Performance of Urea-Formaldehyde Adhesive with Oxidized Cassava Starch

Hui Wang,* Jiankun Liang, Jun Zhang, Xiaojian Zhou, and Guanben Du

Urea-formaldehyde (UF) resins based on different formaldehyde/urea (F/U) mole ratio were synthesized with oxidized cassava starch added at the final stage of the resin synthesis process. The basic characteristics of resins including solid content, viscosity, and curing time were studied, and the dry and wet bond strengths were evaluated by producing a three layer plywood. Additionally, the curing characteristics of different resins were investigated *via* differential scanning calorimetry (DSC). Structural distributions between UF and oxidized cassava starch were examined *via* FT-IR and ^{13}C NMR analysis. The results indicated that the addition of oxidized starch not only improved resin bond strength but also notably reduced the curing start temperature of modified resins. Furthermore, a negative relationship between F/U mole ratio and the extent of reduction was identified. The structural distribution of UF resins changed dramatically because of oxidation cassava starch addition, but the changes varied due to different F/U mole ratios.

Keywords: Oxidation cassava starch; Urea-formaldehyde resin; Bonding strength; Curing characteristics

*Contact information: Southwest Forestry University, Yunnan Key Laboratory of Wood Adhesives and Glued Products, Kunming, Yunnan, P. R. China; *Corresponding author: w20030608016@126.com*

INTRODUCTION

Urea-formaldehyde (UF) resin is an important synthetic resin used in the wood composites industry due to its relatively low cost and excellent properties. Presently, about 90% of UF resin is used for wood products. However, some drawbacks, especially formaldehyde emissions, create a great barrier to the wider utilization of UF resin.

Many methods have been used effectively to decrease formaldehyde emissions, including reducing the formaldehyde/urea (F/U) mole, using a formaldehyde scavenger, optimizing resin formula, *etc*. (Dunky 1998; Nuryawan *et al.* 2014). Currently, the F/U mole ratio can be decreased to a low value of about 1.0. Further decreases in F/U mole ratio reduce the bond strength and water resistance of plywood due to the limitation of cross-linking. Although optimizing resin formula can reduce formaldehyde emissions, the extent of reduction is limited. Therefore, to balance the mole ratio and performance of resins, some kinds of additives, including melamine (Tohmura *et al.* 2001; Young No and Kim 2007; Zhang *et al.* 2013), phenol (Sinha and Khali 2015), tannin (Vazquez *et al.* 2004; Zanetti *et al.* 2014), starch (Zhu *et al.* 2013), hyper-branched polymers (Zhou *et al.* 2013), and fluorinated polyether (Mansouri *et al.* 2010) are extensively used in resin formulation.

Compared with oil-derived materials, biomass materials used as additive agents of UF resin have more advantages, such as abundance, renewability, and non-toxicity (Kaewtatip and Tanrattanakul 2008). In this work, cassava starch was used as an additive because it is colorless, odorless, and is environmentally friendly. In addition, incorporation of cassava starch can also reduce the cost of UF resins. Cassava starch, as a regenerative resource, is widely used in many industries. Its amylopectin to amylose ratio is about 80:20

(Wang *et al.* 2013), which gives the modified resin a higher degree of branching. However, the application of cassava starch in wood adhesives is still limited. Hence, it is necessary to further study its effects on UF performance.

Cassava starch has a complex molecular structure, but the hydroxyl groups of starch are easily subjected to various types of reactions after oxidation. In this work, oxidized cassava starch was applied to modify UF resin, and the performances of UF resin with various F/U mole ratios were evaluated by adding oxidized cassava starch at the final stage of the resin synthesis process. The plywood characteristics, including the bond strength and water resistance, were examined. Moreover, the curing characteristic was investigated by differential scanning calorimetry (DSC). The structures of the resins were characterized by Fourier transform infrared spectroscopy (FTIR) and carbon 13 nuclear magnetic resonance spectroscopy (^{13}C-NMR).

EXPERIMENTAL

Materials

Oxidized cassava starch (90%) was purchased from Xuan Kang Starch Co., Ltd. (Guangxi, China). Poplar veneer with a moisture content of 8% to 10% and 1.5 mm thickness was purchased from Zhi Wei veneer factory (Hebei, China) for the preparation of plywood. All other chemicals used in this work were of reagent grade and supplied by the chemical reagent operation department of Danchi Trading Co., Ltd. (Kunming, China).

Resin Preparation

Resins used in this work were synthesized in the laboratory *via* the following process. First, 37% formaldehyde was added to the reactor with a thermometer, condenser, and mechanical stirrer. The pH was adjusted to between 8.0 and 8.5 with 40% sodium hydroxide, and the first portion of urea was added. When the temperature reached 90 °C, the second portion of urea was added. After 30 min, the pH was adjusted to between 5.0 and 5.5 with 30% formic acid and maintained for 2 h at 90 °C. After the pH was adjusted to between 7.5 and 8.0, the last urea was added. Almost 30 min later, the reaction mixture was cooled to room temperature. By adjusting the addition of the last urea, resins with various F/U mole ratios (1.0, 1.3) were obtained. The resins were named UF1.0 and UF1.3. At the last stage, 3% of oxidized cassava starch, based on the amount of urea in the reaction, was added, and various modified UF resins were also prepared. These resins were defined as UF1.0-3 and UF1.3-3. In previous experiments (one paper accepted by a Chinese journal but not published), the use of 3% oxidized cassava starch was found to produce optimum results.

Characteristic of Resins

The solid content of resins was determined by measuring the weight of the resins before and after drying in a thermostat oven at 120 ± 1 °C for 2 h. The average of three replications was taken. The viscosity of resin was measured with a tu-4 cup at 25 °C. Curing time was evaluated in boiled water with NH_4Cl as a curing agent, and the duration time from fluid glue to highly viscous glue was recorded according to Chinese National Standard GB/T 14074 (2006).

Preparation of Three-layer Plywood and Properties

The bond strengths and water resistances of resins were tested by preparing three-layer plywood and evaluating its dry and wet shear strengths. The plywood was prepared with three poplar veneers of 200 mm × 200 mm × 2 mm, and the veneer moisture content was between 8% and 12%. A total of 1% ammonium chloride (NH_4Cl) solid, based on the resin total weight, was added to the resin mixture. The dosage of adhesive used was 200 g/m^2 (single side). Plywood was hot pressed at 140 °C and 1 MPa for 3 min. After hot pressing, the plywood was stored in the ambient environment (about 20 °C and 12% relative humidity) for 3 days. The dry and wet bond strengths were tested in accordance with the procedure described by Chinese National Standard GB/T 17657 (2013). In this test, 6 specimens of each kind were tested, and the average was used as the final result.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was used to determine the curing characteristics of resins with different oxidized cassava starch content. Each sample was tested using an NETZSCH DSC 204 analyzer (Selb, Germany). Approximately 5 mg of liquid resin sample with 1% hardener was weighed on an aluminum pan and sealed with another aluminum cover. An aluminum pan was used as a reference. The prepared sample was heated from 25 °C to 200 °C with a heating rate of 10 °C/min under a nitrogen flow. The starting temperature, peak temperature, and the end temperature were measured.

FT-IR and 13C-NMR Analysis

Fourier transform infrared spectra of resins were measured in the form of KBr pellets on a Perkin Elmer model spectrum V10 instrument (Waltham, MA, USA). Each sample was prepared with 100 mg of KBr and 1 mg of liquid resin. After water evaporation at 25 °C (room temperature), sample discs were scanned with a wave number range of 500 cm^{-1} to 4000 cm^{-1}. Thirty-two scans were accumulated with a resolution of 4 cm^{-1}.

The ^{13}C-NMR spectra were measured using a Bruker Avance 600 MHz instrument (Karlsruhe, Germany). DMSO was used as a solvent. The sample was prepared by mixing liquid resin with the solvent at a 1:3 volume ratio. The spectra were recorded at a frequency of 125.75 Hz and a relaxation delay of 10 s. The chemical shifts were measured with respect to TMS as the internal standard.

The peaks of FT-IR and ^{13}C-NMR were assigned as previously described (Park *et al.* 2008; Kim 2010; Roumeli *et al.* 2012; Zhang 2013; Li *et al.* 2016).

RESULTS AND DISCUSSION

Properties of Neat and Modified Urea-formaldehyde Resins

The basic performance and bond strength of UF resins with various molar ratios are shown in Table 1. Oxidized cassava starch with 3% content clearly increased the viscosity of resins and reduced their curing time, but the solid contents of the resins were indistinguishable considering the experiment error. This result suggests that there was no direct relationship between solid content and viscosity. It is more likely that the oxidized cassava starch changed the resin molecular structure, which increased the viscosity of the modified resins. The modified resins had a shorter curing time with the same hardener agent content (NH_4Cl).

Table 1 also shows that resin bond strength was greatly improved after adding oxidized cassava starch. In particular, wet shear strength (F/U=1.0) increased 56% from 0.32 MPa to 0.50 MPa. These results further indicate that oxidation cassava starch is not a filler agent, but likely plays the role of a molecular cross-linking agent.

Table 1. Properties of Neat and Modified Urea-formaldehyde Resins

Resin	Solid Content (%)	Viscosity (s)	Curing Time (s)	Dry Shear Strength (MPa)	Wet Shear Strength* (MPa)
$UF_{1.0}$	57.1	82	180	1.19	0.32
$UF_{1.0-3}$	56.0	105	158	1.45	0.50
$UF_{1.3}$	57.3	77	129	1.89	1.14
$UF_{1.3-3}$	55.2	97	112	2.49	1.53

* Wet shear strength are obtained after plywood samples dipping into cold water for 12 hours at room temperature

FT-IR Analysis of Resins

The FT-IR spectra of the different UF resins are shown in Fig. 1. The novel and modified UF resins had quite similar patterns, indicating that there was no free oxidized cassava starch (Sheng *et al.* 2011). The strong absorption of the modified resin band between 3000 cm^{-1} to 3500 cm^{-1} was assigned to hydrogen bonded N-H and O-H or water. When the F/U mole ratio was 1.0, this peak became weaker. Within the range from 1500 cm^{-1} to 1700 cm^{-1}, the absorption peaks of the bending vibration band of the N-H of the amide II functional group also declined.

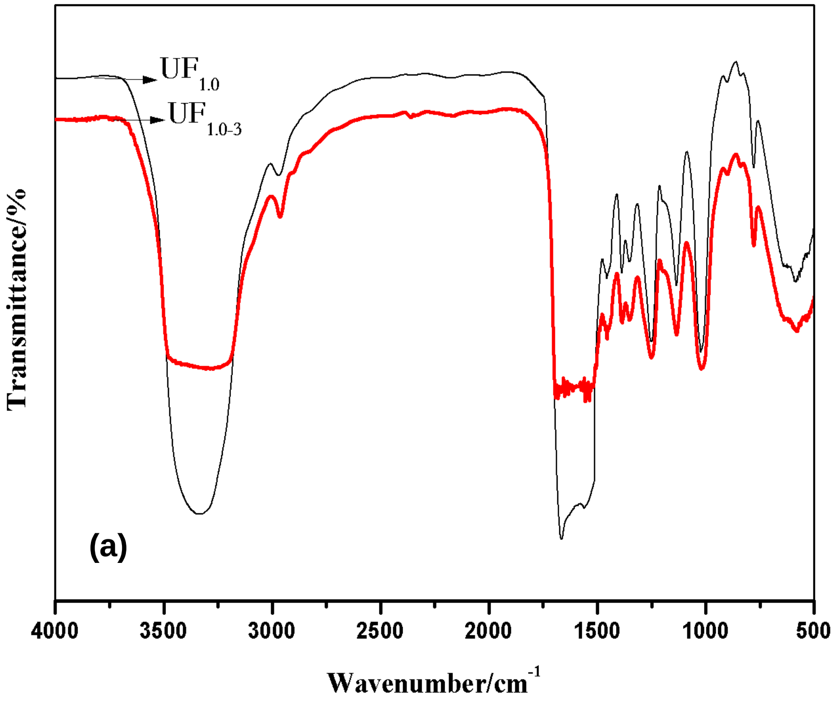


Fig. 1 (a). FT-IR spectra of pure and modified UF resin with oxidized cassava starch. a) UF1.0 resin; b) UF1.3 resin

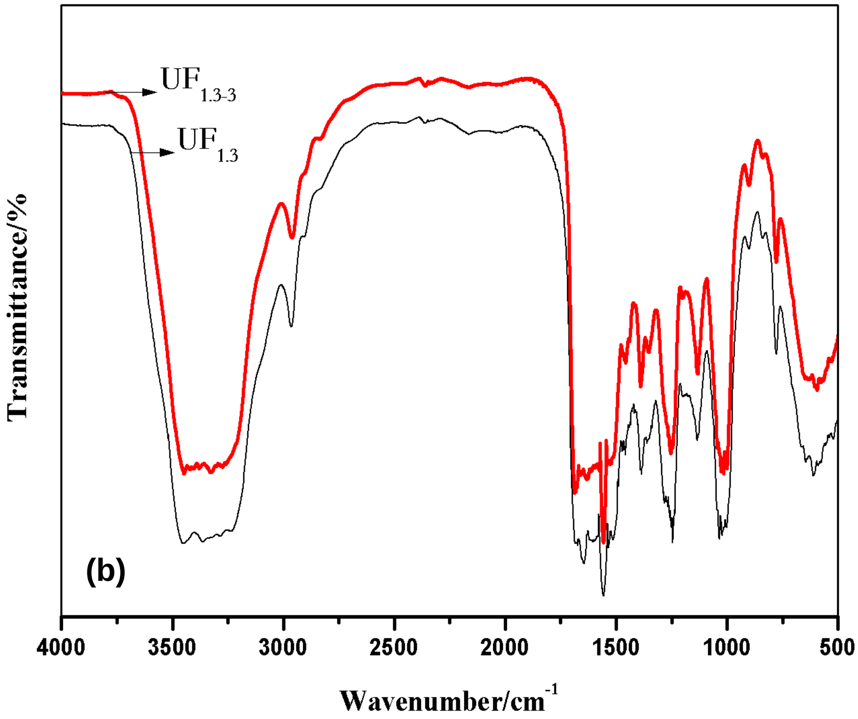


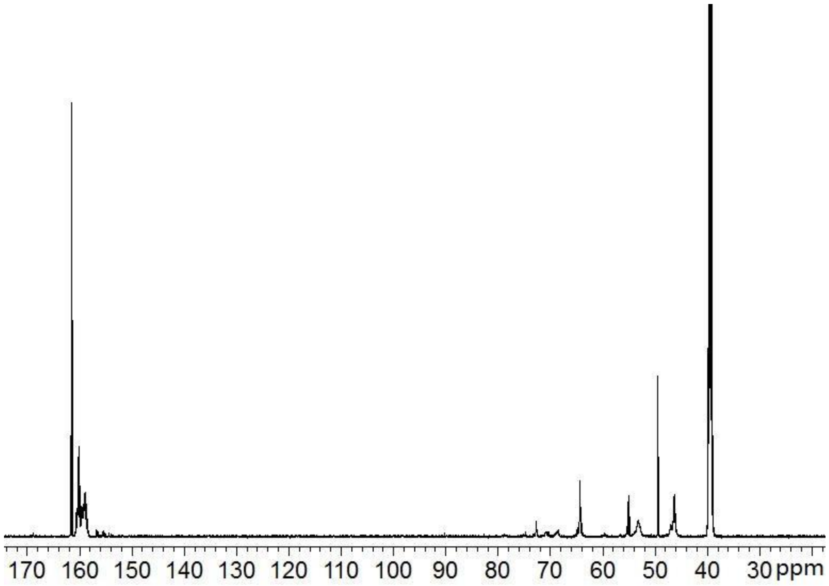
Fig. 1 (b). FT-IR spectra of pure and modified UF resin with oxidized cassava starch. a) UF1.0 resin; b) UF1.3 resin

In the band located at 1658 cm^{-1}, stretching was not observed, meaning that there may have been a reaction between -COOH and N-H or -NH$_2$. Similar variations occurred at the band located at 1264 cm^{-1}, assigned to the stretching C-O-C vibration of ether linkage, and at 1030 cm^{-1}, reflecting the stretching and vibration mode of C-O and O-H linkage in the -CH$_2$OH group. However, the band located at 1141 cm^{-1} assigned to C-N stretching and the band located at 616 cm^{-1} were similar before and after the addition of oxidation cassava starch. When the F/U mole ratio was 1.3, the changes in the spectra were similar to those of the UF$_{1.0}$ resin, but the functional group content was different.

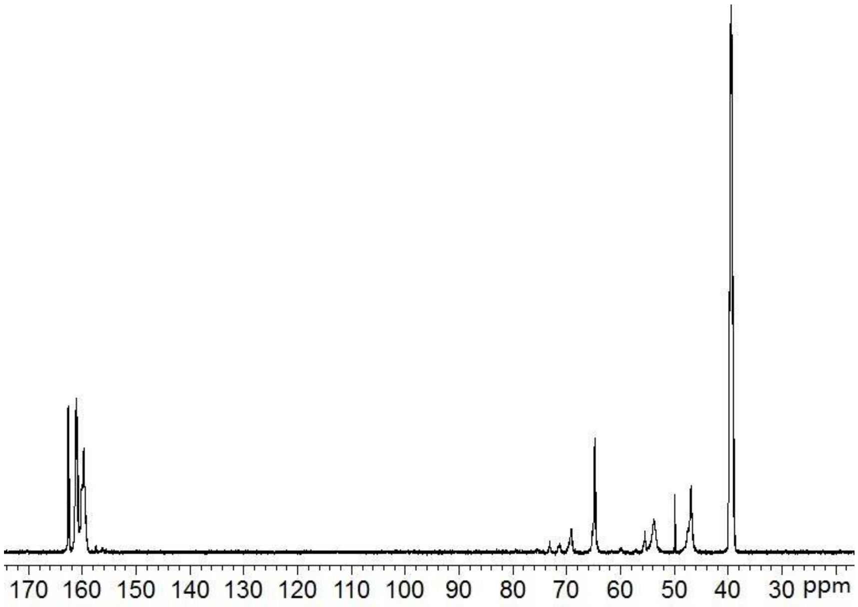
NMR Analysis of Resins

^{13}C-NMR analysis was employed to further study structural changes in the pure and modified resins, as shown in Figs. 2 and 3, respectively. The shift assignments of different groups are listed in Table 2. The signal distribution in these spectra shows that oxidized cassava starch was integrated into the UF resin system. There were also various effects on the structural distribution of resins due to different F/U molar ratios. Moreover, the addition of oxidation cassava starch effectively reduced the content of various types of ether in both resins with low F/U mole ratios and those with high F/U mole ratios. This is the one of reasons why oxidized cassava starch is used to reduce the free formaldehyde content of resins. This phenomenon was also consistent with previously reported results (Li 2001; Zhu 2013).

For lower F/U mole ratios, the reduction of ether content (-CH$_2$-O-CH$_2$-) was slightly more remarkable than higher F/U mole ratio. This was due to the rearrangement of some unstable structures of the UF resin and the relatively high content of final urea and oxidized starch, which could connect with more formaldehyde. Hence, it is easy to produce methylol urea of small molecular weight, which brings about high methylol linkage (-CH_2OH) bond content. However, methylene (-CH_2-) linkage bond content decreases, especially amide I type, resulting in a decrease in the total content of methylene. These changes indicate that oxidized starch may be likely to hinder the reaction between free urea and formaldehyde, reducing the amount of methylene bridge bonds. Hence, in Table 2, the increase of hydroxymethyl content from 22.2% to 28.3% is prominent, but methylene content was reduced from 61.6% to 58.9%. Moreover, for alkaline conditions, it is possible to combine salt compound between remained oxidation starch and urea.

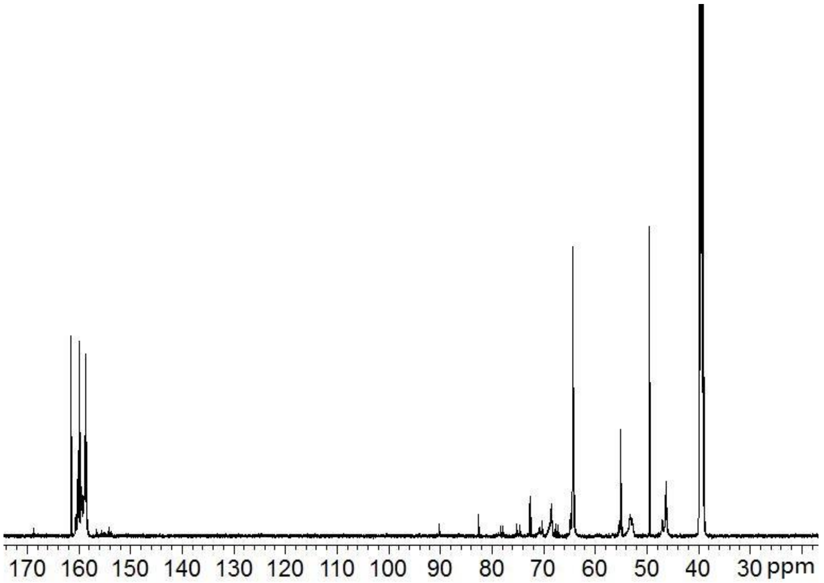


(a) ^{13}C-NMR of pure UF resin (F:U=1.0)

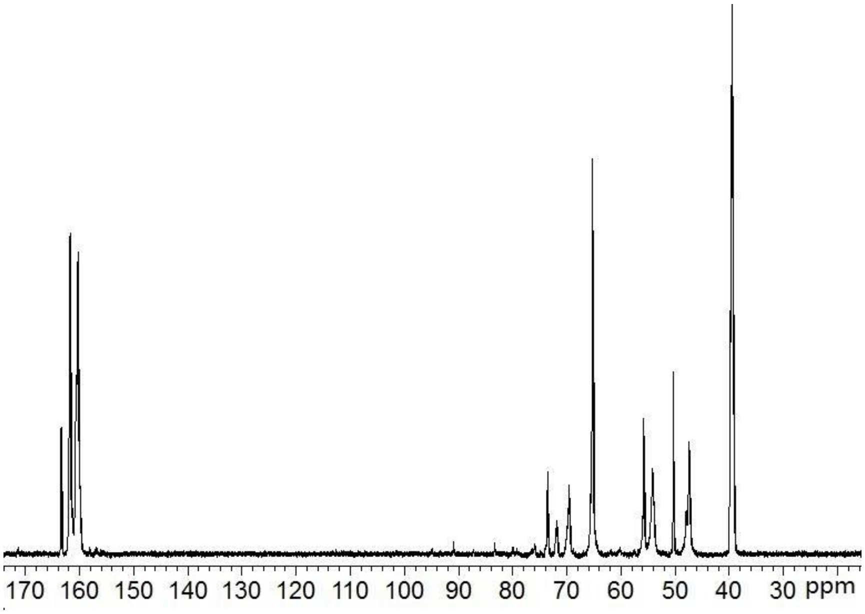


(b) ^{13}C-NMR of modified UF resin (F:U=1.0)

Fig. 2. ^{13}C-NMR spectrum of UF resins (F:U=1.0)



(a) ^{13}C-NMR of pure UF resin (F:U=1.3)



(b) ^{13}C-NMR of modified UF resin (F:U=1.3)

Fig. 3. ^{13}C-NMR spectrum of UF resins (F:U=1.3)

As the F/U mole ratio continued to increase, changes in methylene (-CH_2-) and methylol (-CH_2OH) linkage content can be seen in Table 2 as well, differing from those of lower F/U mole ratios. This may be explained by the relatively high formaldehyde content of the resin due to the lower amount of final urea that was added. Final urea may have first reacted with formaldehyde to form methylol urea after urea addition due to the instability of the ether bond and the remaining formaldehyde content in the resin. The final urea reacted with the aldehyde (-CHO) groups of oxidation starch, forming starch-based polymers. There was higher methylene (-CH_2-) bond content and lower methylol linkage (-CH_2OH) in $UF_{1.3\text{-}3}$, which indicates that methylene (-CH_2-) bridge bonds largely becomes the main combination type between oxidation starch and urea.

Table 2. ^{13}C-NMR Assignment and Content of Pure and Modified UF Resins with Various Molar Ratios

Structure	Chemical Shift	UF$_{1.0}$	UF$_{1.0\text{-}3}$	UF$_{1.3}$	UF$_{1.3\text{-}3}$
$\text{-NH-}\underline{C}H_2\text{-NH-}$ (I)	46~48	36.71	31.67	19.53	18.13
$\text{-NH-}\underline{C}H_2\text{-N=}$ (II)	53~55	24.91	26.30	15.00	27.99
$\text{=N-}\underline{C}H_2\text{-N=}$ (III)	60~61	-	0.93	-	-
	Total	61.62	58.90	34.53	46.12
$\text{-NH-}\underline{C}H_2OH$ (I) $HO\underline{C}H_2\text{-NH-}\underline{C}H_2OH$	63~65	22.22	28.27	40.98	33.50
	Total	22.22	28.27	40.98	33.50
$\text{-NH-}\underline{C}H_2OCH_2NH\text{-}$ (I) $\text{-NH-}\underline{C}H_2\text{-O-}CH_2OH$	68~70	6.07	8.88	12.85	9.15
$\text{-NH-}\underline{C}H_2\text{-O-}CH_3$	72~75	9.80	3.94	9.54	8.87
$HO\underline{C}H_2\text{-O-}CH_2\text{-O-}CH_2OH$ $\text{-NH-}\underline{C}H_2\text{-O-}CH_2OH$ $HO\underline{C}H_2\text{-O-}CH_2\text{-}OCH_2OH$	76~90	-	-	2.76	2.37
	Total	15.87	12.82	25.15	20.39
Glucose Ring Carbon	163~164	-	17.67	-	5.78
$NH_2\text{-}\underline{C}O\text{-NH-}$	161~162	16.81	40.86	6.38	34.33
$\text{-NH-}\underline{C}O\text{-NH-}$ $\text{-NH-}\underline{C}O\text{-N=}$	159~161	81.93	40.37	91.76	59.90
Uron	154~158	1.26	1.10	1.87	-

Differential Scanning Calorimetry

The curing curves of different UF resins shown in Fig. 4 have several common features. The modified resins had lower start temperatures and peak temperatures, meaning that oxidized cassava starch of 3% content notably accelerated the curing of UF resin. However, different F/U mole ratios showed various change trends. The start temperature decreased 20 °C when the F/U mole ratio was 1.0, but the degree of change of the curing start temperature was much smaller when the F/U mole ratio was 1.3. This results agreed with the curing time change summarized in Table 1.

As the F/U mole ratio decreased, the curing speed of the UF resin could be slower because of decreased cross-linking density. In this study, oxidized cassava starch plays the role of the cross-linked agent during the UF resin curing process. Thus, a lower F/U mole ratio resulted in quicker UF resin curing.

Due to different functional group distribution changes in the pure and modified resins, resins showed different curing characteristics and made modified resins have much higher bond strengths and water resistances. The curing and ^{13}C-NMR analysis results of resins confirmed that the mechanism of oxidation through which cassava starch modifies urea-formaldehyde resin is different for different F/U mole ratios, although they have identical oxidized starch addition proportions.

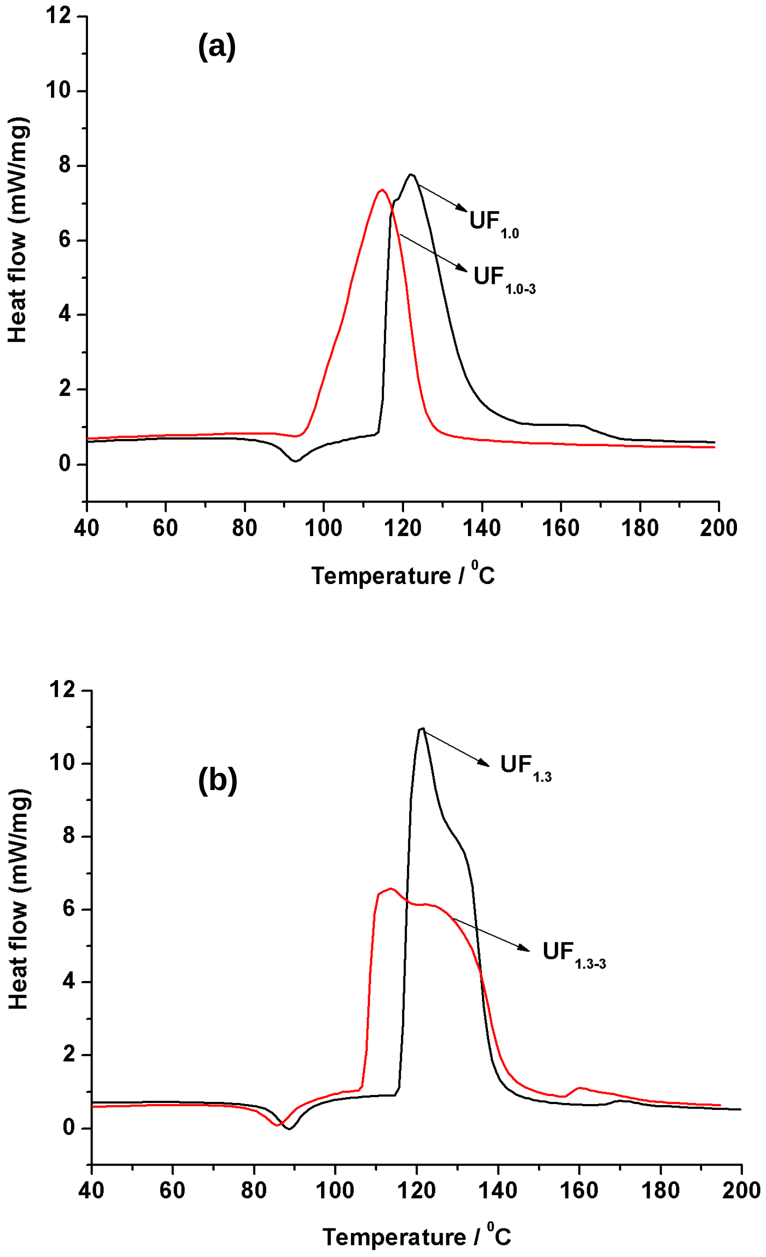


Fig. 4. DSC curves of (a) UF1.0 and (b) UF1.3 resins

CONCLUSIONS

1. Oxidized cassava starch was used to modify UF resins. Oxidized cassava starch was added into the UF resin system at the final stage of resin process. It increased viscosity of resin and bond strength and also reduced curing time and curing start temperature. For resins of lower F/U mole ratios, DSC analysis results indicated that the effects were particularly remarkable.

2. FT-IR and ^{13}C-NMR analyses showed that oxidized cassava starch had a visible influence on the functional group content of resins. It reduced the ether content for both low and high F/U mole ratios. However, when the F/U mole ratio was lower, the addition of oxidized cassava starch hindered the reaction between urea and formaldehyde, leading to relatively lower methylene content. Because of the high final urea usage, $UF_{1.0\text{-}3}$ resin had more hydroxymethyl groups. A higher F/U mole ratio showed different changes because enough formaldehyde was present in the resin. Oxidized starch played a key role in reducing formaldehyde content.
3. The above results demonstrated that oxidized cassava starch modifies UF resin. In complex systems, oxidized starch does not act as a filler, but rather reacts chemically with UF polymers. However, the mechanism of the reaction remains unclear.

ACKNOWLEDEMENTS

This work was supported by the Key Projects in the National Science & Technology Pillar Program during the 12th Five-Year Plan Period (2015BAD14B03) and Scientific Research Foundation of Southwest Forestry University. In addition, the authors thank Pu Long for his assistance with the study.

REFERENCES CITED

Dunky, M. (1998). "Urea-formaldehyde (UF) adhesive resins for wood," *International J. Adhesion Adhesives* 18(2), 95-107. DOI: 10.1016/S0143-7496(97)00054-7

GB/T 14074 (2006). "The methods for testing wood adhesive and resin," Standardization Administration of China, Beijing, China.

GB/T 17657 (2013). "The test methods of evaluating the properties of wood-based panels and surface decorated wood-based panels," Standardization Administration of China, Beijing, China.

Kaewtatip, K., and Tanrattanakul, V. (2008). "Preparation of cassava starch grafted with polystyrene by suspension polymerization," *Carbohydrate Polymers* 73(4), 647-655. DOI: 10.1016/j.carbpol.2008.01.006

Kim, M. G. (2010). "Examination of selected synthesis parameters for wood adhesive-type urea-formaldehyde resins by ^{13}C-NMR spectroscopy III," *Journal of Applied Polymer Science* 80(14), 2800-2814. DOI: 10.1002/app.1397

Li, T. H., Liang, J. H., Cao, M., Guo, X. S., Xie, X. G., and Du, G. B. (2016). "Re-elucidation of the acid-catalyzedurea–formaldehyde reactions: A theoretical and^{13}C-NMR study," *J. Appl. Polym. Sci.* 133(48), 44339-44356. DOI: 10.1002/APP.44339

Mansouri, H. R., Thomas, R. R., Garnier, S., and Pizzi, A. (2010). "Fluorinated polyether additives to improve the performance of urea–formaldehyde adhesives for wood panels," *Journal of Applied Polymer Science* 106(3), 1683-1688. DOI: 10.1002/app.26749

Nuryawan, A., Park, B.-D., Adya P., and Singh, A. P. (2014). "Penetration of urea-formaldehyde resins with different formaldehyde/urea mole ratios into softwood tissues," *Wood Science and Technology* 48(50), 889-902. DOI: 10.1007/s00226-014-0649-9

Park, B. D., Sang, M. L., and Park, J. Y. (2008). "^{13}C-NMR spectroscopy of urea-formaldehyde resin adhesives with different formaldehyde/ureamole ratios," *Journal of Korean Institute of Fire Science and Engineering* 36(2), 63-72. DOI: 10.5658/WOOD.2008.36.2.063

Roumeli, E., Papadopoulou, E., Pavlidou, E., Bikiaris, D., Paraskevopoulos, K. M., and Chrissafis, K. (2012). "Synthesis, characterization and thermal analysis of urea–formaldehyde/nanosio$_2$ resins," *Thermochimica* Acta 527, 33-39. DOI: 10.1016/j.tca.2011.10.007

Sinha, S. K., and Khali, D. P. (2015). "Synthesis and comparison of phenol-urea-formaldehyde (PUF) thermosetting resin with commercial synthetic resins," *Asian Journal of Research in Chemistry* 8(7), 449-452. DOI: 10.5958/0974-4150.2015.00072.3

Sheng, Y., Wang, Q., Xu, X. C., Jiang, W., Gan, S. C., and Zou, H. F. (2011). "Oxidation of cornstarch using oxygen as oxidant without catalyst," *LWT - Food Science and Technology* 44(1), 139-144. DOI: 10.1016/j.lwt.2010.05.004

Tohmura, S. I., Inoue, A., and Sahari, S. H. (2001). "Influence of the melamine content in melamine-urea-formaldehyde resins on formaldehyde emission and cured resin structure," *Journal of Wood Science* 47(6), 451-457. DOI: 10.1007/BF00767897

Vazquez, G., Lopez-Suevos, F., Villar-Garea, A., Gonzalez-Alvarez, J., and Antorrena, G. (2004). "^{13}C-NMR analysis of phenol-urea-formaldehyde prepolymers and phenol-urea-formaldehyde-tannin adhesives," *Journal of Adhesion Science and Technology* 18(13), 1529-1543. DOI: 10.1163/1568561042411231

Wang, S., Zhang, F., Chen, F., and Pang, Z. (2013). "Preparation of a crosslinking cassava starch adhesive and its application in coating paper," *BioResources* 8(3), 3574-3589. DOI: 10.15376/biores.8.3.3574-3589

Young No, B., and Kim, M. G. (2007). "Evaluation of melamine-modified urea-formaldehyde resins as particleboard binders," *Journal of Applied Polymer Science* 106(6), 4148-4156. DOI: 10.1002/app.26770

Zanetti, M., Causin, V., Saini, R., Cardin, A., and Cavalli, R. (2014). "Effect of tannin on increasing UF adhesive performance at high temperature investigated by TMA and TGA analysis," *European Journal of and Wood and Wood Products* 72(3), 385-392. DOI: 10.1007/s00107-014-0795-7

Zhang, J., Wang, X., Zhang, S., Gao, Q., and Li, J. (2013). "Effects of melamine addition stage on the performance and curing behavior of melamine-urea formaldehyde resin" *BioResources* 8(4), 5500-5514. DOI: 10.15376/biores.8.4.5500-5514

Zhou, X., Essawy, H. A., Pizzi, A., Li, X., Pasch, H., and Pretorius, N. (2013). "Poly(amidoamine)s dendrimers of different generations as components of melamine urea formaldehyde (MUF) adhesives used for particleboards production: What are the positive implications?" *Journal of Polymer* Research 20(10), 1-14. DOI: 10.1080/01694243.2012.727166

Zhu, X., Xu, E., Lin, R., Wang, X., and Gao, Z. (2013). "Decreasing the formaldehyde emission in urea-formaldehyde using modified starch by strongly acid process," *Journal of Applied Polymer Science* 131(9), 40202. DOI: 10.1002/app.40202

Article submitted: June 13, 2017; Peer review completed: August 19, 2017; Revised version received and accepted: August 22, 2017; Published: August 30, 2017.
DOI: 10.15376/biores.12.4.7590-7600