

# <sup>13</sup>C NMR Analysis Method for Urea–Formaldehyde Resin Strength and Formaldehyde Emission

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## SYNOPSIS

A method based on the use of <sup>13</sup>C NMR relative peak intensity ratios for different characteristic chemical groups, known or supposed to contribute to urea–formaldehyde (UF) resin strength and formaldehyde emission is presented. The method relates results obtained by <sup>13</sup>C NMR analysis of liquid UF resins with their strength, formaldehyde emission, and percent crystallinity in the resin-hardened state. Correlation of different peak ratios with experimental results allows the proposal of equations relating the sum of a number of different <sup>13</sup>C NMR peak ratios with the three mentioned physical properties of the same resins in their hardened state. Resin strength and percent crystallinity appear to be loosely, inversely related. The equations presented appear to have some applied value in predicting physical properties of hardened industrial-type UF resins from a single <sup>13</sup>C NMR spectrum of the original liquid resins, as well as to render easier comparison between difficult UF resin formulations. This approach has allowed identification of which chemical groups really contribute to the physical properties of the hardened resin, and to what extent.

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## INTRODUCTION

Urea–formaldehyde (UF) resins are widely used as adhesives for the manufacture of interior grade wood products, in particular for wood-based particleboard. However, the formaldehyde released by the UF binder during the board service life has been widely recognised as an indoor air pollutant. Strict standards limiting it have been implemented in many countries.<sup>1</sup> While UF resins of much earlier times had high formaldehyde content that produced boards with very good strength (tensile internal bond = I.B.), they also presented formaldehyde emissions that were unacceptably high by today's standards. Conversely, wood particleboard prepared with today's UF resins of lower formaldehyde to urea molar ratio result in much lower formaldehyde emissions but, in general, result in much lower internal bond strength. The evaluation of the cured strength of a UF adhesive and the determination of its capacity for formaldehyde emission, once it has become the

hardened binder of a board, is a long procedure needing repetitive testing because it is subject to fairly large experimental errors. These are induced by the need to pass through the board manufacturing stage. This article instead presents a much faster and less laborious method of analysis of both the strength and capacity for formaldehyde emission of a UF resin applicable in its liquid stage that can be directly correlated to both the particleboard I.B. strength and its potential formaldehyde emission. The proposed method is based on a single <sup>13</sup>C NMR analysis (by which certain identification of chemical groupings exist in the literature<sup>2,3</sup>) of a liquid UF resin before hardening, correlated to experimental results obtained after particleboard manufacturing.

## EXPERIMENTAL

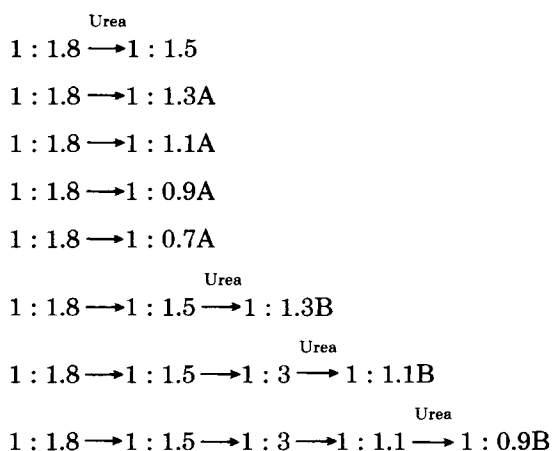
### Resin Preparation

A UF resin of U : F molar ratio of U : F molar ratio 1 : 1.8 was prepared according to an industrial formulation as follows: 2.2 moles of paraformaldehyde is dispersed in 55 mL of water and heated to 50°C.

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The pH is increased to 8.5 using NaOH 30% solution. One mole urea is added to obtain a U : F ratio of 1 : 2.2 U : F molar. The temperature is increased to 95°C and kept there for 15 min. Formic acid is added to decrease the pH to 5.2. The reaction mixture is reacted for a further 15–20 min at 95°C before 30% NaOH solution is added to increase the pH to 6.5. The solution is cooled down to 60°C and a second urea added to have a final U : F molar ratio of 1 : 1.8. The final product is kept at 60°C for 20 min and then cooled to ambient temperature.

This basic resin was used to prepare two sets of resins [A series and B series each in duplicate (I) and (II), Table I] with the same final U : F molar ratio but with a different synthesis approach. The two series of resins were as follows:



For the above schemes, the required amount of urea was added to the 1 : 1.8 resin at 60°C to make up the respective modified resin. The resin was kept at that temperature for 45 min, then cooled and left for 24 h to mature before analysis and application. A waiting period of 24 h was allowed during the synthesis of the multiple-step addition resins before the next addition of urea.

The liquid resins were analyzed by IR and <sup>13</sup>C NMR spectroscopy, respectively. A small sample of the respective resins were cured with 3% NH<sub>4</sub>Cl at 140°C for 1 h. The cured resins were ground and analyzed by X-ray diffraction.

### Particleboard and Resin Strength

Triplicate (*Pinus Radiata*) one-layer core-only particleboards, 12-mm thick, were made from the modified resins to determine the strength of the cured resin. The following set of conditions were kept the same for each of the boards prepared. Pine chips ranging in size from 1 to 25 mm, 7% UF solids content. Hardener used: 2% NH<sub>4</sub>Cl of solid glue. Glue particles moisture content of 12–15% was obtained. Pressing time for each board was 4.5 min: 1 min at 23.5 kg/cm<sup>2</sup>, 1.5 min at 11.7 kg/cm<sup>2</sup>, 2 min at 3 kg/cm<sup>2</sup> at a pressing temperature of 190°C. The boards were left standing in a well-vented room for 2 weeks before analysis.

Strength tests of the particleboard was done by subjecting small blocks of the boards (50 × 50 × 12-

**Table I** Averaged Results for Strength Test and Formaldehyde Emission of Triplicate Particleboards Prepared with UF Resins (I) and (II)

Resin Sample	Average Density (g · cm <sup>-3</sup> )	I.B. Strength (MPa)	Average Formaldehyde Emission, mg/100 g Board
1 : 1.8 (I)	0.650	0.592	
1 : 1.8 (II)	0.704	0.733	44.75
1 : 1.5 (I)	0.685	0.776	
1 : 1.5 (II)	0.676	0.737	21.53
1 : 1.3A (I)	0.695	0.594	
1 : 1.3A (II)	0.665	0.724	10.06
1 : 1.3B (I)	0.687	0.825	
1 : 1.3B (II)	0.685	0.784	8.03
I : 1.1A (I)	0.665	0.629	
1 : 1.1A (II)	0.684	0.655	6.04
1 : 1.1B (I)	0.666	0.520	
1 : 1.1B (II)	0.704	0.651	4.35
1 : 0.9A (I)	0.646	0.274	
1 : 0.9A (II)	0.669	0.336	1.98
1 : 0.9B (I)	0.680	0.405	
1 : 0.9B (II)	0.667	0.358	2.20

mm thickness) to an I.B. tensile-strength test using a Hounsfield tensometer. The tension was subjected perpendicular to the board surface, giving a reading in Newtons. The results in MPa compared to the requirements of standard specifications for interior grade particleboard<sup>4</sup> are shown in Table I.

### Formaldehyde Release

The desiccator method was used to determine the formaldehyde emission of the particleboard prepared with the modified resins. The desiccator method we used is similar to the Japanese Standard desiccator method,<sup>5</sup> with a slight modification to allow for smaller board samples.

This desiccator method used a 2-L desiccator, in which a 200-ml glass dish filled with 100 mL of distilled water was placed. The particleboard specimens were cut (25 × 25 × 12-mm thickness), weighed, and suspended over the water by a porcelain desiccator plate. The desiccators were kept at 25 ± 1°C for 24 h. An average of six samples per board were analyzed. The determination of the formaldehyde in water was done by the fluorometric acetylacetone method.

The desiccator method used was standardized to both the perforator and to the WKI method described by E. Roffael and L. Melhorn.<sup>6</sup> The formaldehyde emission results in Table I and in the formaldehyde emission equation are standardized to

give results of formaldehyde emission according to the WKI method.

### <sup>13</sup>C NMR Spectroscopy

<sup>13</sup>C NMR spectra were obtained on a Bruker AC 200 spectrometer. Chemical shifts were calculated relative to (CH<sub>3</sub>)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>Na for NMR control. (CH<sub>3</sub>)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>Na was dissolved in D<sub>2</sub>O, run separately, and the shifts for the four signals were set. About 1.0 mL of liquid 65% solids resin sample was placed in an NMR tube and diluted with about 0.4 mL deuterium oxide added directly to the sample. The spin-lattice relaxation time of <sup>13</sup>C is an important factor in setting the pulse intervals. Tomita and Hatono<sup>2</sup> suggested a pulse interval of 5 s was needed to obtain a reliable spectrum. No direct quantitative results could be obtained from the raw data, but by considering the peak ratios of certain species, some information between the various synthesis parameters and the final resin's properties could be deduced and some quantitative considerations derived.

The <sup>13</sup>C NMR spectra of UF resins can be split up into four main areas<sup>2,3</sup>:

1. the substituted and unsubstituted urea carbonyl groups with signals from 160–170 ppm;
2. methylene groups with signals from 45 to 60 ppm;

**Table II** <sup>13</sup>C NMR Peak Assignment and Peak Intensities for Different UF Resins

Functional Group (ppm)	1:1.8	1:1.5	1:1.3A	1:1.3B	1:1.1A	1:1.1B	1:0.9A	1:0.9B
Carbonyl group {C}								
NH <sub>2</sub> CONHCH <sub>2</sub> OH (163.6) {C1}	23.7	52.5	42.1	58.8	58.8	18.0	28.9	11.4
=NCON= (162.0) {C2}	4.0	27.7	37.3	14.0	54.2	20.5	25.1	15.0
Methylene group {Me}								
—NHCH <sub>2</sub> NH— (48.8) {A} <sup>2</sup>	2.4	9.0	7.1	3.7	14.0	2.9	8.9	4.7
—N(CH <sub>2</sub> )—CH <sub>2</sub> NH— (55.5) {C} <sup>2</sup>	3.5	9.6	6.2	3.1	12.2	2.3	8.0	3.1
—NH(CH <sub>2</sub> )—CH <sub>2</sub> N(CH <sub>2</sub> )— (61.6) {E} <sup>2</sup>	1.0	2.7	1.0	1.2	1.3	1.0	1.2	0.5
Methylol group {Mo}								
—NCH <sub>2</sub> OH (66.6) {Mo1}	26.3	101.5	68.0	31.0	115.9	28.7	67.1	25.3
—N(CH <sub>2</sub> )—CH <sub>2</sub> OH (71.0) {Mo2}	5.3	18.4	12.2	6.9	21.3	4.7	11.9	6.1
Ether {E}								
—NHCH <sub>2</sub> OCH <sub>3</sub> (73.4) {E1}	10.2	12.9	6.5	2.8	9.5	1.9	9.2	1.8
—N(CH <sub>2</sub> )—CH <sub>2</sub> OCH <sub>3</sub> (77.7) {E2}	1.3	3.2	1.9	1.2	2.8	0.7	2.4	0.9
—NHCH <sub>2</sub> OCH <sub>2</sub> OH (88.7) {E3}	2.0	2.2	—	—	—	—	—	—
—NHCH <sub>2</sub> OCH <sub>2</sub> NH— (70.3) {E4}	—	3.7	2.5	1.5	3.3	0.7	2.4	0.9
—NH(CH <sub>2</sub> )—CH <sub>2</sub> OCH <sub>2</sub> NH— (75.0) {E5}	1.7	3.9	3.1	2.0	5.2	0.9	3.2	1.3
Methanol CH <sub>3</sub> OH (51.7)	1.3	3.5	1.8	—	—	—	—	—
Free formaldehyde (84.7)	7.9	9.4	2.4	1.3	3.3	—	—	—
Urea NH <sub>2</sub> CONH <sub>2</sub> (165.4)	—	6.6	21.3	5.5	55.5	23.5	49.7	20.7

**Table III** NMR Peak Ratios

	Urea/ (C1 + C2)	C1/C2	E1/E2	Crosslinking <sup>a</sup>	Me/Mo	Free F/Me	E1 + E4/ E2 + E5	E1 + E2/ E4 + E5
1 : 1.8	0	5.9	7.85	0.72	0.22	1.15	3.73	4.26
1 : 1.5	0.08	1.9	4.03	0.70	0.18	0.44	2.34	2.12
1 : 1.3A	0.27	1.1	3.42	0.57	0.18	0.17	1.80	1.50
1 : 1.3B	0.18	1.25	2.33	0.69	0.21	0.16	1.34	1.14
1 : 1.1A	0.49	1.1	3.39	0.49	0.20	0.12	1.60	1.45
1 : 1.1B	0.61	0.88	2.71	0.60	0.19	0	1.63	1.63
1 : 0.9A	0.92	1.2	3.83	0.57	0.23	0	2.07	2.07
1 : 0.9B	0.78	0.76	2.00	0.49	0.26	0	2.23	1.23
1 : 1.11	0.90	0.578	5.36	0.68	0.28	0.13	2.50	2.97

$$^a \frac{C + 2E}{A + C + E}$$

3. methylol groups with signals from 65 to 72 ppm; and
4. methylene-ether groups with signals from 69 to 90 ppm.

There are also less important species present at much lower concentrations such as the methylene glycols, but these were not considered.

Peaks assignments and relative intensities are reported in Table II. Potentially significant peak intensity ratios are reported in Table III. Regression equations and their coefficients of correlation between potentially significant <sup>13</sup>C NMR peak inten-

sity ratios and the F : U molar ratio are reported in Table IV.

#### X-Ray Crystallography

X-ray diffraction patterns of the cured resins were collected on an Automated Philips Powder Diffractometer PW1710/00 that recorded the intensity of the X-rays diffracted by the sample as a function of the Bragg angle using the Phillips computer software. Cu radiation ( $\lambda = 1.5405 \text{ \AA}$ ) was used with a nickel filter. The scan speed was  $0.02 (^\circ 2\theta/s)$  with a  $0.02 (^\circ 2\theta)$  step. The different cured resins were

**Table IV** Regression Equations and Respective Coefficients of Correlation Describing Variation of <sup>13</sup>C NMR Species Ratios as Function of F : U Molar Ratio

Series Resin	Regression Equation	r
A	$\ln(\text{urea}/C1 + C2) = -3.962U + 3.596$	0.940
B	$\ln(\text{urea}/C1 + C2) = -3.666U + 3.213$	0.937
A	$\ln(C1/C2) = 1.779U - 1.790$	0.831
B	$\ln(C1/C2) = 2.375U + 2.629$	0.937
A	$\ln(C1 + 2E/A + C + E) = 0.4661 \ln U - 0.621$	0.832
B	$\ln(C1 + C2/A + C + E) = 0.5431 \ln U - 0.595$	0.889
A	$\text{Me}/\text{Mo} = 0.229U^2 - 0.631U + 0.615$	0.996
B	$\text{Me}/\text{Mo} = 0.222U^2 - 0.632U + 0.640$	0.808
A	$E1/E2 = 11.815U^2 - 27.716U + 19.350$	0.996
B	$E1/E2 = 9.765U^2 - 20.186U + 12.494$	0.974
A	$\ln(E1 + E4/E2 + E5) = 0.746U - 0.1955$	0.811
B	$\ln(E1 + E4/E2 + E5) = 1.196U - 0.949$	0.913
A	$\ln(E1 + E2/E4 + E5) = 7.784U^2 - 18.578U + 12.482$	1.000
B	$\ln(E1 + E2/E4 + E5) = 6.021U^2 - 13.126U + 8.339$	0.950
A	$\ln(\text{F}/\text{Me}) = 3.376U - 5.956$	0.932
B	$\ln(\text{F}/\text{Me}) = 3.508U - 6.894$	0.948

U, Final formaldehyde/urea molar ratio; r, coefficient of correlation.

ground to a particle size of about 2–10  $\mu\text{m}$  using a mortar and pestle and packed tightly on an aluminum sample holder.

The percent crystallinity for the different cured resins was determined by considering the areas for the crystalline region to that of the total area. A best smooth curve was drawn to connect the minima between the crystalline peaks. The assumption was made that the intensity above is the contribution by the crystalline region and below by the amorphous region.<sup>7</sup>

## DISCUSSION

The absolute intensities of  $^{13}\text{C}$  NMR peaks can never be taken as a measure of the abundance of a particular chemical group. In a resin such as UF in which all chemical groups are closely interrelated, ratios of the intensities of peaks characteristic of chemical groups known or suspected to contribute to the cured strength and formaldehyde emission appear to indicate excellent correlation with the experimental reality. The two series of resins prepared, of U : F molar ratios, 1 : 1.8; 1 : 1.5; 1 : 1.3; 1 : 1.1; 1 : 0.9; and 1 : 0.7 were prepared by two different methods. The UF resins in one series were prepared starting at a 1 : 1.8 molar ratio and were brought to the final ratio by a single-step second-urea addition (series A). The UF resins in the other series were instead brought to the final U : F molar ratio by the addition of urea in several steps (series B). Both methods are used extensively for the preparation of industrial UF resins, the first one being the most commonly used. As an initial assessment of the possible strength of UF strength from the liquid resin  $^{13}\text{C}$  NMR spectra, Tomita and Hatono<sup>2</sup> formulated an equation that considered the peak intensity ratios exclusively of the methylene linkages in the liquid

resin. The equation gave some indication of the degree of crosslinking present after curing the resin. Although methylene linkages already formed in the liquid resin are important contributors to the final crosslinking and strength of the hardened resin, they are not the only contributors. What this still important equation fails to consider is the contribution of the species that will be converted to methylene and methylene ether linkages during the curing process.

In Table I the experimental results for internal bond strength and formaldehyde emission are reported, and the experimental  $^{13}\text{C}$  NMR results are reported in Table II. Tables III and IV show the values of the peak intensities of species known or suspected to contribute or potentially contribute to the hardened strength of the resin and its formaldehyde emission. In Table I it must be noted that the difference in I.B. for resins 1 : 1.8 (I) and 1 : 1.8 (II) is due to the excessive difference in average board densities in the two series of samples. The densities were in the range 0.670–0.700  $\text{g}/\text{cm}^3$  in which directly comparable results can generally be obtained.<sup>4</sup> Maintaining average densities within such a narrow range is not easy for laboratory particleboard. The fact that the densities reported are in the main in the narrow board density range defined indicate that reproducibility of results within such a range is acceptable and significant enough for the correlations to be meaningful within the internationally accepted range for particleboard density.<sup>4</sup> These ratios were chosen among others because not only are they potentially significant to the physical reality of the situation but also because they correlated well with the variation in F : U molar ratio (Table IV).

Table V shows the  $^{13}\text{C}$  NMR species ratio correlation to I.B. strength for the two series of resins. As can be seen, only certain group's ratios appear

**Table V**  $^{13}\text{C}$  NMR Species Ratio Correlation to I.B. Strength

	NMR Species Ratio	Correlation for A-Series Resins	Correlation for B-Series Resins
Y1	Urea/(C1 + C2)	0.888	0.895
Y2	C1/C2	0.228	0.412
Y3	E1/E2	0.145	0.357
Y4	Crosslinking (C + 2E)/(A + C + E)	0.410	0.919
Y5	Me/Mo	0.780	0.482
Y6	(E1 + E4)/(E2 + E5)	0.139	0.336
Y7	(E1 + E2)/(E4 + E5)	0.063	0.277
Y8	Free F/Me	0.424	0.456

to correlate well with the I.B. strength. It can also further be deduced that ratios such as Me/Mo are likely to play an important role in the final I.B. strength of a board. As discussed, the equation by Tomita and Hatono<sup>2</sup> for possible crosslinking can also be considered as summing up important contributions. From the correlation studies in Table V, the urea/(C1 + C2) ratio appears also to play a role in the final strength. This makes some sense because an increase in the free urea content of a resin should adversely affect hardened resin strength and hence board strength. The ether species do not correlate as well, and their final contribution to the I.B. strength of a board might be low. But, since ethers decompose on hot curing of the resin and in time emit formaldehyde, they are likely to play instead an important role in the final formaldehyde emission from particleboard. It can be noticed that none of the peak ratios, when taken alone, explain the phenomenon to a high enough level. The highest correlation in Table V is given by Y1, but this is a negative contribution, subtracting rather than adding to the I.B. strength. The only other contribution with a high level of correlation is Y4, but only for the B series of resins. All the other contributions' correlation coefficients are able to explain only part of the phenomenon. For this reason a composite equation to improve total correlation, explain the greater part of the phenomenon to a reasonable extent and in a conceptually correct manner in regards to the expected contribution of chemical species to crosslinking, must be used. Composite equations, describing at the 95% level the contribution of the different chemical species to resin crosslinking thus much higher than any single term, can then be derived from Table V.

Three ratios from the results in Table V can then be related to resin crosslinking and hence to the experimental I.B. strength

$$\text{I.B. strength} = a\{(C + 2E)/(A + C + E)\} + b\{\text{urea}/(C1 + C2)\} + c\{\text{Me}/\text{Mo}\}$$

where  $a$ ,  $b$ , and  $c$  are coefficients characteristic for each unique homologous series of UF resins, at an average density of 0.680 g/cm<sup>3</sup>.  $A = \text{—NH}\underline{\text{C}}\text{H}_2\text{—NH—}$  (peak at 48.8 ppm);  $C = \text{—N}(\text{CH}_2)\underline{\text{C}}\text{H}_2\text{NH—}$  (peak at 55.5 ppm);  $E = \text{—N}(\text{CH}_2)\underline{\text{C}}\text{H}_2\text{N}(\text{CH}_2)\text{—}$  (peak at 61.6 ppm);  $C1 = \text{NH}_2\underline{\text{C}}\text{ONHCH}_2\text{OH}$  (peak at 163.0 ppm);  $C2 =$  larger molecular species,  $\text{=N}\underline{\text{C}}\text{ON=}$  groups ( $\text{HOCH}_2\text{NH}\underline{\text{C}}\text{ONHCH}_2\text{OH}$ ) (peak at 162.0 ppm); urea = free urea (peak at 165 ppm); Me = A + C

+ E, total methylene species (peak from 45 to 60 ppm); Mo = total methylol species (peak from 65 to 72 ppm).

For the A-series resins

$$\text{IB} = 0.43Y4 - 0.36Y1 + 2.39Y5$$

with an estimated standard deviation = 0.20 for an I.B. strength range of 0.776–0.274 MPa.

Similarly for the B-series resins

$$\text{IB} = 1.08Y4 - 0.11Y1 - 0.14Y5$$

with an estimated standard deviation of 0.11 for an I.B. strength of 0.825–0.358 MPa. where IB = I.B. strength (MPa); Y1 = urea/(C1 + C2) peak ratio; Y4 = possible crosslinking peak ratio from the Tomita and Hatono equation<sup>2</sup>; Y5 = Me/Mo peak ratio. It must however be remembered that the equation coefficients are unique for each specific homologous resin series. The coefficients would change for resins synthesized and boards made under different conditions.

An important factor that can be deduced from the above is that the physical properties of a cured resin (such as I.B. strength) can be related to the ratio of species present in the resin before cure. There are also other group ratios that could be considered, but their significance would appear to be low. Species such as the ethers appear to contribute little to the I.B. strength. Species such as the free F/Me ratio seem to correlate, but only due to the type of experimental setup used where the formaldehyde content was decreased sequentially by the addition of urea. This is true in most industrial applications, but for resins synthesised by simple first urea addition, this relationship would not hold.

A similar approach can be taken for relating <sup>13</sup>C NMR peak ratios of different chemical groups to the formaldehyde emission. Table VI shows the <sup>13</sup>C NMR ratios correlation to formaldehyde emission for the two series of resins.

Most of the ratios appear to correlate with the formaldehyde emission. As clearly expected, the free F/Me ratio correlates excellently with the formaldehyde emission from particle boards. The effect other groups' ratios, such as the C1/C2, have on the final emission of formaldehyde from the board is less clear. An equation relating only the free F/Me ratio to the formaldehyde emission can be obtained for the A-series resins.

$$F = 2.927 + 37.11Y8 \quad r = 0.996.$$

Table VI  $^{13}\text{C}$  NMR Species Ratio Correlation to Formaldehyde Emission

NMR Species Ratio		Correlation for A-Series Resins	Correlation for B-Series Resins
Y1	Urea/(C1 + C2)	0.805	0.786
Y2	C1/C2	0.954	0.973
Y3	E1/E2	0.927	0.986
Y4	Crosslinking (C + 2E)/(A + C + E)	0.844	0.705
Y5	Me/Mo	0.099	0.153
Y6	(E1 + E4)/(E2 + E5)	0.939	0.985
Y7	(E1 + E2)/(E4 + E5)	0.909	0.966
Y8	Free F/Me	0.996	0.997

Similarly for the B-series resins

$$F = 2.847 + 36.35 Y8 \quad r = 0.997$$

where F = formaldehyde emission (mg F/100 g of board); Y8 = free F : Me. The above correlation could only be applicable for shorter periods of time because it has been shown that the formaldehyde emission from boards made with a resin that initially contained high amounts of free formaldehyde in the liquid resin (1 : 1.5), shows a considerable decrease when tested again after 3 months. This as total formaldehyde emission is recognised as being due to the contribution of (i) free unreacted formaldehyde,<sup>1</sup> (ii) species that can slowly release formaldehyde in the longer term,<sup>1,8,9</sup> and (iii) the long-term susceptibility to slow hydrolysis of urea amidomethylene linkages.<sup>8,9</sup> Clearly then the good correlation shown to exist between just the unreacted formaldehyde and emission is only valid in the short term. These two equations then do not take into consideration the contribution of the other two factors outlined above. Such contributions are proportionally small when unreacted formaldehyde is still present, but gain in proportional importance when unreacted formaldehyde keeps decreasing with time.

Furthermore the equations in Table IV show that all the  $^{13}\text{C}$  NMR peak ratios are shown to depend on the F : U molar ratio, although according to different laws. Thus the F : U ratio is definitely the most important factor but suffers, from an analytical point of view, from having to be known in advance: it cannot be used then when the resin under analysis has an unknown F : U ratio. It has also been shown that the F : U ratio, by simple regression, can explain at best only 70% of the formaldehyde emission phenomenon.<sup>10</sup> Thus any single peak ratio, including F/Me, can only explain the total phenomenon, at best to the 65–70% significance level, leading to the

conclusion that a composite equation including several factors must be used.

The correlations of formaldehyde to the other NMR peak ratios were also reasonably good. Thus, they could also be considered to play a role in the formaldehyde emission of particleboard and be included in a final equation that expresses the formaldehyde emission of a UF-bonded board to the  $^{13}\text{C}$  NMR peak ratios of the groups present in the liquid resin.

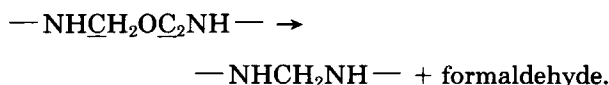
The urea/(C1 + C2) (Y1) ratio should logically belong to the equation. This as the presence of free urea in the system would affect the final formaldehyde emission by "capturing" free formaldehyde during the curing stages of the resin, with urea being more efficient but more random in this effect than the C1 and C2 species.

The correlation of the C1/C2 ratio seems to be very good, but its contribution to the final formaldehyde emission of a board is not clear. Since the carbonyl ratios have already been indirectly considered in the urea/(C1 + C2) ratio, one of the two ratios is likely to be redundant. The latter is likely to be the C1/C2 as the urea/C1 + C2 takes into consideration not only C1 + C2 but also the free urea.

The crosslinking ratio (Y4) from Tomita and Hatono<sup>2</sup> should also have some influence on the formaldehyde emission of a particleboard. This is especially true for boards in service for long periods of time and exposed to higher humidity conditions. Because with time most of the free formaldehyde that considerably influences the emission has almost disappeared, the presence of  $-\text{CH}_2-$  groups then plays a role. Hence, an increase in crosslinking of a resin means that there is a higher concentration of  $-\text{CH}_2-$  groups present, which with time might slowly hydrolyse and emit formaldehyde.

The next ratios to consider are those due to the

ethers. The correlation of all three ratios ( $Y_3$ ,  $Y_6$ , and  $Y_7$ ) appear to be good. But only one of the ratios can be considered. This is because looking at the chemistry of each of the ethers present, one must then consider which of them would contribute to the formaldehyde emission. The  $E_1/E_2$  ratio where  $E_1 = -\text{NH}\underline{\text{C}}\text{H}_2\text{OCH}_3$  and  $E_2 = -\text{N}(\text{CH}_2-)\underline{\text{C}}\text{H}_2\text{OCH}_3$  would not influence the emission because the species would only decompose and emit methanol rather than formaldehyde. The  $(E_1 + E_2)/(E_4 + E_5)$  species ratio was the one preferred to describe the contribution of the ethers to the formaldehyde emission, even though the correlation of the second ratio appeared at first to be slightly better. There is a well-defined experimental reason for this:  $E_4 = -\text{NHCH}_2\text{OCH}_2\text{NH}-$  and  $E_5 = -\text{N}(\text{CH}_2-)\underline{\text{C}}\text{H}_2\text{OCH}_2\text{NH}-$ . These species can decompose and emit formaldehyde as follows



Hence, a decrease in the abundance of the ( $E_4 + E_5$ ) species is likely to decrease the emission of formaldehyde in the cured resin. Only one ether ratio is then necessary to describe the effect because using all three ratios would mean considering the same or similar effects three times and give a false impression of the importance of the ethers to the emission.

From the above an equation can be obtained unique for a specific homologous series of UF resins. This is also unique to the particular formaldehyde emission determination method (desiccator)<sup>5</sup> although this is easily correlated to other methods<sup>1,6,10</sup> and in the form given below the results are given in the WKI method mg/100 g board. This general equation linking the <sup>13</sup>C NMR intensity ratios of free F/Me, Tomita and Hatono crosslinking ratio,<sup>2</sup> urea/( $C_1 + C_2$ ),  $(E_1 + E_2)/(E_4 + E_5)$  and  $E_3/\text{Me}$  to the formaldehyde emission of a board should be expressed conceptually as:

$$\text{F emission} = a\{\text{free F/Me}\} + b\{(C + 2E)/ \\ (A + C + E)\} + c\{\text{urea}/(C_1 + C_2)\} \\ + d\{(E_1 + E_2)/(E_4 + E_5)\} + e\{E_3/\text{Me}\}$$

where  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $e$  are coefficients characteristic for each unique homologous UF resin series.

Conceptually the species  $E_3/\text{Me}$ , keeping in mind that it is a blocked, not reactive, group derived by reaction of methanol generated during reaction with a methylol group, might subtract then material that

could contribute to emission. FF = free formaldehyde (peak at 84.7 ppm); Me = sum of all methylene groups;  $A = -\text{NH}\underline{\text{C}}\text{H}_2\text{NH}-$  (peak at 48.8 ppm);  $C = -\text{N}(\text{CH}_2-)\underline{\text{C}}\text{H}_2\text{NH}-$  (peak at 55.5 ppm);  $E = -\text{N}(\text{CH}_2-)\underline{\text{C}}\text{H}_2\text{N}(\text{CH}_2-)-$  (peak at 61.6 ppm);  $C_1 = \text{NH}_2\underline{\text{C}}\text{ONHCH}_2\text{OH}$  (peak at 162.0 ppm);  $C_2 =$  larger molecular species,  $=\text{N}\underline{\text{C}}\text{ON}=\text{}$  groups (peak at 162.0 ppm); urea = free urea (peak at 165 ppm);  $E_1 = -\text{NH}\underline{\text{C}}\text{H}_2\text{OCH}_3$  (peak at 73.4 ppm);  $E_2 = -\text{N}(\text{CH}_2-)\underline{\text{C}}\text{H}_2\text{OCH}_3$  (peak at 88.7 ppm);  $E_4 = \text{NH}\underline{\text{C}}\text{H}_2\text{O}\underline{\text{C}}\text{H}_2\text{NH}-$  (peak at 70.3 ppm);  $E_5 = -\text{N}(\text{CH}_2-)\underline{\text{C}}\text{H}_2\text{OCH}_2\text{NH}-$  (peak at 75.0);  $E_3 = -\text{NH}\underline{\text{C}}\text{H}_2\text{OCH}_2\text{OH}$  (peak at 88.7 ppm). Therefore these ratios can be related to the formaldehyde emission for the specific series of resins by taking the respective experimental data and obtaining the following equation for the A series resins.

$$F = 19.18Y_8 - 11.66Y_1 + 7.17Y_4 + 4.13Y_7$$

with an estimated standard deviation of 0.389 for a formaldehyde emission range of 44.75–1.98 mg F/100 g board.

Similarly for the B-series resins

$$F = 21.71Y_8 - 6.09Y_1 + 2.39Y_4 + 4.35Y_7$$

with an estimated standard deviation of 2.01 for a formaldehyde emission range of 44.75–2.20 mg F/100 g board, where F = formaldehyde emission (mg F/100 g of board);  $Y_1 = \text{urea}/(C_1 + C_2)$  peak ratio;  $Y_4 =$  possible crosslinking peak ratio from the Tomita and Hatono equation<sup>2</sup>;  $Y_8 =$  free F/Me peak ratio;  $Y_7 = (E_1 + E_2)/(E_4 + E_5)$  peak ratio.

The above sets of equations can be used in predicting some of the physical properties of the hardened resin by studying the <sup>13</sup>C NMR peak ratio of certain species in the liquid UF resin.

### X-Ray Diffraction

A further indication of the effects indicated in regard to strength of the cured UF resin is a study by X-ray diffraction of the UF resins prepared after they were cured. The crystallinity of the hardened resins changes from an almost amorphous material (U : F = 1 : 1.8) to a semicrystalline one (U : F = 1 : 0.7A). The proportion of crystallinity of the respective resins cured alone is summarized as follows:

	Increase in urea molar proportion					
Crystallinity	17%	21%	24%	43%	47%	74%
	1 : 1.8;	1 : 1.5;	1 : 1.3A;	1 : 1.1A;	1 : 0.9A;	1 : 0.7A



**Table VII**  $^{13}\text{C}$  NMR Species Ratio in Liquid Resin Correlation to Percent Crystallinity of Hardened UF Resin

	NMR Species Ratio	Correlation for A-Series Resins
Y1	Urea/(C1 + C2)	0.941
Y2	C1/C2	0.621
Y3	E1/E2	0.569
Y4	Crosslinking (C + 2E)/(A + C + E)	0.800
Y5	Me/Mo	0.439
Y6	(E1 + E4)/(E2 + E5)	0.631
Y7	(E1 + E2)/(E4 + E5)	0.542
Y8	Free F/Me	0.759

The two methods of synthesis had no apparent effects on the final cured resin crystallinity. Previous studies<sup>8</sup> showed that the crystallinity of UF resins disappears when cured on wood, this being also supported by previous theoretical considerations.<sup>9</sup> This also occurred for the resins under examination. For this reason the crystallinity of the hardened UF resins were determined by X-ray diffraction only to present additional evidence of why the strength of the final resin is connected to the U : F molar ratio.

As remarked previously this suggests that the crystallite regions of the resin are not separate from the bulk amorphous region but rather consists of small regions where crystalline order is formed by sections of the molecules. These are regions where  $-\text{CH}_2-$  bridges linking tridimensionally single chains of resin do not occur and thus secondary forces adjust the molecules in a crystalline state. There should then be some correlation between extent of crystallinity of the resin when cured alone and strength of the same UF resin when used as an adhesive. The higher the percent crystallinity, the lower the amount of tridimensional crosslinking and hence the weaker the strength of the hardened resin.

The correlation results in Table VII indicate that percent crystallinity is mostly correlated to the urea/(C1 + C2) (Y1)  $^{13}\text{C}$  NMR peak intensity ratio, and less well to the (C + 2E)/(A + C + E) (Y4)  $^{13}\text{C}$  NMR ratio. The influence of the latter term is expected because as the tridimensional crosslinking of the resin decreases the percent crystallinity should increase (the proportion of linear species increases) allowing for a higher degree of ordered packing to occur. Similarly the influence of the urea/(C1 + C2) term is expected because as the monomeric urea and mono- and dimethylol ureas increase, the proportion of linear species increases and the per-

cent crystallinity should also increase. Thus, the following equation correlating crystallinity to  $^{13}\text{C}$  NMR species ratios can be proposed.

$$\% \text{ crystallinity} = 25.75 Y_1 + 40.64 Y_4$$

with standard deviation of 6.85 for the cases considered. The above equation presents two of the terms relating I.B. strength with  $^{13}\text{C}$  NMR peak ratios, clearly indicating that correlation between resin strength and its percent crystallinity exist. Interestingly and expected is the fact that in the above equation the urea/(C1 + C2) term has a coefficient of opposite sign than in the strength equation indicating that these species contribution to strength and percent crystallinity are inversely proportional. This equation, however, does not give a very good correlation. This could be explained by the fact that not all possible factors that could contribute to crystallinity have been considered. Finally correlation between I.B. strength and percent crystallinity was attempted. But since not all the terms considered in the I.B. strength equation are present in the percent crystallinity equation, no good correlation was obtained. Thus I.B. strength and percent crystallinity seem to somewhat influence one another, but are not really correlated.<sup>8</sup>

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