

INFLUENCE OF URON RESINS ON THE PERFORMANCE OF UF RESINS AS ADHESIVES FOR PLYWOOD

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ABSTRACT

Uron resin, a kind of urea-formaldehyde (UF) resin containing much more uron structure, were prepared. Several modified UF resins were obtained from mixing uron resins with normal UF resins as well as synthesizing UF resin with uron resin as raw material. This work demonstrated that the introducing of the uron structure reduced free formaldehyde content of UF resin and formaldehyde emission levels in bonded plywood panels significantly, the former were reduced by 76% and 84% in the latter. The synthesis time of uron resin can be shortened to 8 hours. The test result of free formaldehyde content, formaldehyde emission levels and bond strength indicated that specimen of 20 parts uron resin synthesized in 8 hours mixed with 100 parts UF resins (F/U molar ratio of 1.3) had a potential advantage to industrial application. The beneficial effect of uron resin on the performance of UF resin can be attributed to the opening of uron cycle structure and the following reaction with free formaldehyde and its oligomeric glycol forms.

Keywords: Uron structure; UF resin; plywood; formaldehyde emission; ¹³C NMR.

INTRODUCTION

The contamination from formaldehyde emission on the environment limits the wide application of urea-formaldehyde (UF) resin. Thus, considerable efforts have been paid on reducing formaldehyde emission level from UF bonded wood composites, such as mending the prescription and procedure of UF resin synthesis, optimizing the application craft of adhesives, as well as the use of formaldehyde scavengers with adhesives (Abdullah and Park 2010). Uron initially aroused interest due to its lower formaldehyde emission effect on UF resin which was synthesized at very acid pH (Gu *et al.* 1995). The following research confirmed that the introduction at lower reaction temperatures of the additional strongly acid condensation step was the formation of sometime considerable quantities of Uron (Gu *et al.* 1995). Thus, the critical parameters for maximizing the portion of Uron present at the end of the UF resin synthesis was proposed, and the particle board bonded with uron-rich resins showed the considerable bond strength (Soulard *et al.* 1999). However, the preparation of UF resins containing high proportion of urons is not feasible in practice simply because the quantity of free formaldehyde left at the end of the reaction is too high and would lead to a very high formaldehyde emission from panels. Futher, little is known about the mechanisms of the reduction effect of uron structure on reducing free formaldehyde content and formaldehyde emission levels.

The approach of this work is attempted to simplify the preparation process of uron resin and develop it as a type of additive to UF resin. Furthermore, the special objective is to reduce formaldehyde content of UF resin and formaldehyde emission levels of it bonded plywood via introducing uron resins, as well as to interpret the reaction mechanism of the former result.

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EXPERIMENT

Resin preparation and testing

Urea formaldehyde resins

Three different UF resins were prepared according to the following typical resin procedure: 955.9g (11.79mol) of a 37% formaldehyde solution (AR) was charged under continuous mechanical stirring in a glass reactor equipped with a reflux condenser, thermometer and pH electrode and temperature raised to 45°C. The pH of the formalin was adjusted to 7.5-8.0 with 30% NaOH water solution. The first urea of 353.7g (5.90mol) was added to the reactor and the temperature was slowly raised to 90±2°C within 40-60min and maintained at 90±2°C for 60min. After that, the pH was adjusted to 4.4 with 20% formic acid and kept refluxing for 15min. Small samples of the reaction mixture were then extracted with a pipette and charged to 20°C water to examine for signs of turbidity. Immediately, after reaching turbidity, the pH was adjusted to 7.5, followed by 88.4g (1.47mol) second urea. The temperature was decreased rapidly to 70-80°C and maintained for 30min. Then 102g (1.7mol) of the third urea were added and also refluxing for 30min. Finally, the system was adjusted to pH 7.5-8.0 and cooled to room temperature, which was marked as UF-B. By changing the amount of the third urea, different F/U molar ratio resins were obtained: UF-A: F/U=1.4:1, UF-B: F/U=1.3:1, and UF-C: F/U=1.2:1.

Uron-UF mixtures

574.7g (7.09mol) of a 37% formaldehyde solution was charged into a glass reactor equipped with a reflux condenser, thermometer and pH electrode. The pH of the formalin was adjusted to 11.0 with 30% NaOH water solution following 88.6g (1.48mol) of the first urea. The temperature was raised to 90±2°C in 30min, and 32.9g (0.55mol) of the second urea was added and then the pH was reduced from 11.0 to 1.5 within 24 hours by adding 20% formic acid in small amounts at different times. After that, the reaction mixture was made alkaline to pH 8.7 with 30% NaOH water solution and cooled to 60°C. 303.8g (5.06mol) of the third urea was added and the reaction mixture was maintained at 60°C for 1 hour. Lastly, the reaction was adjusted to pH 7.5-8.0 and cooled to room temperature, which was marked as Uron-A. By changing the time of reducing pH from 11.0 to 1.5, different kinds of uron resins were taken: Uron-A: 24h, Uron-B: 12h, Uron-C: 8h.

Uron-UF mixtures were prepared by mixing uron resins with UF resins at various weight ratios as indicated in table 1, stirred at 60°C for 1 hour and then cooled to room temperature.

Table 1. Weight ratio of Uron to UF for the mixtures

Mixtures (Uron : UF)	Sample							
	1	2	3	4	5	6	7	8
A-A	0:100	20:100	33:100	50:100	100:100	150:100	200:100	100:0
B-A	0:100	20:100	33:100	50:100	100:100	150:100	200:100	100:0
C-A	0:100	20:100	33:100	50:100	100:100	150:100	200:100	100:0
B-B	0:100	20:100	33:100	50:100	100:100	150:100	200:100	100:0
C-B	0:100	20:100	33:100	50:100	100:100	150:100	200:100	100:0
C-C	0:100	20:100	33:100	50:100	100:100			100:0

Synthesis of UF resins using uron resin as raw material

The procedure was the same as the one used above to synthesize UF resins, except that the addition of the first urea was replaced by uron resins. So the amount of formalin, the amounts of 2nd and 3rd urea were changed according to the weight ratio of uron resin to the end UF resins. The F/U molar ratio of this series UF resins (UF-U) was 1.3:1.

UF-U1: 20% of Uron-C (80g), the amount of the formaldehyde, the 2nd and 3rd urea were separately 208.9g (2.58mol), 23.6g (0.39mol), and 27.2g (0.45mol), UF-U2: 30% of Uron-C (120g) and 186.0g (2.29mol) of formaldehyde, UF-U3: 40% of Uron-C (160g) and 163.0g (2.01mol) of formaldehyde, UF-U4: 55% of Uron-C (220g) and 127.5g (1.57 mol) of formaldehyde. The amount of the 2nd and 3rd urea of UF-U1 to UF-U4 was equal. The final pH of all resins were adjusted to 7.5-8.0. Viscosity and gelation time of all samples were tested according to GB/T 14074 -2006.

¹³C-NMR Tesing

NMR resin samples (Uron-C and C-B2) were prepared by mixing liquid resins (2.0g) with D₂O (1.0g). Carbon spectra were obtained with a Bruker DPX300 nuclear magnetic resonance spectrometer at a frequency of 75.47MHz. Acquisition time was 0.544 s with the number of transients about 1000. Pulse width was 3.00 usec. The assignments of the different peak shifts observed (Table 3) were obtained from literatures and calculation.

Preparation and testing of plywood panels

Three layer plywood panels were prepared using Chinese white poplar (*Populus tomentosa*) veneers of 300(W)×300(L)×1.5(T) mm, which were obtained from a local manufacturer and dried to approximately 3% moisture content before manufacturing. The glue spread used was a 300g/m² double glue line (which was aimed to maximize the effect of different type adhesives as well as evaluate the effect significantly) with a mixture of 100 parts UF liquid resin with 5-15 parts wheat flour and 1 part NH₄Cl solid powder. After 15 min ageing stage, the mat was pressed for 4.5 min (1min/mm), at 120°C and 1.5MPa. After hot pressing, the panels were cooled down and conditioned at 22±1°C, 65±2% relative humidity till a constant weight prior to testing. The bond strength with seven repetitions after 3 hours 63°C water step followed by a 10 min drying in air was tested according to Chinese Standard GB/T 17657-1999 for plywood. The formaldehyde emission level were determined in accordance with the following procedure: one specimen with a dimension of 100±2(W) × 30±1(L) × 4.5±0.2(T) mm was maintained for 24 hours at 20 °C and 40 % RH in a 500 ml jar sealed with airproof. The formaldehyde concentration in the jar was measured using a F400 formaldehyde-meter (Wales). Seven replicates were tested for each condition.

RESULTS AND DISCUSSION

Effects of Uron resin on the performance of UF resins

Viscosity and gelation time

Table 2 shows that the higher the weight ratio of uron resins to UF resins, the lower viscosity values and the longer gelation time of mixed UF resins. The viscosity values of three types of uron resins are 6.8-10.1 mPa.s. Mixing uron resins with UF resins under the conditions in table 1 made the viscosity of mixed UF resins decreased rapidly. The probable reason for this is that the uron cyclic structures are series of relatively independent ingredients in the mixed UF resin. For both unsubstituted uron



as  and substituted uron as , the reaction activity is low because of less active sites in molecular. So the higher percentage of Uron resins added to UF the lower is the viscosity. Additionally, according to the general method for determination of gelation time of UF resin (GB/T 14074.7-93), all uron resins charged in 100°C water longer than 500 sec could not cure and still kept in liquid. This may be due to the existence of uron cycles in synthesized uron resins, which made the amount of active groups (the content of methylol) declined, and molecule chains could not react with each other to form the polymerized network. Thus, even the molecular weight of uron resins was low, the viscosity values decreased and gelation time became longer than normal UF resins and could not cure.

Table 2. Viscosity and gelation time of UF resins mixed with uron resins.

Specimens	Viscosity (mPa.s)	Gelation time (s)	Specimens	Viscosity (mPa.s)	Gelation time (s)
UF-A (AA-1)	121.5 (9.1) a [*]	96 (7) a	UF-B	81.3 (5.3) a	74 (4) a
BA-1,CA-1)			(BB-1,CB-1)		
AA-2	107.5 (7.3) a	148 (10) b	BB-2	36.8 (3.2) b	121 (9) b
AA-3	47.3 (3.5) b	168 (11) b	BB-3	29.8 (2.1) b	187 (11) c
AA-4	28.5 (1.7) c	218 (17) c	BB-4	23.3 (1.7) bc	253 (17) d
AA-5	22.0 (1.1) c	298 (19) d	BB-5	17.8 (1.1) c	320 (25) e
AA-6	17.3 (1.1) cd	455 (20) e	BB-6	15.5 (0.6) c	390 (31) f
AA-7	15.0 (0.9) d	-	BB-7	15.1 (0.6) c	-
Uron-A (AA-8)	10.8 (0.9) d	-	CB-2	40.8 (3.1) b	155 (11) b
BA-2	51.0 (2.5) b	145 (12) b	CB-3	33.8 (2.7) b	205 (17) c
BA-3	32.0 (1.9) c	208 (15) c	CB-4	27.2 (1.5) bc	260 (19) d
BA-4	26.0 (1.8) c	247 (20) c	CB-5	18.5 (1.2) c	320 (26) e
BA-5	15.0 (0.8) d	335 (25) def	CB-6	15.2 (0.9) c	390 (29) f
BA-6	13.3 (0.7) d	390 (28) g	CB-7	14.3 (0.8) c	-
BA-7	12.2 (0.7) d	-	CC-1	41.5 (3.5) b	89 (5) b
Uron-B(BA-8)	6.8 (0.5) e	-	CC-2	35.5 (2.4) bc	167 (11) c
CA-2	87.0 (3.7) ab	110 (8) a	CC-3	32.1 (2.6) bc	199 (13) d
CA-3	36.8 (2.5) c	150 (11) b	CC-4	25.0 (1.2) bc	250 (17) e
CA-4	24.5 (1.9) c	257 (20) cd	CC-5	16.0 (0.8) c	320 (25) f
CA-5	28.9 (1.7) c	263 (19) cd	UF-U1	50.5 (3.7) b	138 (9) b
CA-6	15.5 (1.1) d	313 (25) def	UF-U2	26.5 (1.9) bc	203 (11) c
CA-7	13.8 (1.1) d	-	UF-U3	20.5 (1.5) bc	405 (31) g
Uron-C (CA-8, CB-8,CC-6)	8.1 (0.7) de	-	UF-U4	13.9 (0.7) d	-

*Values represent means of seven replicates per treatment, while figures in parentheses are the standard deviation. Means with a column followed by the same letter are not significantly different using Tukey's Studentized Range Test ($\alpha = 0.05$)

"-" means the corresponding samples can not be cured in 100°C water, while figures in parentheses are the standard deviations.

Free formaldehyde contents

The free formaldehyde content in the three types of UF resins synthesized in this experiment are 0.35%, 0.19%, and 0.11% separately. The pure uron resin's free formaldehyde content are very low (0.08–0.12%) as shown in figure 1. The addition of uron resins reduced the free formaldehyde contents notably, the highest extent of decrease recorded measuring 76%. Especially, Uron-C performed a surprising reduction effect that the free formaldehyde content of Uron-C (0.12%) was higher than that of UF resins' (UF-C 0.11%), but after mixing 20 part of Uron-C with 100 part UF-C, the free formaldehyde contents of mixed UF resins was lower than the corresponding values of both pure Uron-C and UF-C. The same result was obtained while mixing Uron-C with UF-B (in Figure 1). These results indicate the promising potential obtaining of low formaldehyde emission plywood panels bonded with above modified UF resins.

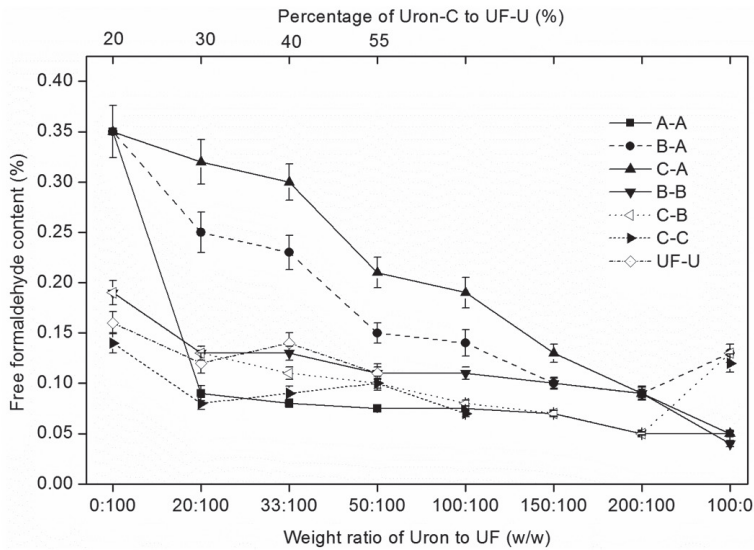


Figure 1. Free formaldehyde content of pure UF and modified UF resins.

Formaldehyde emission levels of plywood

The addition of uron to UF resins clearly decreased the formaldehyde emission levels of plywood as shown in figure 2. The highest formaldehyde emission level of the plywood belongs to the one glued with UF-A and the lowest to Uron-C. The more the addition of uron resins, the lower the formaldehyde emission levels of plywood. While mixing Uron-C with UF-B at weight ratio of 200:100, the formaldehyde emission values reduced by almost 84%. This reduction effect was very significant regardless of the mixture type of uron resins with high F/U molar ratio UF resins (such as 1.4:1 and 1.3:1), but relatively insignificant in mixtures of lower F/U molar ratio of UF resins (such as 1.2:1).

The formaldehyde emission levels of plywood made with UF-U which were synthesized by urea, formaldehyde and Uron-C as its raw material are relatively high, although these values reduced as the amount of uron resin addition increased. On the whole, there is no predominance compared with mixed UF resins.

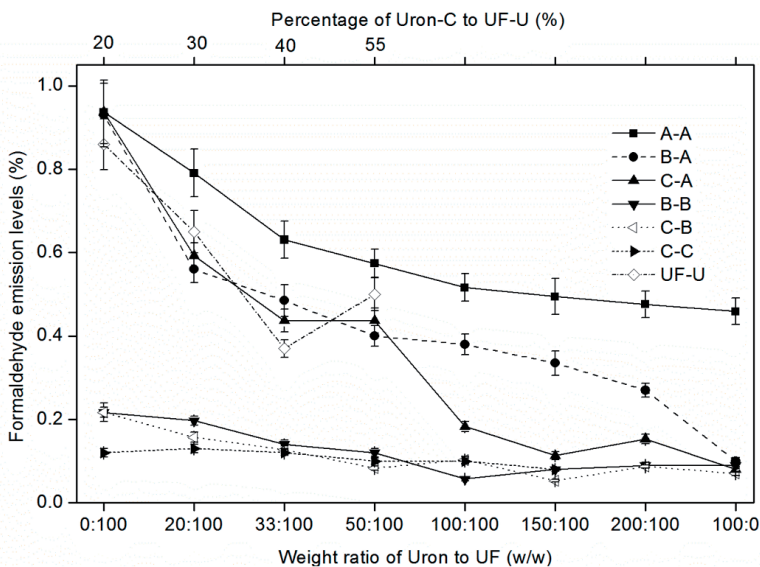


Figure 2. Formaldehyde emission levels of plywood panels bonded with various UF resins.

Bond strength of plywood

In general, bond strength is considered to be controversial to formaldehyde emission levels of UF resin glued wood composites. Figure 3 indicates that the effect of uron resin on the bond strength of plywood panels is not as clear as on formaldehyde content and formaldehyde emission levels above. Uron-A dropped the bond strength to 0 MPa immediately when it was mixed with UF-A, as well as the similar decreasing trend of Uron-B. However, Uron-C presented completely different result that the bond strength improved while it was mixed with UF resin by weight of Uron/UF of 20:100. The bond strength of sample C-B2 approached 1.2 MPa which is significantly different with other CBs using Tukey's Studentized Range Test ($\alpha = 0.05$). Meanwhile, it showed a very low formaldehyde emission values as well, which indicates that it is potential to be applied in industry.

Cyclic uron structures are a kind of outgrowth while synthesizing UF resins and appear in all synthesis procedures. Previous studies have indicated that the definite pH ranges of formation and satisfying stability of uron were higher than 6 and lower than 3 (Soulard *et al.* 1999). The combined effect of the experimental results with respect to free formaldehyde content, bond strength and formaldehyde emission levels in this research confirm that the introducing of uron resin improved the performance of normal UF resins, but which is irrespective of the preparation time of uron. So long as the reaction mixture is maintained enough at the strongly acid and alkaline step, the preparation time of uron resins can be shortened obviously. This is potentially beneficial to industrial applications.

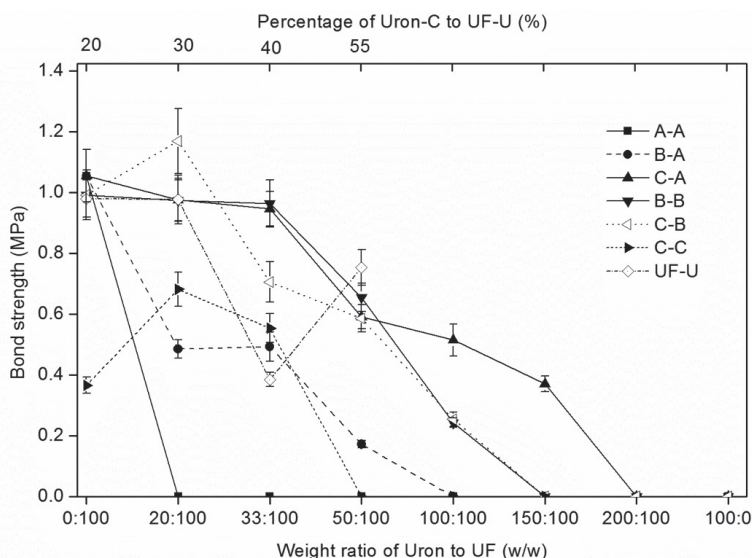


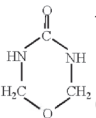
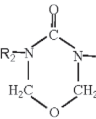
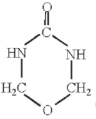
Figure 3. Bond strength of plywood panels manufactured by various UF resins.

Mechanisms of the effect of uron resin on the performance of UF resins

¹³C-NMR analysis

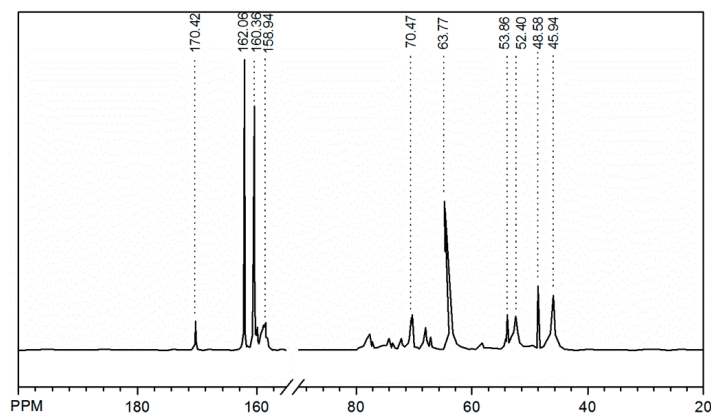
There are many reports about the structure of UF resins and ¹³C NMR peak chemical shifts assignments, which can be divided into four ranges (Ferg *et al.* 1993): 155-170 ppm region belongs to urea and its ramification (such as carbonyl of methylol urea or uron), 45-60 ppm to methylene (-CH₂-), 65-72 ppm to methylol, and 69-95 ppm to methylol ether bridge (including both free formaldehyde and its oligomeric glycol forms). The assignments of the different peak shifts of sample CB-2 and Uron-C shown in Table 3 were obtained from literatures and calculation.

Table 3. ^{13}C -NMR peak shift assignments of CB-2 and Uron-C

Group	Shift (ppm)	References
H- <u>C</u> OO-	170.31	173.0 (Soulard <i>et al.</i> 1999), 171.6 (Pretsch <i>et al.</i> 2009)
NH ₂ - <u>C</u> O-NH-	162.06, 162.13	163.6 (Pizzi 1999), 161-162 (Du 1999), 162.2 (Kim <i>et al.</i> 2003)
-NH- <u>C</u> O-NH-	160.49, 160.55	162.0 (Pizzi 1999), 159-160 (Christjanson <i>et al.</i> 2002), 160.7 (Kim <i>et al.</i> 2003)
-NH- <u>C</u> O-N=	160.44, 160.36	159-160 (Du 1999)
 (unsubstituted)	158.91, 158.94	157-158 (Du 1999), 157.4 (Soulard <i>et al.</i> 1999)
 (substituted)	154.80	154-157 (Du 1999), 153.1 (Soulard <i>et al.</i> 1999)
 (unsubstituted)	78.13	78.8 (Soulard <i>et al.</i> 1999), 78.7-78.9 (Gu <i>et al.</i> 1995)
Uron- <u>C</u> H ₂ -O-CH ₃	77.90	76-77 (Du 1999)
Uron- <u>C</u> H ₂ -O- <u>C</u> H ₂ -Uron	74.21	73.5 (Soulard <i>et al.</i> 1999), 74.5 (Soulard <i>et al.</i> 1999)
-NH- <u>C</u> H ₂ -O- <u>C</u> H ₂ -NH-	70.47	70.5 (Soulard <i>et al.</i> 1999), 69-70 (Christjanson <i>et al.</i> 2002)
Uron- <u>C</u> H ₂ OH	67.25	67.2 (Soulard <i>et al.</i> 1999)
-NH- <u>C</u> H ₂ -OH	63.77, 63.84	62.2-65.6 (Soulard <i>et al.</i> 1999), 65.2 (Gu <i>et al.</i> 1995)
-N(CH ₂ -) <u>C</u> H ₂ -NH-	52.40, 53.86, 53.94	53-54 (Du 1999), 53.0 (Soulard <i>et al.</i> 1999)
-NH- <u>C</u> H ₂ -NH-	45.94, 46.17, 48.58	46-48 (Du 1999), 45.6-47.4 (Gu <i>et al.</i> 1995)

Effect of Uron resins on the properties of UF resins and plywood

Unsubstituted cyclic uron structures can be obtained from the chemical shift of its carbonyl ($-\text{CO}-$) and methylene ($-\text{CH}_2-$) groups, which are present firstly at 158.80-158.91 ppm and secondly at about 78.13ppm. All of the peaks in this range in figure 4 are so weak, even to the point of disappearing, meaning that the amount of unsubstituted cyclic uron structures in CB-2 is too less to be neglected.

**Figure 4.** ^{13}C -NMR spectra of CB-2.

Peaks in 73.71 to 77.90 ppm in figure 5 belong to several types of methylene group connected to the branches of cyclic uron structures, such as Uron- CH_2 -O- CH_2 -Uron, Uron- CH_2 -O- CH_3 and Uron- CH_2 -NH-CO-NH₂ etc. However, all of these peaks in the ¹³C NMR spectrum of CB-2 are so weak that they disappear as well. Thus these differences also show that the relative amount of any type of cyclic uron structures in sample CB-2 was extremely small and can be ignored.

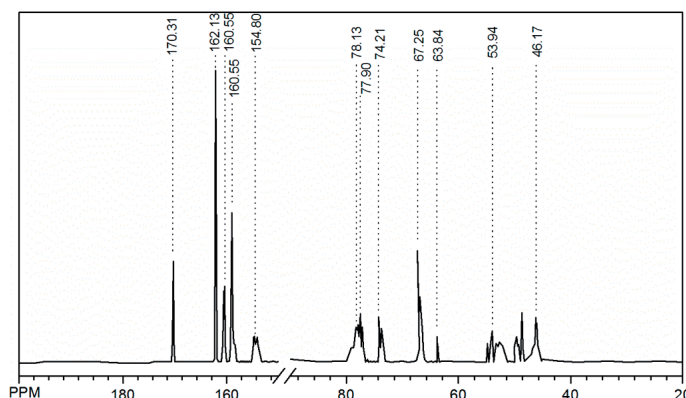
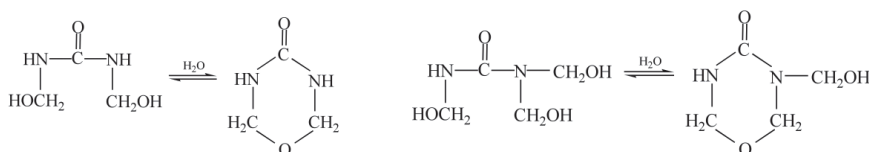


Figure 5. ¹³C-NMR spectra of Uron-C

The relative carbonyl peak areas of Di-substituted urea to Tri-substituted urea (at 158.94-160.49 ppm) of CB-2 is 30%, which is higher than 20.8% of Uron-C. In general, one unsubstituted uron cycle can be created from a Di-hydroxymethyl urea molecular, and a uron cycle connected with a hydroxymethylene (the methylol uron) can be obtained from a Tri-hydroxymethylene urea molecule as shown in the following equation.



Forming reaction equation of two kinds of Uron structure

From these two NMR figures the following facts are evident: various types of cyclic uron structures (both substituted and unsubstituted) opened to reform several kinds of Di-hydroxymethyl urea and Tri-hydroxymethyl urea while mixing Uron-C with UF-B under 60°C, in pH 7.0 and reacting 1 hour. In the neutral or weakly acid condition, the reaction of substituted urea species with free formaldehyde to form various types of methylene glycols and oligomeric methylene glycols in original mixed UF resins resulted in the formation of methylol urea and methylene methylol urea, so the free formaldehyde content of mixed UF resins was reduced and the bond strength was improved for the effect of increased activation groups like methylol group. And this tendency became more significant with increasing adding amounts of uron resin. In addition, the pH range of lower uron stability was proved to be 4.5-6.0 in previous study (Soulard *et al.* 1999), in this experiment the pH value of the mixture was about 7 at the beginning of mixing the uron resin with the UF resin, and it decreased to nearly 6 at the end of the reaction. This is strong evidence supporting the viewpoint mentioned above that the uron cycle structure opened while mixing the uron resin with the UF resin in the neutral pH condition.

Furthermore, the reaction of the cyclic uron structure opening to reform several kinds of methylol urea and connecting with free formaldehyde in the original mixed UF resin to form methylol urea was prevented or even terminated in the following condensation polymerization step in acidic con-

ditions, since the proportion of crosslinked polymer structures to mixed UF resins was not increased, which resulted in the improvement of bond strength at beginning and the following declining as shown in figure 3. However, the amount of the low molecular weight polymer and short chains polymer accumulated only by increasing the amount of uron resin. Many methylene ether bonds formed in the reaction and were easily broken, so the bond strength decreased obviously. This interpretation of the opening of the uron cyclic structure and the resulting reactions based on the analysis of NMR and physical and mechanical properties of plywood is different with previous reports.

Although the cyclic uron structure opened under the above conditions, they didn't absolutely disrupt at all. In Figure 4, the peak of 68.10 ppm belongs to the methylol connected with uron rings (Uron-CH₂-OH), which indicated that a small proportion of uron was still present in the mixed UF resins. This is explained by the fact that the cyclic uron ring is a kind of outgrowth when synthesizing UF resins and will appear in any kind of synthesis procedure.

CONCLUSIONS

Uron resins showed a distinct effect on decreasing free formaldehyde content and formaldehyde emission levels of UF resin and its bonded plywood, the former can be reduced by 76% and the latter 84%. The period for uron resin synthesis can be shortened to 8 hours. In this study, the mixture of 20 part uron resin (synthesized in 8 hours) with 100 part UF resins (F/U molar ratio of 1.3) has a potential advantage on industrial application according to the testing of free formaldehyde content, formaldehyde emission levels and bond strength. The improved effect of uron resin on the performance of UF resin can be attributed to the opening of uron ring structure and the following reaction with free formaldehyde and its oligomeric glycol forms. In this article, the tolerance of plywood in water and the station of cyclic uron structure in the cured UF resin in the presence of wood were not included, which will be focused in the future study.

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