# Uron and Uron–Urea-Formaldehyde Resins

C. SOULARD, C. KAMOUN, A. PIZZI

ENSTIB, University of Nancy 1, Epinal, France

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ABSTRACT: The favored pH ranges for the formation of urons in urea-formaldehyde (UF) resins preparation were determined, these being at pH's higher than 6 and lower than 4 at which the equilibrium urons  $\leftrightarrow N, N'$ -dimethylol ureas are shifted in favor of the cyclic uron species. Shifting the pH slowly during the preparation from one favorable range to the other causes shift in the equilibrium and formation of a majority of methylol ureas species, whereas a rapid change in pH does not cause this to any great extent. UF resins in which uron constituted as much as 60% of the resin were prepared and the procedure to maximize the proportion of uron present at the end of the reaction is described. Uron was found to be present in these resins also as linked by methylene bridges to urea and other urons and also as methylol urons, the reactivity of the methylol group of this latter having been shown to be much lower than that of the same group in methylol ureas. Thermomechanical analysis (TMA) tests and tests on wood particleboard prepared with uron resins to which relatively small proportions of urea were added at the end of the reaction were capable of gelling and yielding bonds of considerable strength. Equally, mixing a uron-rich resin with a low F/U molar ratio UF resin yielded resins of greater strength than a simple UF of corresponding molar ratio indicating that UF resins of lower formaldehyde emission with still acceptable strength could be prepared with these resins. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 277-289, 1999

**Key words:** uron; uron resins; urea-formaldehyde resins; wood adhesives; reactivity; pH range; equilibrium; formaldehyde emission

# INTRODUCTION

The potential introduction of a reaction step at very acid pH inducing the formation of some uron in the preparation of urea-formaldehyde (UF) resins of lower formaldehyde emission has caused some interest, but no known action in Europe.<sup>1</sup> The only formal research work that can be found in the worldwide literature on this subject deals with the introduction of just such a strongly acid condensation step in the preparation of UF resins.<sup>2</sup> This work came to the conclusion that introduction of such an acid step can lead to UF resins of improved bonding strength but also of higher

Correspondence to: A. Pizzi.

postcure formaldehyde emission. One of the remarked effects of the introduction at lower reaction temperatures of the additional strongly acid condensation step was the formation of sometime considerable quantities of uron,<sup>2</sup> thus of the wellknown structure of a cyclic intramolecular urea methylene ether.<sup>3,4</sup> Equally, in the same work it also was stated that minimization of the formation of urons yielded better UF resins when the strongly acid condensation step is introduced in the reaction.<sup>2</sup>

The findings of this thorough research work<sup>2</sup> are not in question. However, so little is known of the effect of the formation of uron on the performance of UF resins and so unusual is this compound that it awoke our curiosity. For example, what would the effect be of maximizing the formation of uron in a UF reaction? In which pH

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		Time		Time		
Time (h)	pH	(h)	pH	(h)	pH	
Long reaction						
0	10.3	6h00	5.02	19h30	2.99	
1h00	7.5	9h00	5.01	20h30	2.40	
2h30	7.0	13h00	4.57	21h30	2.30	
3h00	6.2	16h00	3.98	23h00	2.02	
Short reaction						
0	10.3	2h10	1.94	4h30	2.20	
0h45	6.68	3h35	2.50	4h50	1.80	
2h00	6.35	3h40	2.20	6h00	2.05	
2h05	4.5	4h10	2.27			

Table I Variation of pH as Function of Reaction Time for Uron Preparation Reaction<sup>a</sup>

<sup>a</sup> Times indicated are those at which samples for NMR analysis were taken.

ranges would urons mainly be formed and be stable? Could they be used to improve or impart particular properties to UF resins or not, etc. Thus, our approach was not the introduction of a strongly acid condensation step under conditions minimizing uron formation as in the study quot $ed^2$  to seek a method to improve a UF wood adhesive. Our approach, instead, concentrated on maximizing by any possible method the proportion of uron and its derivatives during the reaction of urea and formaldehyde and only after having achieved this to explore if something useful could be done with such a resin. This article reports this work as well as its applied consequences.

# **EXPERIMENTAL**

#### **Resins Preparation**

The reaction mixture was composed of 72.4% of a commercial formaldehyde concentrate in water (formurea, Elf Atochem) containing 23.0 wt % urea and 55.05 wt % formaldehyde, already incorporated of a buffer, and of formaldehyde to urea molar ratio of 4.8:1, to which were added 8.33 wt % urea and 19.23 wt % water. The reaction mixture was brought initially to a pH of 10.3 by addition of 33% NaOH solution and then heated to 93°C in a reactor equipped with reflux condenser and under continuous mechanical stirring. Formic acid in small amounts was added at different times during the reaction to achieve a variation of pH as a function of time as indicated in Table I, for a total period of reaction of 23 h, and afterward for reaction times of 6 h (Table I), after which the reaction mixture was cooled or left standing at ambient temperature or by immersion of the reactor in iced water. At the end of the reactions the pH was adjusted to 8.7. The reaction pH was followed throughout the whole reaction.

To the ambient temperature cooled resin variable amounts of urea were added, at the end of the reaction, and the uron–UF resins so obtained were tested for gel time, by <sup>13</sup>C-NMR and to prepare wood particleboard.

# <sup>13</sup>C-NMR in Liquid and Solid Phase

The solid state CP-MAS <sup>13</sup>C-NMR spectra of the uron-formaldehyde resin and of the same resin with 16.7% postadded urea hardened by addition of 1% ammonium chloride were obtained with a Bruker MSL 300 Fourier-transform-nuclear magnetic resonance (FT-NMR) spectrometer at a frequency of 75.45 MHz and at sample spin of 3.5 kHz. Chemical shifts were calculated relative to TMS for NMR control. Acquisition time was of 0.026 s with number of transients of about 1000. The spectra were accurate to 1 ppm. Typical spinlattice relaxation times for the types of compounds analyzed as well as peak interpretation were taken from the literature<sup>5</sup> or calculated.<sup>6</sup>

The liquid <sup>13</sup>C-NMR spectrum of the uron resin with and without postadded urea throughout the reaction of preparation of the uron resin and at the end of the preparations was obtained on a Brüker MSL 300 FT-NMR spectrometer. Chemical shifts were calculated relative to  $(CH_3)_3Si(CH_2)_3SO_3Na$ dissolved in D<sub>2</sub>O for NMR shifts control.<sup>7</sup> The spectra were done at 62.90 MHz for a number of transients of approximately 1000. All the spectra were run with a relaxation delay of 5 s and chemical

Group	Shift <sup>a</sup> (ppm)	Shift <sup>b</sup> (ppm)	References
	49.0	48-49	$45.6{-}47.4,{}^{2}49,{}^{2}47.7,{}^{18}\\46.3{-}47.4,{}^{19}49.0,{}^{20}47.2^{21}$
$-N(CH_2-)\underline{C}H_2-NH-$	$53.0 \\ 53.2 \\ 56.3$	51.8-54.5	$51.7,^2 53.8,^{18} 54.5 - 54.8,^{19} 51.7,^{20} 55.5,^{20} 53.5^{21}$
Uron— <u>C</u> H <sub>2</sub> —uron	57.5	57	
$-N(CH_2-)\underline{C}H_2-N(CH_2-)-$	$\begin{array}{c} 59.8\\ 61.5\end{array}$		$59.4{-}61.0,^2\ 60.0,^{18}\ 59.4{-}61.0,^{19}\\ 61.6^{20}$
-NH-CH <sub>2</sub> OH		62.2-65.6	${}^{63.7-65.2,^2}_{66.6,^{20}} {}^{65.1,^{18}}_{64.5-65.2,^{19}}_{66.6,^{20}}$
Uron—CH <sub>2</sub> OH	67.2	65.8, 66.8	$67.2,^2 68.6^{18}$
$-NH-\underline{C}H_2-O-\underline{C}H_2-NH-$	70.5	68.8, 69.0	${\begin{array}{*{20}c} 69.4,^{2,18} 68.3 - 69.9,^{19} \\ 69.6^{21} \end{array}} 70.3,^{20}$
$ \begin{array}{c} -\mathrm{N}(\mathrm{CH}_2-)\underline{\mathrm{C}}\mathrm{H}_2\mathrm{OH} \text{ and } -\mathrm{N}\mathrm{H}(\underline{\mathrm{C}}\mathrm{H}_2\mathrm{OH})_2 \text{ and}^4 \\ -\mathrm{N} \underbrace{\overset{\mathrm{CH}_2\mathrm{O}}{\underset{\mathrm{CH}_2\mathrm{O}}{}}}_{\mathrm{CH}_2} \mathrm{CH}_2 \end{array} $	71.4	72.7	$71.6 - 72.8,^{2,19}, 71.7,^{18,21}, 71.0^{20}$
Uron— $\underline{C}H_2$ —O— $\underline{C}H_2$ —uron	$73.5 \\ 74.5 \\ 75.2$		
$\begin{array}{c c} HN-CO-HH & uron \\ & \\ CH_2-O-\underline{C}H_2 \end{array}$	78.8		$78.7 - 78.9^2$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$80.9 \\ 81.3 \\ 81.6$	76.0-76.1 76.3 76.7-76.8	
$\begin{array}{l} HO - \underline{C}H_2 - OH \\ HO - \underline{C}H_2 - O - \underline{C}H_2 - OH \\ - NH - \underline{C}H_2 - O - \underline{C}H_2 - OH / - NH - \underline{C}H_2 - O - \underline{C}H_3 \\ HO - \underline{C}H_2 - O - \underline{C}H_3 \\ \end{array}$	85.0 88.5 89.0 89.2		83.1, <sup>18</sup> 84.7, <sup>20</sup> 82.9 <sup>21</sup> 89.8, <sup>2</sup> 90.6, <sup>18</sup> 90.5 <sup>21</sup>
$HO - \underline{C}H_2 - O - \underline{C}H_2 - O - \underline{C}H_3$	92.3		93.4, <sup>2</sup> 95.0 <sup>18</sup>
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	157.4	$152.4 \\ 152.7 \\ 153.1$	152.6 - 155.4, <sup>2</sup> $155.8 - 157.2$ <sup>10</sup>
HN— <u>C</u> O—NH— Substituted ureas	161.61	156.8 156.9 157.3	$\begin{array}{c} 157.1\!-\!161.0,^2\ 159.6\!-\!163.3,^{18} \\ 159.3\!-\!169.6,^{19}\ 161\!-\!163.6^{20} \\ (\text{substituted}) \\ 165.0^{20}\ (\text{nonsubstituted}) \end{array}$
$H - \underline{C}OO^{-}$ $H - \underline{C}OOH$	173.0	168.6	$171.6^6$ $166.3^6$

 Table II
 Uron Resins Liquid <sup>13</sup>C-NMR Peak Shift Assignments

<sup>a</sup> Ref. 22. <sup>b</sup> Ref. 23.

Cooling Method		NMR Peak Areas (Relative %)						
	Water Tolerance (%)	Uron	Substituted Urons	Urea	Substituted Urea			
Before cooling	_	38.7	3.5	52.4	5.4			
Slow	220	50.0	8.6	36.4	5.0			
Rapid	400	69.8	10.3	12.3	7.6			

Table III Relative Proportion of Urons and Ureas by Liquid <sup>13</sup>C-NMR Analysis

shifts were accurate to 1 ppm. The assignments of the different peak shifts observed (Table II) were obtained from both the relevant literature and calculated.<sup>6</sup> The relative proportions of urons and urea, substituted and unsubstituted, were obtained from the relative peak areas of the liquid phase NMR spectra (Table III).

## **Thermomechanical Analysis**

The uron–UF resins above were tested dynamically by thermomechanical analysis (TMA) on a Mettler apparatus. Triplicate samples of beech wood alone and of two beech wood plies each 0.6-mm thick bonded with each system for a total samples dimensions of  $21 \times 6 \times 1.15$  mm were tested in nonisothermal mode between 40 and  $220^{\circ}$ C at a heating rate of  $10^{\circ}$ C/min with a Mettler 40 TMA apparatus in three points bending on a span of 18 mm exercising a force cycle of 0.1/ 0.5N on the specimens with each force cycle of 12 s (6 s/6 s). The classical mechanics relation between force and deflection  $E = [L^3/(4bh^3)][\Delta F/(\Delta f)]$  allows the calculation of the Young's modulus E for each case tested.

## **Gel Times and Particleboard Preparation**

Gel times at 100°C of the uron-formaldehyde resin as a function of the proportion of postadded urea were carried out in triplicate (Fig. 3). Duplicate single-layer laboratory particleboards of dimensions  $350 \times 300 \times 14$  mm were bonded with both a uron-formaldehyde resin of 16.7% postadded urea and mixtures of the uron-formaldehyde resin with a commercial UF resin of molar ratio U : F = 1 : 1.2 using 1% ammonium chloride as hardener on total resin solids (uron + UF) in the proportions by weight of uron : UF = 0 : 100, 25 :75, 50: 50, and 75: 25. Adhesives solids percentage on dry wood was of 12% in the first case and of 6% in the following series of UF-uron mixes. The boards were pressed at 195°C and maximum pressure of 30 kg/cm<sup>2</sup> and pressing time of 180 s,

namely, of 12.8-s/mm panel thickness. The boards were tested for internal bond (IB) strength dry (V20) (DIN 68763).<sup>8</sup>

## DISCUSSION

The first reaction involved was a reaction, at 93°C throughout, of urea with an excess of formaldehyde, namely, at molar ratio U : F = 1 : 3.2, carried out starting from an industrial formurea (a formaldehyde/urea concentrate) already additioned of a strong buffer by the manufacturer. The reaction time used was very long, namely, 23 h because formic acid was added progressively to the reaction throughout the whole period to lower the pH, while the buffer worked against such acid addition to reestablish the pH. The shortened list of pH's reached throughout the reaction are reported in Table I. The pH of the reaction was monitored continuously throughout the whole reaction and 11 samples were taken at different times during the reaction to monitor what happened by liquid <sup>13</sup>C-NMR. Figures 1 and 2 show what was found with this reaction. Figure 1(a)and (b) details the <sup>13</sup>C-NMR of the liquid resin after 23-h reaction and shows a number of interesting features: the peaks assignments are reported in Table II. Comparing Figure 1(c) with Figure 1(b) it is possible to see that as the reaction proceeds several more uron signals appear, indicating that as the reaction proceeds uron becomes progressively more substituted. Figure 2 reports the variation throughout the pH range, during the reaction, of the peak areas of the carbonyl peak of urons (the NMR spectra were quantitative spectra) and the variation of the reacted urea : uron peak areas ratios throughout the same range of pH. From these two figures the following facts are evident:

1. The maximum quantity of urons at the end of the reaction, at pH 2.3, approaches al-





152.29	-	-	-	•	-	•	•	•	•	•		•	-	•	•	 -	-	÷	·	*
152.63			-	-	-	-	-	-					-	-				-	-	
152.80	÷		·	-		-	•		-		•••	-	•	-	-	 -	-			-
152.92		~			-	-		-	-	-	• •	-	-	-	-	 -	-	-	-	-



most 50% of the total urea present (uron + urea) [Fig. 2(a) and (b)]. More interesting, once the pH of the reaction mixture is reestablished at 8.7 at the end of 23 h of reaction the relative amount of uron increases to 58% of the total urea present (uron + urea).

2. There are definite pH ranges of formation and greater stability of the urons, these being at pH's higher than approximately 6 and at pH's lower than 4 but particularly lower than 3. The pH range of lower uron stability and lower uron proportion is 4.5– 6.0, but particularly 5.0–5.5.



**Figure 2** (a) Variation of the <sup>13</sup>C-NMR carbonyl peak areas of urons as a function of pH during the total reaction. (b) Variation of the urea : uron ratio of the <sup>13</sup>C-NMR carbonyl peak areas as a function of pH during the total reaction.

There are several more conclusions of interest that can be obtained by this NMR investigation, from Figures 1 and 2, and Table II. From the calculation of possible NMR shifts<sup>6</sup> a considerable proportion of urons is present as methylol urons, methylene urons, or methylene ether urons, hence as structures of the type



as can be seen by the existence of three welldistinct peaks at 80.88, 81.26, and 81.59 ppm, the peak areas of which are not all that dissimilar. The presence of two types of methylol group peaks at 66-67 ppm, one belonging to methylol groups on urea and one to methylol groups on uron, indicate not only that at least monomethylol uron is present, but also that the three peaks mentioned above in the 80-82 ppm range do belong exclusively to methylene urons and to methylene ether urons. It is difficult to interpret this region because no previous data on it has ever been given: the signals are the -CH<sub>2</sub>-signals of substituted cyclic uron structures. As the signals are three indicating three different conditions in which the methylene within the uron cycle finds itself this means the signals only can indicate uron-CH2and -CH2-uron-CH2- structures without being able to determine what other group is attached to the  $-CH_2$ . Because the region of the methylols indicate that there is only one other type of methylol other than the normal one on urea, it means by deduction that one of the three peaks in the 80.9–81.6 ppm region belongs to the cycle methylene of the methylol uron. The other two peaks can only belong to methylene urons or to methylene ether urons. Thus, these two peaks can be uron— $CH_2$ —uron or uron— $CH_2$ —urea equally uron— $CH_2$ —O— $CH_2$ —uron and and uron-CH2-O-CH2-urea for one peak, whereas the second peak can only belong to -CH<sub>2</sub>-uron- $CH_2$ — or  $-CH_2$ —O— $CH_2$ —uron— $CH_2$ —O— CH<sub>2</sub>—, whatever group they are connected to. It is not possible to distinguish them from their relative shifts better than this because they are very close to each other hence the way they are defined in Table II. This means that the uron structure does not just exist as a separate structure from the resin, but rather it is copolymerized with the UF resin or that methylenediurons and dimethylenetriurons are present too.

Also, it is clear that urons are formed mostly in the alkaline pH range around pH's 7–9, mainly at pH of  $\pm 8$ . The decrease in the amount of urons as the pH is lowered during the slow reaction indicates that many of the uron structures formed in the alkaline range of pH open to form methylol ureas and methylene methylol ureas in the 4.5–6 pH range. The stability of the cyclic uron ring can be explained by hyperconjugation theory: in the cyclic uron structure the carbons of the two methylene groups are  $sp^3$  hybrids and the four bonds on the carbon are all  $\sigma$  bonds, but because the hydrogens bound to the methylene carbons are out of the plane of the molecule each C-H bond has a more marked p orbital character. In hyperconjugation theory the methylene can be --CH--+ H<sup>+</sup>; hence as one proton leaves the C retrieves an electron; as a consequence two electrons (one for each carbon of the methylene groups) are perpendicular to the plane of the uron molecule and then can participate in the  $\pi$  orbital. Thus, in hyperconjugation theory, delocalization of the pelectrons on all atoms of the uron cycle and formation of a  $\pi$  orbital on the whole cycle are possible. This leads to stabilization of the uron cycle at a lower energy as it presents some aromatic character.

The reopened structures reform the intramolecular uron methylene ether cycle as the pH reaches the acid range in which the cyclic structure is again stable. Thus, the uron structure is in equilibrium with the open dimethylol ureas form and the pH range determines the direction toward which such an equilibrium is more or less shifted.



The rate of opening or closure of the cycle is not very rapid because, at the end of the reaction, when the pH is adjusted rapidly from the very acid to the alkaline range, the proportion of cyclic structures present does not alter much, while during the slow descent of the pH during the reaction, passing through the middle pH range causes the disappearance of the greater proportion of the uron cyclic structures, which then form again once the acid pH range is reached. An important characteristic of the uron resins formed is the high amount of free formaldehyde in the form of various types of methylene glycols and oligomeric methylene glycols present (peaks at 85, 88.51, 89.04, and 93 ppm, Fig. 1).

Following the identification of the ranges of formation and stability of the uron resin the preparation procedure was reduced from 23 to only 6 h. The variation and proportion of urons formed were exactly the same with the short preparation time as that obtained with the much longer preparation time.

An interesting phenomenon is the influence of the temperature, hence of the quickness of cooling at the end of the reaction, on the water tolerance point of the uron-rich resin. When cooling is slow (overnight) rather than very rapid (in ice/water) the proportion in the cooled resin of nonsubstituted urons is higher than the proportion of methylol-substituted urons and the total amount of uron structures is much higher than the proportion of methylol ureas left in the resin. Also, the relative proportions of unsubstituted and substituted urea change on cooling in favor of the latter. Because the solubility in water of the cyclic uron structures, particularly of the unsubstituted urons, and of reacted urea is lower, this yields a resin that presents a noticeably lower water tolerance (Table III).

The uron resin formed is not capable of gelling either by addition of an acid (HCl) at ambient temperature or by addition of NH<sub>4</sub>Cl at 100°C. For this reason urea was added to it after its preparation, namely, 20% urea solid on uron resin solids in one case and 12% urea in another case. The new amounts of urea added were not copolymerized at higher temperature but just added, predissolved in water, at ambient temperature. Notwithstanding this, comparison of the <sup>13</sup>C-NMR spectra obtained indicated that the urea reacted well with the free formaldehyde present in the uron resin as noticeable from the decrease of the relative areas of both monomeric methylene glycol and oligomeric methylene glycol peaks (85–93 ppm) as well as the increase in the area and relative intensity of the substituted ureas peak (161–162 ppm). Equally interesting is that the methylol urons have not reacted with the postadded urea, indicating that the reactivity of the methylol groups on the uron is much lower than that of the methylol groups on the noncyclic structures of urea. This statement stems from the



**Figure 3** Gel time in seconds of the uron-rich resin as a function of the percentage on uron-rich resin of ambient temperature postadded urea.

consideration that in an environment in which there is only free HCHO (and its oligomeric methylene glycol forms), small amounts of  $-CH_2OH$ groups on urea and big amounts of  $-CH_2OH$ groups on the uron, the NMR signal of the C=O group of the substituted urea will increase only if the added urea reacted with (1) the free HCHO (which it does) and (2) with the methylol groups on urea (which it does). This means that the methylol group on the uron did not react, otherwise this could be seen from the various uron signals, or reacted very little; hence we conclude that the  $-CH_2OH$  group of the uron is less reactive of both free HCHO and of the  $-CH_2OH$ group on urea.

As the preparations in which additional amounts of urea were added at ambient temperature were capable of gelling, the variation of the gel time as a function of the proportion of postadded urea was studied. The results are shown in Figure 3 and show the variation of gel time as a function of the percentage of urea solids added on uron resin solids. The fastest gel time obtained is in the range of 16-25% (in particular 16-20%) postadded urea solids on uron resin solids, equivalent to say in a range of 14-21% (particularly 14-18%) postadded urea on total resin mix. Because the uron resin so modified is capable of gelling, its capability to form bonded wood joints and their characteristics was investigated both by TMA according to newly developed but already reported procedures<sup>9-14</sup> and by preparing laboratory particleboard. The minimum deflection in micrometers obtained for different amounts of NH<sub>4</sub>Cl hardener for a uron resin with 20% postadded urea is shown in Table IV, where also shown are the equivalent deflections obtained with normal UF resins all catalyzed with 2% NH<sub>4</sub>Cl for comparison. The urea : formaldehyde molar ratio of the uron-rich resin is calculated as being 1: 1.77. Table IV shows that the minimum deflection obtained, related to the tightness of the hardened resin network, to the inverse of the joint modulus<sup>12-14</sup> and hence to the mechanical resistance of the joint is slightly better (of about 5%) than that obtainable with a pure UF resin of similar molar ratio. It means that in some manner the uron resin is capable of reacting and contributing to the strength of the final joint. Equally interesting is that decrease of the proportion of NH<sub>4</sub>Cl actually improves the results obtained by almost 9% (Table 4).

As regards particleboard the following two types of glue mixes were tried: (1) a uron resin with 16.7% postadded urea and 1% NH<sub>4</sub>Cl on

Resin Type	$\mathrm{NH_4Cl}_{(\%)}$	Minimum TMA Deflection (µm)	Maximum Elastic Modulus (MPa)
Uron + 16.7% urea	5	23.8	2424
(total U : F = 1 : 1.91)	2	20.2	2856
	1	18.6	3101
UF $1: 2.0$ control	2	20.8	2774
UF 1 : 1.8 control	2	21.1	2735
UF 1 : 1.2 control	<b>2</b>	27.7	2083

Table IVMinimum TMA Deflection and Maximum Elastic Modulus ofBeech Joints Bonded with Uron-Based Resins

Resin Type	Resin Load (%)	Density (kg/m <sup>3</sup> )	IB (MPa)	Minimum TMA Deflection (µm)
Uron + 16.7% urea UF : uron	12	740	1.1	_
100:0	6	704	0.90	21.4
75:25	6	710	1.11	19.9
50:50	6	710	1.14	17.9
25:75	6	715	0.84	23.7

Table VParticleboard IB and TMA Tests Results for Mixes of Uron Resinwith UF Resin of Molar Ratio 1 : 1.2

total resin solids and (2) a series of glue mixes in which a 1:1.2 molar ratio commercial UF resin was mixed with the pure uron resin in different proportions, namely, weight proportion by resin solids of UF : uron resin of 100 : 0, 75 : 25, 50 : 50, 25:75, and 0:100. Because at the beginning it was not known how the uron resin in (1) above would perform on a particleboard, 12% resin solids on dry wood was used. For the series of resins in (2) above, only 6% total resin solids on dry wood were added instead, and pressing was carried out at 12.8-s/mm panel thickness. The results obtained are shown in both Table V and Figure 4. Table V and Figure 4 also give the results of the TMA done on the same series of resin mixes in (2)above. The results show that, first of all, the uron resin alone (postadditioned of some urea) is capable to give a particleboard. The exceptionally high internal bond is caused by the very high resin solids content used, but it leaves in no doubt that the uron resin can contribute, and contribute markedly, to the IB of the panel. The results of the mix UF/uron resin are more interesting. At parity of pressing conditions there is a marked maximum value of the IB in the range of 25 : 75-50:50 UF: uron resin, with the value of the IB between 24 and 27% higher than the UF resin alone. The particleboard IB result is confirmed by the TMA results, which also show a minimum value of deflection in the same range of proportions. This is an important finding, because it indicates for the first time that UF resins containing very high proportions of uron can yield strengths higher than plain UF resins: an unexpected result considering what was found previously in the literature.<sup>2</sup>

The correlation between particleboard IB and TMA deflections has a coefficient of correlation r = 0.92 and a form IB (MPa) = -0.0576 (TMA deflection in  $\mu$ m) + 2.188. Correlation at r = 0.99



**Figure 4** (a) Variation of wood particleboard IB as a function of the relative proportion of resin solids content by weight of uron-rich resin and a UF resin of molar ratio 1 : 1.2. (b) Variation of beech wood joints TMA minimum deflection (in  $\mu$ m) bonded with uron resin + UF resin as a function of the uron-rich resin relative proportion by weight of resin solids content.



Figure 5 Solid state CP-MAS  $^{13}$ C-NMR spectrum of the final products of the 23-h reaction of urea with formaldehyde to form the uron-rich resin, after hardening, showing that the uron cyclic structure is maintained and predominates even in the hardened resin.

between TMA and particleboard IBs has been demonstrated already for normal UF resins.<sup>11</sup>

Figure 5 shows the solid phase CP-MAS  $^{13}$ C-NMR spectrum of the uron-rich resin + 16.7% urea after hardening by addition of 1% ammonium chloride. The predominance of the peaks at 79–82 ppm of the methylene groups of the substituted uron structures and the clear predominance of the urons carbonyl signal at 156 ppm over the substituted ureas carbonyl signal at 160 ppm indicate that the uron cyclic structure is conserved and predominates even after the hardening of the resin and that the uron participates in the hardening of the resin.

This article would not be complete without some discussion as regards the industrial applicability of what was found. It is evident that 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. This cannot be avoided because the condition essential to the preparation of very high proportions of urons is to conduct the reaction with urea under a considerable excess of formaldehyde. Postaddition of urea to a uron resin as the one described above already reduces noticeably the amount of free formaldehyde, but not even near enough to a level that would lead to acceptable panel emission because higher additions of urea slow down the uron resin as seen from the gel time data. The most promising alternative is the one of mixing two resins in the glue mix, namely, a UF resin and the urea postadded uron resin: the results have shown that the uron increases considerably the IB of a relatively low molar ratio UF resin. As a consequence the use of very low molar ratio UF resins (well below the U : F 1 : 1) coupled with the uron resin appears capable of overcoming the inherent weakness of such UF resins while decreasing the formaldehyde emission to

more acceptable levels. The concept of mixing two different resins, or preresins, in the glue mix is not new and is used industrially today for some UF resins<sup>15-17</sup> and hence it would not constitute a difficulty. However, optimization of the separate UF–uron system to achieve this is needed.

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