

**AN ECO-FRIENDLY UREA-FORMALDEHYDE RESIN:  
PREPARATION  
STRUCTURE AND PROPERTIES**

ZHIGANG WU, XUEDONG XI, LIPING YU, LI SU  
GUIZHOU UNIVERSITY, COLLEGE OF FORESTRY  
GUIZHOU, P.R. CHINA

ZHIGANG WU, XUEDONG XI, HONG LEI, GUANBEN DU, ZHIWEI YIN  
SOUTHWEST FORESTRY UNIVERSITY, YUNNAN PROVINCIAL KEY LABORATORY OF WOOD  
ADHESIVES AND GLUED PRODUCTS  
KUNMING, YUNNAN, P.R. CHINA

XUEDONG XI  
UNIVERSITY OF LORRAINE, ENSTIB-LERMAB  
EPINAL, FRANCE

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**ABSTRACT**

The preparation, structures and properties of UF resin prepared with concentrated formaldehyde at a low molar ratio  $F/U=1.1$  were studied in this paper. According to the results obtained from  $^{13}C$ -NMR, FT-IR and DMA, UF resin prepared with concentrated formaldehyde showed better mechanical properties and heat resistance and lower formaldehyde emission responsible for its high degree of polycondensation and crosslinking than that of UF prepared with common formaldehyde, but its stability was so bad due to its high content of ether bridges. However, it was stated that adding hydrolyzed soy protein to this UF resin at the first alkali preparation stage of "alkali-acid-alkali", its stability got improved due to the increase of methylene bridges, which was the key contribution to polycondensation.

**KEYWORDS:** UF resin, concentrated formaldehyde, soy protein, structures, properties.

**INTRODUCTION**

Urea-formaldehyde (UF) resins are the most widely used in wood industry, such as particle board, plywood, medium-density fiberboard, and so on. UF resins possess several advantages

such as clear glueline, high initial viscosity, lower press temperature, good performance, lower cost, and also have been widely used in manufacturing products. Unfortunately, the formaldehyde used in the synthesis process will release from the preparation, practical application and the subsequent UF-bonded boards (Kandelbauer et al. 2007, Dunky et al. 1998, 2004). Besides that, the cured UF resins are very difficult to degrade. There was no evidence of biodegradation after the UF resins under soil for over 32 years (Okada, 2002, (Qu et al. 2015a, 2015b). The efforts have never stopped in order to resolve this problem. With the increase focus on the health risks of UF resins, many works have been done on the development of low-formaldehyde emission UF resins. Studies showed that the key to reduce formaldehyde emission of UF resins' products was cutting down the molar ratio (F/U). However, only dropping the molar ratio will decline the degree of crosslinking and the initial viscosity of UF resins, and the mechanical properties of UF resins are so poor that it can't meet the requirement of use (Steinhof et al. 2014, Despres et al. 2007, Chung et al. 1994).

Although UF resins consist of only two monomers, urea and formaldehyde, the reaction between them is rather complex due to the high reactivity of urea and formaldehyde. The classical preparation procedure between urea and formaldehyde can be divided into three stages "alkali-acid-alkali": usually an alkaline methylation followed by an acid condensation and stored in alkaline condition (Li et al. 2016, Cao et al. 2016). It proved that the preparation conditions, such as molar ratio, pH, reaction temperature, and so on, had great effects on the structures and properties of UF resins (Li et al. 2015, 2014).

The content of concentrated formaldehyde is more than 42%. UF resins prepared with urea-formaldehyde concentrate (UFC) have better performance than common UF resins, such as higher curing reactivity, short curing time, lower free formaldehyde emission and products with better mechanical properties, and so on (Wu et al. 2016a, Lei et al. 2006). But the study on the preparation of UF resins directly with concentrated formaldehyde is rather few. In this paper, concentrated formaldehyde was used to replace the common formaldehyde 37 wt% to compound UF resin at a low molar ratio F/U=1.1. Besides, biomass soy protein was introduced into three preparation stages. Lower cross-linking degree of UF resins with low molar ratio, improved chain flexibility, and introduced natural molecular may enhance the susceptibility of the modified UF resins to enzymatic hydrolysis (Arancibia et al. 2014, Okada et al. 2002). Soy proteins consist of the amino acid units, the possible reactive groups in the soy protein structure mainly include -OH, -SH, -COOH and -NH<sub>2</sub> groups, which may react with UF (Wu et al. 2016b, Lei et al. 2014). Hence, the incorporation of biodegradable soy protein molecular chains along with a low molar UF may be an effective strategy for enhancing the biodegradability of UF resins (Wu et al. 2013a). The objective of this work was to analyze the structures and properties of the UF resins prepared with concentrated formaldehyde and soy protein.

## MATERIALS AND METHODS

### Materials

Soy protein isolate (SPI, 90% protein content) was purchased from Yuxin Soybean Protein Co., Ltd, China. Two kinds of formaldehyde solution with concentration of 37 wt% and 50 wt% were purchased from Sinopharm Chemical Reagent Co., Ltd, PR China and Kunming Xinfeilin Panel Board CO., LTD, PR China. Oak veneer, with moisture content less than 15% and density more than 0.5 g·cm<sup>-3</sup>, was come from Banna district of China, respectively. All other chemicals mentioned in this paper were all of reagent grade.

### Degradation of SPI protein

In a three-neck round-bottom flask equipped with a mechanical stirrer, thermometer, and condenser was charged with water (140 g), NaOH (7.56 g), a phase transfer agent ethylene glycol (1.6 g) and silicon oil (10 drops) and then heated to 70°C. SPI (84 g) was then charged to the rapidly stirring solution. The mixture was heated to 90°C (treating temperature), with rapid agitation, and held between for 3h (treating time). The mixture was cooled to 35°C in an ice bath. Test methods of viscosity and pH value referred to Chinese national standard GB/T 14074-14074.

### Preparation of UF adhesive

The UF adhesive with molar ratio F/U=1.1:1 was prepared as follows: 113 parts of formaldehyde 37 wt% or 83.4 parts of formaldehyde 50 wt% was charged to a three-neck 500ml flask equipped with a mechanical stirrer, thermometer and condenser and. The first urea (34.8 g) was then charged to the rapidly stirring solution. The pH was adjusted to 8.0-8.5 with NaOH 30% solution. Once the temperature was brought to 90 °C, the second urea (17.4 g) was added to the mixture and the reaction was maintained for 20 minutes. The pH was adjusted to 5.0-5.3 with formic acid 10%. After the desired water tolerance was arrived, the resin was cooled to 60°C. The pH was brought to 7.5-8.0 and the third urea (23.4 g) was added. After 15 minutes, the resin was cooled to room temperature. The UF resin samples prepared with formaldehyde 37% and 50% called as UF1 and UF2, respectively.

And then hydrolyzed soy protein was respectively charged into three preparation stages of "alkali-acid-alkali" of UF2, S1-UF2, S2-UF2 and S3-UF2 were gotten.

The properties of the final UF resin, including viscosity, pH, the content of free formaldehyde and methylol groups, were measured according to the method introduced by the Chinese national standard (GB/T 14074-2006).

### Formaldehyde reaction ability of hydrolyzed soy protein

In a three-neck round-bottom flask equipped with a mechanical stirrer, thermometer, and condenser was charged with hydrolyzed soy protein 64g (W1), formaldehyde 37.2 wt% 30g (W2), then adjust pH to 8.2-8.5 with orthophosphoric acid (W3). The mixture was heated to 85 °C, and held the temperature for 3h. The formaldehyde reaction ability of hydrolyzed soy protein was measured according to the method introduced by the Chinese national standard (GB/T 14074-2006).

$$\text{Formaldehyde reaction ability} = 1000 \times [37.2\% \times W_2 - (W_1 + W_2 + W_3) \times F\%] / (0.375 \times W_1).$$

### Preparation of lap samples

Oak sapwood was cut into pieces with dimensions of 30×25×10 mm. Adhesive was spread on the surface of pieces. The usage of the adhesive was 200 g·m<sup>-2</sup> (two sides) on a dry weight basis. Two pieces were then lapped together to have a 25×25 mm surface area, and were pressed into a specimen at pressure 2.0 MPa and 140°C press temperature. The total press time was 8 min. For one press, 24 specimens could be gotten at the same time.

### <sup>13</sup>C-NMR analysis

The 400μl liquid UF resin was directly mixed with 50μl DMSO-d<sub>6</sub> for <sup>13</sup>C-NMR determination. The spectra were obtained on a Bruker AVANCE 600 NMR spectrometer using 12μs pulse width (90°). The relaxation delay was 6s. To achieve a sufficient signal-to-noise ratio, inverse-gated proton decoupling method was applied. The spectra were taken at 150MHz with

400–600 scans accumulated. The molar distribution of the structural elements was described by the percentages calculated from the obtained spectral peak integration values (Lei et al. 2016, Guo et al. 2014).

### FT-IR analysis

Liquid UF sample was put in the preparation of KBr pills. The FT-IR spectra were gotten on a Varian 1000 infrared spectrophotometer.

### DMA measurement

DMA analysis was conducted by using NETZSCH DMA-242 thermomechanical analyzer with NETZSCH Proteus software for data treatment. All experiments were tested under the same conditions: 0.125 g of resin, heating rate 5 K·min<sup>-1</sup> at the temperature range 20–260°C. Deflection curves, which allow determining the modulus of elasticity, have been obtained in three point flexion mode on two beech wood veneers of dimensions 50×10× 3 mm for each specimen while the liquid resin layer was spread between the two specimens. The measurements of the thermomechanical properties were made in triplicates on three similar specimens and the average value was taken.

## RESULTS AND DISCUSSION

### Performance of hydrolyzed soy protein

Performance of hydrolyzed soy protein was shown in Tab 1. As the treating time from 1h to 3h, formaldehyde reaction capacity of hydrolyzed soy protein increased from 116.6 mg·g<sup>-1</sup> to 214.3 mg·g<sup>-1</sup>, which showed that the longer the treating time, the more active groups in hydrolyzed soy protein. SPI protein treated by alkali, and then secondary and tertiary structure destruction, polar groups and hydrophobic groups inside soy protein released. The following hydrolyzed soy protein (treating time 3h) was to modify UF resin.

Tab. 1: Effects of degradation conditions on performance of hydrolyzed soy protein.

Treating time (h)	Viscosity at 45°C (mPa·s)	pH	Formaldehyde reaction ability (mg·g <sup>-1</sup> )
1.0	49.0	13.45	116.6
1.5	36.5	13.24	148.9
2.0	32.5	13.40	160.4
2.5	25.0	13.36	181.6
3.0	22.3	13.14	214.3

### Performance of UF resins

The performance of UF1, UF2, S1-UF2, S2-UF2 and S3-UF2 were given in Tab. 1. It was obvious that the solid content and the viscosity of UF2 prepared with concentrated formaldehyde was higher than that of UF1 with formaldehyde 37 wt%. Content of free formaldehyde of UF2 was near to that UF1, but methylol groups and bonding strength was more than UF1.

At the acid preparation stage of UF2, adding hydrolyzed soy protein, S2-UF2 had poor stability and bad bonding strength. Because hydrolyzed soy protein might hinder polycondensation of UF, which resulted to low crosslinking degree, poor stability and bad bonding strength of S2-UF2.

At the last alkali preparation stage of UF2, adding hydrolyzed soy protein, bonding strength of S3-UF2 increased by only 4%, but free formaldehyde decreased by 18%. Partial charging urea to prepare UF was a classical method, and the role of the last batch of urea was to absorb free formaldehyde which had little contribution to the crosslinking polymerization of UF resin (Kim et al. 1999). So was the role of hydrolyzed soy protein adding at the last stage.

At the first alkali preparation stage of UF2, adding hydrolyzed soy protein, S1-UF2 had better performance. Content of free formaldehyde of UF2 and S1-UF2 were near to that UF1, methylol groups more than UF1, which normally affected the curing and water resistance of UF resin. All of the UF resins arrived at the similar water tolerance. Compared with UF1, bonding strength of UF2 and S1-UF2 increase by 64% and 76% indicated that content of formaldehyde might affect the final structures of UF.

Tab.2: Effects of amount of soy protein on performance of UF2 resin.

Adhesives	Viscosity (mPa*s)	Solid content (%)	Methylol (%)	Free formaldehyde (%)	Bonding strength (MPa)
UF1	66.8	50.0	5.62	0.088	3.95±0.77
UF2	456	63.3	13.51	0.088	6.48±1.59
S1-UF2	967	62.4	12.81	0.088	6.95±0.94
S2-UF2	--	--	--	--	--
S3-UF2	2665	64.1	12.64	0.072	4.07±0.60

"--": The data can't be measured

### <sup>13</sup>C-NMR analysis

The chemical structure of UF1 and UF2 was analyzed by <sup>13</sup>C-NMR to find the connection between the chemical structure and the properties of resins (Figs. 1 and 3). The assignments of the observed chemical shifts were listed as in Tab. 3 (Kim et al. 2000, 2001a, 2001b, 2003, 2007, Despres et al. 2007). The percentages calculated by the integration methods for different methylenic carbons were also given in this table.

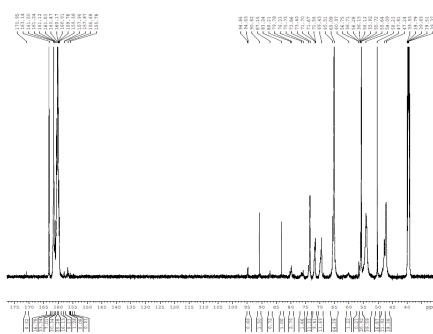


Fig. 1: <sup>13</sup>C-NMR spectrum of UF1 resin

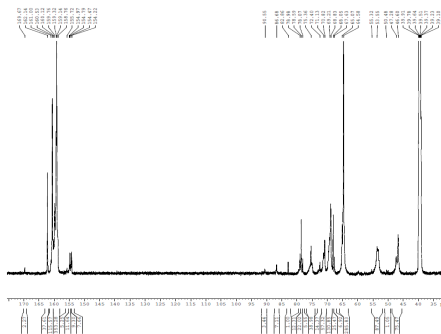


Fig. 2: <sup>13</sup>C-NMR spectrum of UF2 resin

The peaks at 64-66ppm and 71-72ppm were assigned as mono- and di-methylol groups, respectively. The peaks at 47ppm, 54ppm and 60ppm belong to the carbon in type I, II and III methylene bridges. The peaks at 69ppm, 75ppm and 79ppm were methylene ether bridges. Urons could also be seen from the peaks at 154-158ppm.

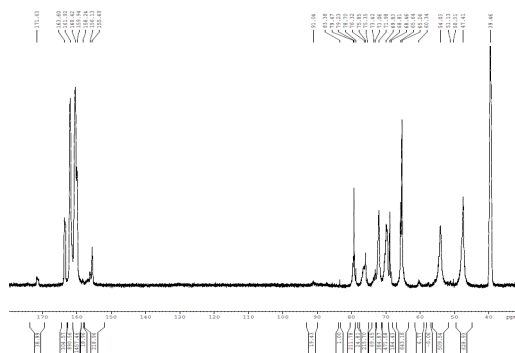


Fig. 3:  $^{13}\text{C}$ -NMR spectrum of S1-UF2 resin

Methylol groups were the basis and key of molecular chain increasing and crosslinking reaction during the preparation of UF resin. The formation of methylene bridges and ether bridges generated by consuming methylol groups indicated that both contents of methylene bridges and ether bridges could show the degree of polycondensation. Seen from Tab. 3, the content of methylene bridges of UF2, 21.05%, was lower than that of UF1, 40.37%. However, there were more ether bridges in UF2 than in UF1, specifically, 31.28% vs. 9.08%. The sum content of methylene bridges and ether bridges indicated that there was higher degree of polycondensation in UF2 than that of UF1, which was good for the mechanical property of UF2 in some degree.

As the basis of the cross-linking of UF resin with branches structure, the content of di-methylol groups which can show the degree of crosslinking is the most important key to contribute to the mechanical property. Seen from Tab. 3, the content of di-methylol groups of UF2, 8.4%, was higher than that of UF1, 5.31%. So, the higher content of methylene bridges, ether bridges and di-methylol groups should be responsible for the better mechanical property of UF2 in Tab. 3. As is well-known that the formation of methylene and ether bridges often occur simultaneously and competitively during the preparation of UF resins. Ether bridges are thought to be not as stable as methylene bridges and be more likely to be rearranged to methylene bridges by splitting off formaldehyde (Du et al. 1999). UF2 resin contained so many ether bridges, which was bound to affect its usability. Besides that, more urons observed in UF2 adhesive was good for formaldehyde emission decrease and the water resistance improvement in some degree.

UF2 had higher degree of polycondensation and crosslinking, and the unfavorable ether bridges were the majority. So, UF2 need to do some modification. Hydrolyzed soy protein was charged into the first alkali preparation stage of UF2, the chemical structure of S1-UF2 was analyzed by  $^{13}\text{C}$ -NMR to find the connection between the chemical structure and the properties as Fig. 3. Seen from Tab. 3, the content of methylene bridges of S1-UF2, 33.96%, was higher than that of UF2, 21.05%. There were more ether bridges in S1-UF2 than in UF2, specifically, 32.88% vs. 31.28%. The sum content of methylene bridges and ether bridges was of S1/UF<sub>2</sub>, 66.87%, higher than that of UF2, 52.33%, which indicated that there was higher degree of polycondensation in S1-UF<sub>2</sub> system. And what's the most important thing was that content of methylene bridges increasing which was the key contribution to polycondensation was critical in improving stability of UF resin.

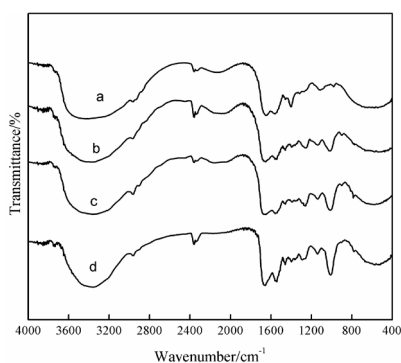
Besides, the content of di-methylol groups of S1-UF2 was higher than that of UF2, 11.42% VS 7.40%. It also showed that adding hydrolyzed soy protein at the first alkali preparation stage of UF<sub>2</sub>, properties of S<sub>1</sub>/UF<sub>2</sub> adhesive had further improvement.

Tab. 3:  $^{13}\text{C}$ -NMR assignments and its quantitative analysis results of UF resins.

Structures	Chemical shifts (ppm)	UF1 (%)	UF2 (%)	S1-UF2 (%)
-NH-CH <sub>2</sub> -NH-(□)	46-48	17.68	9.75	18.65
-NH-CH <sub>2</sub> -N=(□)	53-55	22.36	11.30	15.11
=N-CH <sub>2</sub> -N=(□)	60-61	0.69	-	0.20
	<b>Total</b>	40.37	21.05	33.96
-NH-CH <sub>2</sub> OCH <sub>2</sub> NH-(□)	68-70	6.60	21.09	19.46
-NH-CH <sub>2</sub> OCH <sub>2</sub> N=(□)	75-77	0.94	5.04	6.40
=N-CH <sub>2</sub> OCH <sub>2</sub> N=(□)	78-80	1.52	5.15	7.02
	<b>Total</b>	9.06	31.28	32.88
-NH-CH <sub>2</sub> OH(□)	64-66	36.37	36.92	19.08
-NH(-CH <sub>2</sub> )-CH <sub>2</sub> OH(□)	71-72	5.31	8.40	11.42
	<b>Total</b>	41.68	44.32	30.50
HO-CH <sub>2</sub> -OH	83-84	0.56	0.13	0.03
HOCH <sub>2</sub> -O-CH <sub>2</sub> -OCH <sub>2</sub> OH	86-87	0.41	0.92	-
HOCH <sub>2</sub> -O-CH <sub>2</sub> -OCH <sub>2</sub> OH	90-91	0.85	0.44	0.58
H(CH <sub>2</sub> O) <sub>n</sub> OCH <sub>2</sub> OCH <sub>3</sub>	94-95	0.37	-	-
	<b>Total</b>	2.19	1.49	0.61
-NH-CH <sub>2</sub> -O-CH <sub>3</sub>	72-73	6.42	1.86	2.06
NH <sub>2</sub> -CO-NH <sub>2</sub>	163-164	10.68	6.97	10.54
NH <sub>2</sub> -CO-NH-	161-162	25.10	21.39	30.81
-NH-CO-N=	159-161	63.22	65.38	50.42
Uron rings	154-158	1.00	6.26	8.23

### FT-IR analysis

A typical infrared absorption of UF resin was seen from the reference (Wu et al. 2013b). Peak at 3300~3500 cm<sup>-1</sup> was stretching vibration of O-H and N-H. -CO-NH- at 1530~1600 cm<sup>-1</sup>, -NH-CO-NH- at 1600~1630 cm<sup>-1</sup>, -CH<sub>2</sub>OH at 1010 cm<sup>-1</sup>, -CH<sub>2</sub>-O-CH<sub>2</sub>- at 1050 cm<sup>-1</sup>, uron at 780-800 cm<sup>-1</sup> were observed.



a. soy; b. UF1; c. UF2; d. S1-UF2

Fig. 4: FT-IR cures of UF resins.

A typical infrared absorption of soy protein was seen from the reference (Sun et al. 2014). C=O band at 1647  $\text{cm}^{-1}$ , COO- at 1390  $\text{cm}^{-1}$  and carbinol at 1053  $\text{cm}^{-1}$  was observed. Peak at 1533  $\text{cm}^{-1}$  came from bending vibration of N-H and stretching vibration of C-N. Peak at 3381  $\text{cm}^{-1}$  were identified as O-H and N-H.

The FT-IR results of UF1, UF2 and S1-UF2 were given as Fig. 4. The spectra for the two resin samples looked very similar. The broad band observed at 3300-3500  $\text{cm}^{-1}$  was assigned to the bound -OH and -NH groups. The absorption band of -CO-NH- and -NH-CO-NH- was observed at 1530-1600  $\text{cm}^{-1}$  and 1600-1630  $\text{cm}^{-1}$ , respectively. Compared the spectra of the two samples, it was observed that the absorption at both 1000-1110  $\text{cm}^{-1}$  and 786  $\text{cm}^{-1}$  increased in UF2 resin sample. The former absorption was assigned as the methylene and methylene ether bridges. The latter was from urons. Both the results confirmed what the  $^{13}\text{C}$ -NMR analysis showed.

Peak of S1-UF2 at 1530-1600  $\text{cm}^{-1}$  and 1600-1630  $\text{cm}^{-1}$  had a strong absorption, and 3300-3500  $\text{cm}^{-1}$  turning sharp was a typical associating example of -OH stretching vibration and N-H bond stretching vibration superposition. It indicated that soy protein structures were introduced into UF2.

### DMA analysis of UF resins

It is well-known that DMA analysis is an effective method to evaluate the curing behavior of thermosetting adhesives (Lei et al. 2015a, 2015b). The DMA curves of UF1, UF2 and S1-UF2 with curing agent 1%  $\text{NH}_4\text{Cl}$  were given as Figs. 5 - 7. In Figs. 5, 6, and 7, from 20°C to around 40°C, the storage modulus of the three UF resin systems were at a lowest plateau. At this time, the storage modulus ( $E'$ ) was mainly determined by the supporting substrate wood. As the temperature going up, there would be two changes happened during adhesive system. One was resin softening resulted to the decrease of the resin stiffness, the other one was curing reaction contributed to the stiffness increase. For UF1 40°C to around 88°C, UF2 40°C to around 90°C and S1-UF2, 40°C to around 100°C, the decrease of the stiffness caused by the softening greatly outpaced the increase of the stiffness of UF resin caused by the curing reaction. Once the temperature was higher than the parabolic Temperature (UF1 88°C, UF2 90°C, S1/UF2 100°C), the gelation point of UF resins were arrived and their storage modulus increased abruptly. At around 110, 120, 130°C, the maximum storage modulus of UF1, UF2 and S1-UF2 could be seen respectively, which indicated the complete of the curing of UF adhesives. Till 200, 220, 210°C, the  $E'$  of UF1, UF2 and S1-UF2 began to decrease because of the resins or wood decomposition. UF1, UF2 and S1-UF2 showed the similar curing behavior from DMA curves, but there were still three differences:

(1) The gelation point of UF2 and S1-UF2 were higher than that of UF1, indicated that UF adhesives prepared with concentrated formaldehyde cured at a higher temperature than that of UF resins with formaldehyde 37 wt%.

(2) When the complete of the curing of UF resins, the storage modulus of UF1, UF2 and S1-UF2 were 6424.4 MPa, 9320.8 MPa, 8312.4 MPa, respectively. As the increase of the temperature, the stability of UF2 was so much worse than that UF1, which might attribute to the higher content of methylene ether link in UF2. S1-UF2 prepared with concentrated formaldehyde as the same as UF2, showed better stability than UF2 was an unexpected outcome. There was higher content of methylene bridges, degree of polycondensation and crosslinking in S1-UF2 than that of UF2, which might offset instability produced by ether bridges fracture and rearrangement.



(3) The decomposition temperature of UF2 220°C, S1-UF2 210°C were higher than that of UF1 200°C, which indicated UF resins prepared with concentrated formaldehyde showed better heat resistance than that of UF resins with formaldehyde 37 wt%.

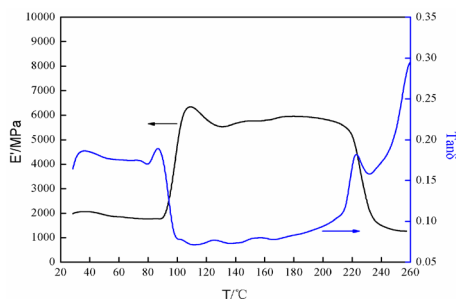


Fig. 5: DMA curves of UF1.

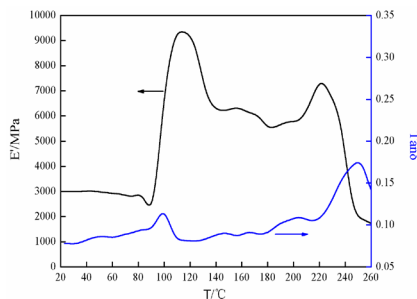


Fig. 6: DMA curves of UF2.

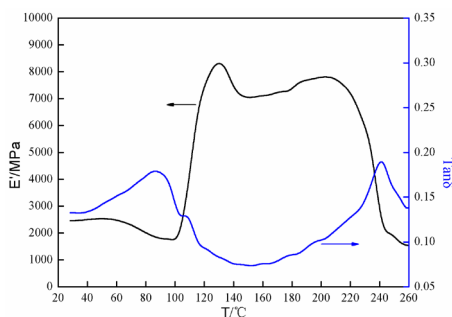


Fig. 7: DMA curves of S1-UF2.

## CONCLUSIONS

The preparation, structures and properties of UF resin prepared with concentrated formaldehyde at a low molar ratio  $F/U=1.1$  were studied in this paper. The  $^{13}\text{C}$ -NMR, FT-IR and DMA results indicated that UF resin prepared with concentrated formaldehyde showed better mechanical properties and heat resistance and lower formaldehyde emission responsible for its high degree of polycondensation and crosslinking than that of UF prepared with common formaldehyde, but its stability was so bad due to its high content of ether bridges. However, it was stated that adding hydrolyzed soy protein to this UF resin at the first alkali preparation stage of “alkali-acid-alkali”, its stability got improved due to the increase of methylene bridges, which was the key contribution to polycondensation.

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ZHIGANG WU, XUEDONG XI#, LIPING YU, LI SU  
GUIZHOU UNIVERSITY  
COLLEGE OF FORESTRY  
GUIYANG 550025  
GUIZHOU  
P.R. CHINA

ZHIGANG WU, XUEDONG XI, HONG LEI\*, GUANBEN DU, ZHIWEI YIN  
SOUTHWEST FORESTRY UNIVERSITY  
YUNNAN PROVINCIAL KEY LABORATORY OF WOOD ADHESIVES AND GLUED PRODUCTS  
KUNMING 650224  
YUNNAN  
P.R. CHINA  
Corresponding author: lfxgirl@163.com.

XUEDONG XI  
UNIVERSITY OF LORRAINE  
ENSTIB-LERMAB 88051  
EPINAL  
FRANCE