore, the FR/F substitution ratio did not have much impact on the curing time of UFFR resins catalyzed by $(NH_4)_2S_2O_8$. Once again, this is because $(NH_4)_2S_2O_8$ can produce acid by its decomposition. By comparison with the case of NH_4Cl, the free formaldehyde content had less influence on the curing time of UFFR resins in the case of $(NH_4)_2S_2O_8$.

Plywood was manufactured under different hot-press temperatures by using UFFR resins and different curing agents and their bond strengths and formaldehyde emissions were investigated. Results are shown in Table 3.

Table 3. Properties of Plywood Bonded with UFFR Resins

Curing agent		Temperature [°C]	Bond strength [MPa]			Formaldehyde emission [ppm]		
			1/5	1/3	1/2	1/5	1/3	1/2
NH_4Cl	1%	120	0.56	0.71	0.27	0.90	0.80	0.22
		130	0.57	0.61	0.43	0.66	0.49	0.17
		140	0.59	0.63	0.57	0.93	0.59	0.20
	2%	120	0.34	0.39	-	0.46	0.25	0.08
		130	-	0.62	0.25	0.26	0.66	0.12
		140	0.36	0.25	0.23	0.54	0.42	0.15
$(NH_4)_2S_2O_8$	1%	120	0.59	0.72	-	0.52	0.31	0.12
		130	0.69	0.84	0.34	0.41	0.23	0.12
		140	0.75	0.64	0.77	0.54	0.51	0.15
	2%	120	0.29	0.31	-	0.43	0.42	0.17
		130	0.41	0.32	0.24	0.39	0.16	0.09
		140	0.52	0.65	0.49	0.65	0.15	0.11

On the whole, the bond strength increased and the formaldehyde emission decreased as the hot pressing temperature increased. In general, an elevated hot pressing temperature can improve the curing degree of these resins, which leads to a higher bond

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strength and a lower formaldehyde emission. It was observed that $(NH_4)_2S_2O_8$ yielded better performances than NH_4Cl, indicating that $(NH_4)_2S_2O_8$ is more efficient than NH_4Cl as a curing agent for UFFR resins. This matches well with curing time data of UFFR resins. Moreover, it is interesting to find that the bond strength of plywood deteriorated when the amount of curing agent was increased from 1% to 2% for both NH_4Cl and $(NH_4)_2S_2O_8$. A possible reason is that too much curing agents might result in weak boundary layers between the resin and veneer, which might cause deterioration of glue lines and then the bond strength. In terms of the FR/F substitution ratio, the UFFR resin with the FR/F substitution ratio of 1/3 yielded the highest bond strength of the resulting plywood. Meanwhile, the formaldehyde emission of plywood was ordered according to the following sequence: $FR/F=1/2 < FR/F=1/3 < FR/F=1/5$. Although the UFFR resin with the FR/F substitution ratio of 1/2 endowed plywood with the lowest formaldehyde emission, the bond strength could not meet the interior usage requirements with a minimum value of 0.7 MPa. In conclusion, the optimized parameters were selected to balance the bond strength and formaldehyde emission as follows: a FR/F substitution ratio of 1/3; 1% $(NH_4)_2S_2O_8$ as the curing agent; and a hot pressing temperature of 130 °C. The bond strength and formaldehyde emission of plywood prepared under optimized parameters were 0.84 MPa and 0.23 ppm, respectively.

CONCLUSIONS

1. Furfural was effective for the partial substitution in place of formaldehyde to prepare UFFR resins as wood adhesives. The free formaldehyde content decreased significantly with the increase of the FR/F substitution ratio. A major drawback of UFFR resins is the prolongation of curing time, which can be solved by adding suitable curing agents, such as $(NH_4)_2S_2O_8$.
2. The spectra of MALDI-TOF and FTIR confirmed the co-condensation of urea-formaldehyde-furfural both in uncured and cured resin. Hence, it is feasible to partially substitute for formaldehyde by using furfural to prepare UFFR resins as wood adhesives for plywood.
3. The optimized parameters to prepare plywood were as follows: the FR/F substitute ratio of 1/3; 1% $(NH_4)_2S_2O_8$ as the curing agent; the hot pressing temperature of 130 °C. The bond strength and formaldehyde emission of plywood manufactured under the optimized parameters were 0.84 MPa and 0.23 ppm, respectively.

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