

# The Curing of UF Resins Studied by Low-Resolution $^1\text{H}$ -NMR

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**ABSTRACT:** A series of UF resins and one MUF resin were studied by low-resolution  $^1\text{H}$ -NMR. The mobility of the resin during curing could be followed by measuring the spin-spin relaxation time ( $T_2$ ) with curing time. The relative curing behavior was similar to that found by traditional gel time measurements. In addition, extra features in the  $T_2$  plots with curing time showed at what point the bulk of the condensation reactions took place. The speed of cure was also related to the chemical groups in the liquid resin, and it was found that the linear methylol groups were mainly responsible for the curing speed of the resins. By studying the curing with different hardener levels and glue concentrations it was found that a UF resin is more sensitive to the glue mix concentration than an MUF resin. A cured resin was also studied after curing to investigate postcuring effects. Water seemed to play the biggest role in the postcure, with substantial amounts present immediately after cure, which decreased with curing time and aging. For the low mol ratio resins studied here further curing reactions did not seem to play a major role in the post curing phenomenon. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 754–765, 2000

**Key words:** low resolution NMR; UF resins; curing; solid-state NMR

## INTRODUCTION

Urea formaldehyde (UF) resins are used in the wood industry to bind wood products, such as plywood, particleboard, and medium density fibreboard (MDF), together. One of the most important properties of the resin is the curing or hardening time of the glue mix because this controls the rate at which the product can be produced. In this context, curing refers to both polymerization and crosslinking of the resin molecules. If the resin is too slow, this may result in poor board properties, while a too fast resin can result in precure, also leading to poor properties. It is of some interest to accurately define the curing of the resin and try and find which chemical groups

in the resin are responsible for the curing behavior. In addition, the state of the cured matrix after cure is also of interest because this can affect the final properties of the bound wood product.

The traditional way to measure the hardening time is to place the glue mix in a test tube at the curing temperature and vigorously agitate the mixture until the glue becomes hard. The point at which the glue solidifies is taken as the hardening time. This method is rather subjective, because it relies on the experience of the operator to decide when the resin is cured. DSC has also been used<sup>1,2</sup> to study the curing of UF resins, and this is a promising method for determining the speed and heat of reaction during curing.

Low-resolution  $^1\text{H}$ -NMR has been used widely in the food industry,<sup>3,4</sup> and is an attractive method for the study of curing phenomena because the mobility of the sample under examination can be studied *in situ* during the cure by

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measurement of the spin-spin relaxation time  $T_2$ . The instrument required for these type of measurements is of relatively low cost because very simple pulse sequences are used, and high resolution is not necessary. The data obtained is given in the time domain, so Fourier transformation is not necessary. This method has been used before,<sup>5</sup> especially for studying the curing of polyester resins<sup>6-8</sup> and the gelation of UF resins.<sup>9</sup> In these studies, the whole <sup>1</sup>H-NMR free-induction decay (FID) was analyzed to obtain a complete picture of the various components present in the curing mixtures. In this way, both the mobility and relative amounts of each component could be measured during the cure.

In the first and second part of this study only the  $T_2$  of the most mobile fraction of the glue mix was analyzed during curing. As seen before,<sup>9</sup> the <sup>1</sup>H-NMR FID generally consists of two components during the cure—the rigid (short  $T_2$ ) component, due to the more crosslinked material, and the mobile (long  $T_2$ ) component, due to residual monomers or oligomers. The reason for examining only the long  $T_2$  component was because the rate at which the reaction proceeds at normal curing temperatures is quite fast. This means that only the spin echo (CPMG)<sup>10</sup> experiment, measuring the long  $T_2$  component, can be performed at each time increment. In the CPMG experiment the short  $T_2$  component is “invisible” due to the long refocusing delay. Because the idea was also to develop a more “routine” method for analyzing the curing of the glue mix, this seemed appropriate here, because large changes in the mobility are to be expected in this mobile component with curing time. Some of the characteristic  $T_2$  curves obtained were compared with the chemical “structure” of the liquid resin to see if any correlation between the chemical groups present and the curing behavior could be found.

In the third part of the study the glue mix was cured and then allowed to cool to room temperature, after which the <sup>1</sup>H-NMR FID was measured. In this case, the whole of the FID was collected and analyzed. The time of cure was varied to see the effect of this on the FID. The FID was also measured at different times after curing to examine any post curing effects.

### <sup>1</sup>H-NMR FID

After excitation by a 90° pulse the <sup>1</sup>H-NMR signal decays with time in the x-y plane. The rate at which

the signal decays depends on the motion of the nuclei within the system. For rigid molecules the decay rate, characterized by the time constant  $T_2$ , can be very short; of the order of  $\mu$ s, due to strong dipole-dipole interactions, whereas in liquids, where these interactions are averaged to zero, it can be several seconds long. In most low-resolution NMR spectrometers the NMR signal decay from a liquid is dominated by the inhomogeneity of the magnetic field and thus the real  $T_2$  of the sample is lost. To overcome this, refocusing pulses can be applied to create echoes as in the Carr-Purcell-Meiboom-Gill (CPMG) sequence<sup>10</sup> and the data points collected at the top of the echoes. The top of the echoes then represents the true  $T_2$  decay of the sample. This method has been used previously to study the mobile  $T_2$  component in cured resins.<sup>7,8</sup> For the short  $T_2$  component the shape of the decay curve is usually approximated by a Gaussian or an Abragam<sup>11</sup> decay function:

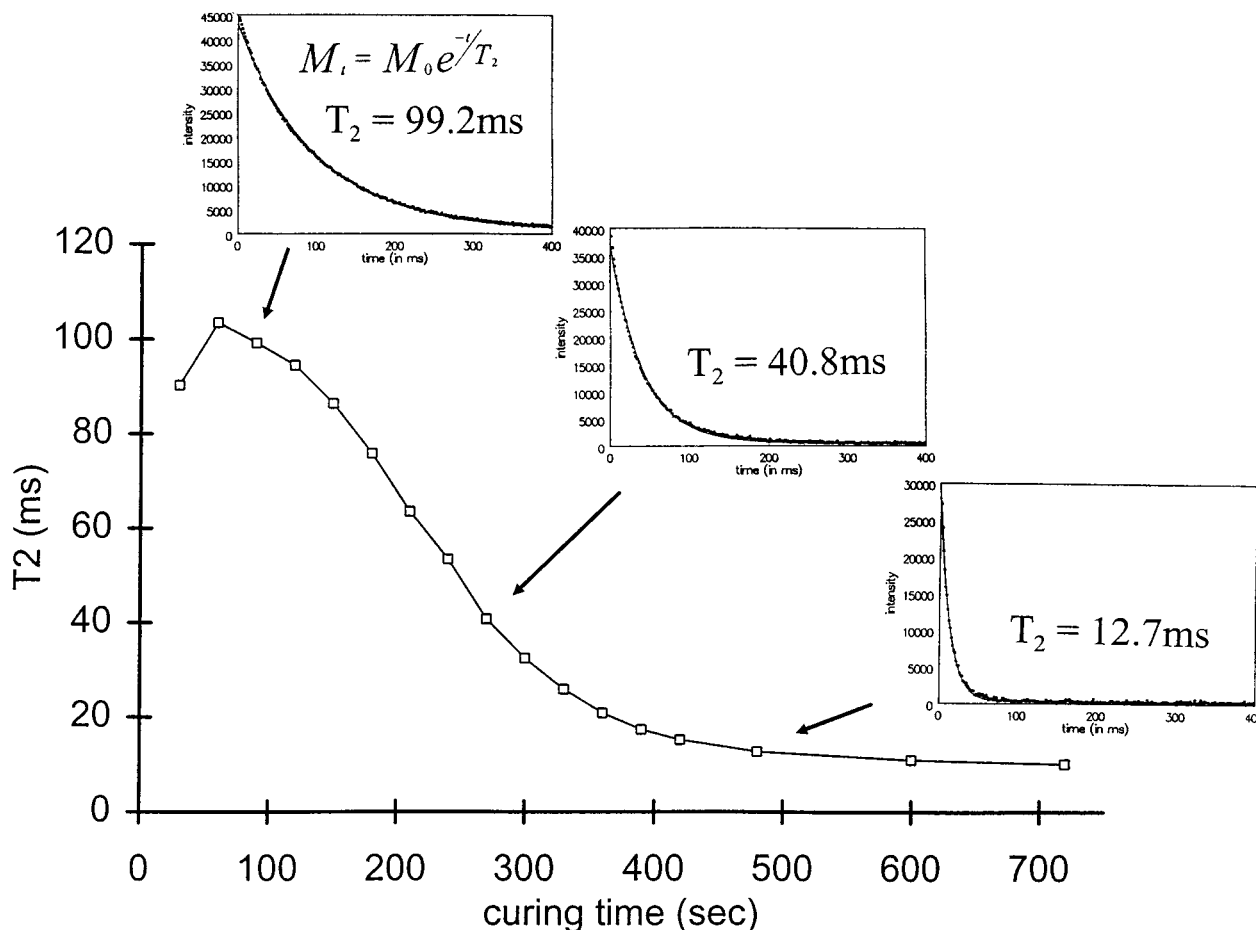
$$\text{Gaussian: } I_t = I_0 e^{-(t/T_2)^2}$$

$$\text{Abragam: } I_t = I_0 \frac{\sin 2\pi\nu}{2\pi\nu} e^{-(t/T_2)^2}$$

For the cured resins examined here at probe temperature after curing, the shape of the fast decaying component of the FID fitted more closely the Abragam function (see Fig. 10). The theoretical justification of this decay function has been discussed elsewhere,<sup>11</sup> and in this work we will consider this short component as due to the rigid areas of the cured resin.

### EXPERIMENTAL

All experiments were carried out using a home-built 60-MHz <sup>1</sup>H low-resolution pulsed NMR instrument. For the *in situ* experiments the resin was mixed with the hardener (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and then placed into a small length of glass 5-mm NMR tube whose bottom was sealed with a tight-fitting PTFE plug. This was then attached via a hollow length of PTFE tube to another length of 5-mm NMR tube, and the whole arrangement placed in the NMR probe set at the curing temperature. The reason for this arrangement was that the glue mix was difficult to place at the bottom of a normal 17.5-cm long 5-mm NMR tube, with most of the glue sticking to the walls of the tube and very little at the bottom. The moment of



**Figure 1** Plot of  $T_2$  vs. curing time for MUF1 at 80°C, together with the  $^1\text{H-NMR}$  FIDs at different stages.

insertion was taken as the  $t = 0$  point along the curing time curve. At various times after this the spin echo FID was recorded using the CPMG pulse sequence, and at the end of the curing experiment the collected FIDs were fitted to a single exponential decay to obtain the  $T_2$  value for each point. For each CPMG experiment generally 1000 echoes were accumulated using  $180^\circ$  pulses of  $3\text{-}\mu\text{s}$  duration with an echo spacing of 1 ms. Some effects of diffusion were noticed with this echo spacing because decreasing the echo time to  $500\ \mu\text{s}$  resulted in a  $T_2$  around 15% higher. However, in our experiments we were restricted to acquiring 1000 data points and, therefore, an echo time of 1 ms was used to accurately define the  $T_2$  decay. Either one or two accumulations were carried out using a recycle delay of 5 s. The  $T_2$  values vs. curing time were then plotted on a graph. Figure 1 shows the  $^1\text{H-NMR}$  FID at various curing times and the resulting  $T_2$  values plotted for an MUF resin cured at 80°C.

The time taken for the sample to reach a typical set temperature of 80°C was found to be around 2 min. The optimum curing temperature was chosen as 80°C because at higher temperatures the rate of reaction was so fast that the resin was probably cured before it had reached equilibrium (see below). At higher temperatures there was also the problem of bubbling of the glue mix out of the coil detection area.

The standard amount of hardener used was 2.5 wt % of  $(\text{NH}_4)_2\text{SO}_4$  of the dry solids content of the resin. For example, for 5 g of resin of 67% dry solids, 2.5 wt % corresponds to 0.08375 g of  $(\text{NH}_4)_2\text{SO}_4$ . In these experiments a 20 wt % solution was used, corresponding to 0.419 g of solution. In experiments where more or less hardener was used, more or less solution was added to the resin. This meant, however, that more or less water was also added to the glue mix and, therefore, both the hardener content and glue concentration changed at the same time. The effect of this is discussed below.

**Table I** Distribution of Formaldehyde in Resins UF1–5 in Terms of the % of Total Formaldehyde Found in Each Chemical Structure

Chemical Groups in Resin	UF1	UF2	UF3	UF4	UF5	Aged UF4
—N(H)CH <sub>2</sub> N(H)—	11.0	11.5	8.0	11.0	13.0	32.0
—N(C)CH <sub>2</sub> N(H)— + —N(C)CH <sub>2</sub> N(C)—	15.0	14.5	14.0	17.0	14.5	19.0
—N(H)CH <sub>2</sub> OH	56.0	50.5	49.0	44.5	41.5	24.5
—N(C)CH <sub>2</sub> OH	8.0	12.0	17.0	15.5	17.0	8.0
—N(H)CH <sub>2</sub> OCH <sub>2</sub> N—	7.0	8.0	7.5	8.0	9.0	12.0
—N(C)CH <sub>2</sub> OCH <sub>2</sub> N—	2.0	2.5	3.0	3.0	3.5	3.5
—NCH <sub>2</sub> OCH <sub>3</sub>	1.0	1.0	1.5	1.0	1.5	1.5
Total	100.0	100.0	100.0	100.0	100.0	100.0
Summary:						
Total methylene bridges	26.0	26.0	22.0	28.0	27.5	51.0
Total methylol groups	64.0	62.5	66.0	60.0	58.5	32.5
Total ether bridges <sup>a</sup>	10.0	11.5	12.0	12.0	14.0	17.0
% Free urea	37.5	39.0	43.0	41.0	41.0	20.5
Curing time/s	49	58	65	65	69	—

The % free urea represents the % urea of the total urea present as free urea.

<sup>a</sup> Including —NCH<sub>2</sub>OCH<sub>3</sub>.

The resins used for the *in situ* curing experiments were mainly UF resins with a F/U of 1.03. Five of these, denoted as UF1–5, were characterized by high-resolution <sup>13</sup>C-NMR to obtain the different chemical groups present in each resin. This method of characterisation has been described elsewhere,<sup>12,13</sup> and gives the distribution of the formaldehyde into the different chemical groups present using the peaks in the area 40 to 100 ppm. The percentage of free urea of the total urea present can also be calculated from the carbonyl area around 150 to 165 ppm. Using this, the correlation of chemical groups with curing behavior could be investigated. The results of the <sup>13</sup>C-NMR analysis for resins UF1–5 are given in Table I. Also included is the analysis for an “aged” resin, where aged means that the resin has been at room temperature for 6 weeks.

The effect of hardener content on curing of a UF resin (UF6, F/U = 1.03) and an MUF resin (MUF1, melamine 24 wt %, F/(NH<sub>2</sub>)<sub>2</sub> = 1.12) was also carried out.

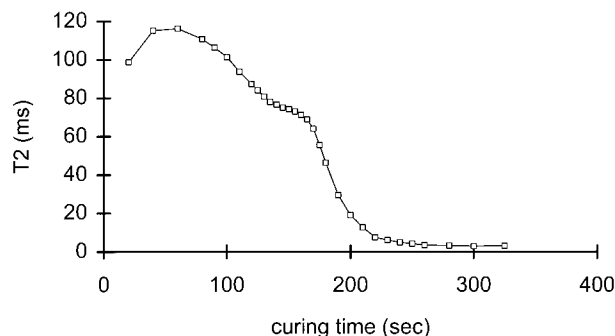
Postcuring effects were investigated using a UF resin with a F/U of 1.07 (UF7). In these experiments the resin (5 g) was cured with 2.5 wt % hardener, as described above, in an aluminium foil dish at 100°C for 10, 20, 30, and 60 min. The <sup>1</sup>H FIDs of the cured resins were then measured at probe temperature (37°C) using a single 90° excitation pulse of 1.5 μs. Approximately 64 tran-

sients of known weight of sample were acquired using a dwell time of 2 μs and a recycle delay of 5 s. In this case, refocussing echoes were not employed because the T<sub>2</sub> of the sample was much shorter than the decay of the magnetization due to the magnetic field inhomogeneity.

Before these samples were measured, a reference sample of a known amount of adamantane was also measured. The initial *t* = 0 intensity of the signal from the adamantane was compared with that due to the sample. Because the number of Hs in adamantane is known, the absolute number of Hs in the sample could be obtained.

The <sup>1</sup>H FID signal was measured for the four samples cured at 10, 20, 30, and 60 min on the day of curing, 1 day later, and then again a week later. The samples were stored in a desiccator between measurements. In general, the FID had two components that could be fitted using an Abragam function for the short decay, and an exponential for the long decay, as shown in Figure 10.

The <sup>13</sup>C CPMAS NMR spectra were obtained with a Chemagnetics CMX270 MHz spectrometer using a 4.5-μs 90° pulse, a 2-ms contact time, and a 3-s recycle delay. The number of transients acquired was around 1000, and the MAS speed was 4.6 kHz. The resin used for these experiments was a UF resin with a F/U of 1.03, called UF8.



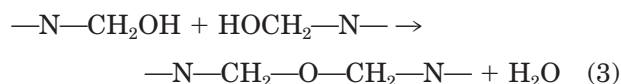
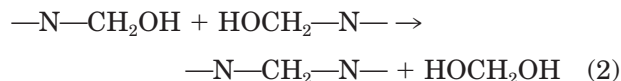
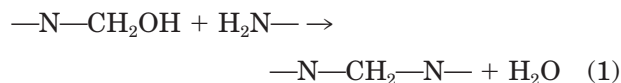
**Figure 2** Plot of  $T_2$  vs. curing time for UF2 at 80°C.

## RESULTS AND DISCUSSION

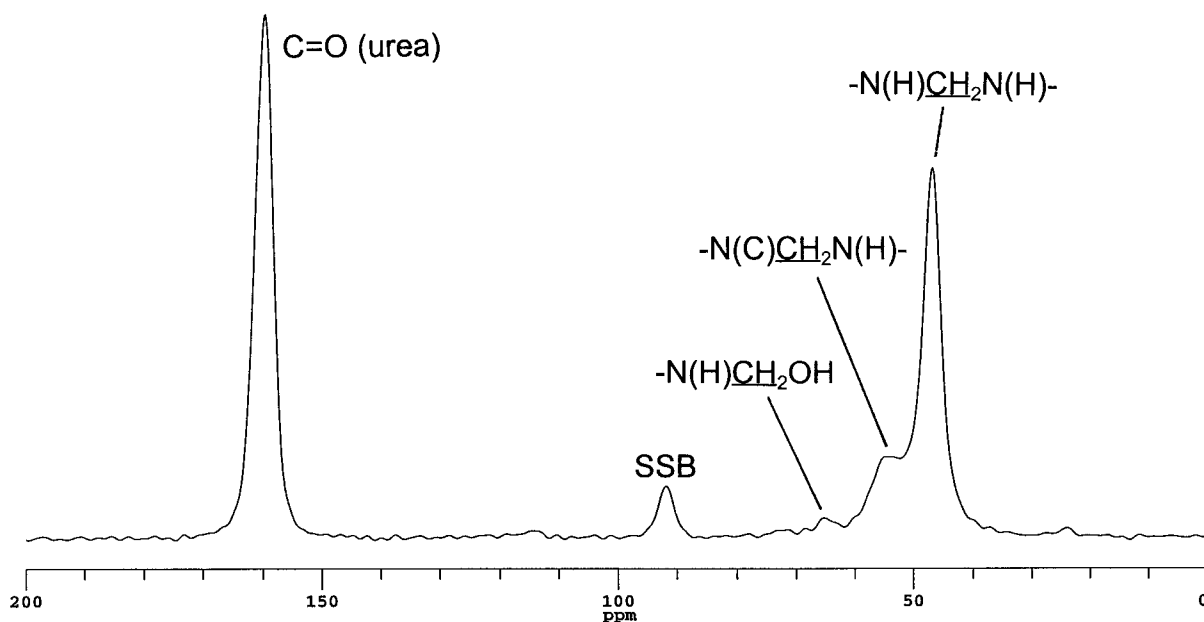
### In Situ Curing

As shown in Figure 1, the long component  $T_2$  gradually decreases as the cure progresses for an MUF resin. The initial rise is due to the decrease in viscosity as the sample temperature increases, but before significant curing occurs. The decrease in  $T_2$  with curing time is to be expected because the mobility of the molecules decreases as curing progresses. However, this simple decay curve is not always obtained, as can be seen in Figure 2, which shows the same graph for resin UF2 cured at 80°C. In this case, there is a hump in the curve at around 170 s. This corresponds to a temporary increase in  $T_2$ , and probably a decrease in viscos-

ity. This decrease in viscosity is unlikely to be due to a reduction in the crosslinking, but rather due to the production of large amounts of small molecules. This is to be expected if the polymerization is due to condensation reactions producing small molecules as in reactions (1), (2), and (3).

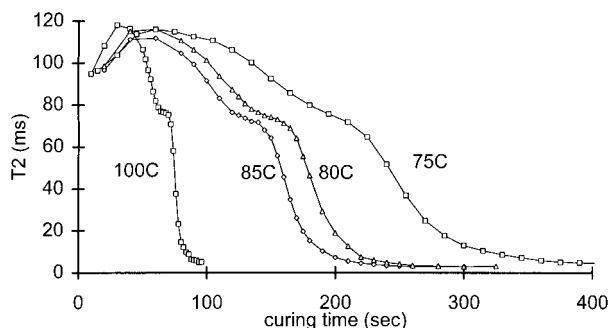


Reaction (3) is ruled out because there are practically no ether bridges produced when these low mol ratio resins are cured. This can be seen quite clearly in Figure 3, which shows the  $^{13}\text{C}$  CPMAS NMR spectrum of the UF8 resin with a mol ratio of 1.03 cured at 75°C. The main chemical groups present in the formaldehyde area are due to linear methylene bridges (47 ppm) and branched methylene bridges (54 ppm). Very few ether bridges can be seen, because there is very little intensity at 68 ppm (due to  $\text{—N(H)—CH}_2\text{OCH}_2\text{—N—}$ ) or 74 ppm (due to  $\text{—N(C)—CH}_2\text{OCH}_2\text{—}$



**Figure 3**  $^{13}\text{C}$  CPMAS NMR spectrum of cured UF8 (F/U = 1.03). SSB stands for spinning sideband.





**Figure 4** Plots of  $T_2$  vs. curing time for UF2 at 75, 80, 85, and 100°C.

N—). There may be some reaction (2), but this is probably quite small also, because there is usually so much free urea present in resins with such a low mol ratio. Therefore, the decrease in viscosity is probably due to the production of significant amounts of water at this critical point in the curing curve due to reaction (1).

The effect of curing temperature on this resin (UF2) is shown in Figure 4. The curing temperature has a big effect on the time taken to cure, as expected. The cure at 100°C is probably too fast to be used routinely because the resin is cured before the sample reaches equilibrium. The temperature of 75°C is getting rather low to be representative of the curing of pressed wood products, so the temperature of 80°C was chosen for the investigations here.

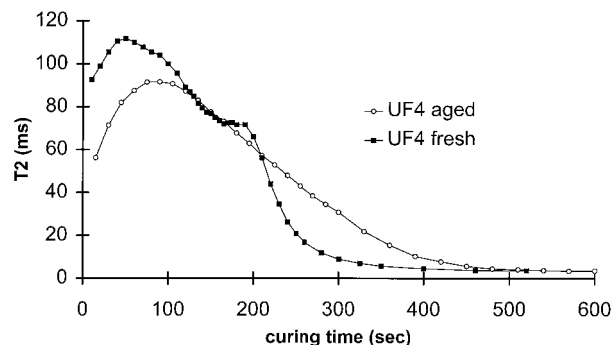
Even at 75°C the hump in the curing curve for UF2 (Fig. 4) is still evident, if somewhat smoothed out. This increase in  $T_2$  during curing does not occur for the MUF1 resin (Fig. 1). The time taken for the resin to cure is also longer, as can be seen by comparing Figures 1 and 2. This phenomenon is also seen for an aged UF resin. Figure 5 shows the  $T_2$  vs. curing time curve for a fresh and aged sample of UF4 at 80°C. The aged resin cures more slowly, and does not have any hump in the curve where the  $T_2$  value increases. From Table I it can be seen that the number of methylol groups and free urea in the aged resin are much lower than for the fresh resin. This is mainly due to aging reactions of type 1, which produce methylene bridges, resulting in a reduction in the amount of methylol groups and  $\text{NH}_2$  groups. One main reaction seems to be the reaction of monomethylol urea (MMU) with urea giving methylene diurea (MDU). This loss of MMU and production of MDU can be seen in the carbonyl area of the high resolution  $^{13}\text{C-NMR}$  spec-

trum of the aged resin (not shown). There is probably higher molecular weight material also produced during aging. Clearly, there are less reactive groups, both methylol and  $\text{NH}_2$ , so this means that during the cure less condensation takes place, which would reduce the amount of water produced.

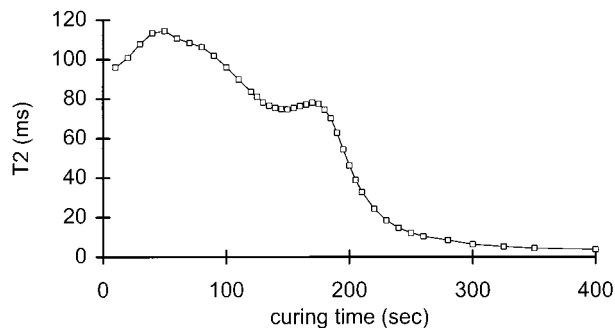
However, this explanation does not appear to hold for the MUF resin. From a similar analysis of the chemical groups present in MUF1 it was found that the % of  $-\text{NR}_2$  groups on the melamine, which are present as  $-\text{NH}_2$  groups, is 38.5%, while the % of urea present as free urea is 33.0%. Sixty-five percent of the formaldehyde is present as methylol groups. Therefore, there would seem to be plenty of reactive groups available. This implies that either the methylol or  $\text{NH}_2$  group on the melamine are less reactive than those on urea. To confirm this, a melamine (MF) resin with the same mol ratio as the UF resins should be examined. This was not carried out here. It should also be remembered that factors other than reactive groups may play a role in reactivity, such as molecular weight distribution of the liquid resin. This was also not investigated here.

Figure 6 shows the curing curve for UF3 at 80°C. Comparing this with the equivalent curve for UF2 shown in Figure 2, it can be seen that resin UF3 exhibits a more pronounced hump in the curing curve than resin UF2. As can be seen from Table I, this resin has the highest amount of methylol groups and free urea. This confirms the above conclusion that the amount of these groups in the resin determines the amount of water produced during the condensation.

Ether bridges are present in these resins, but there is very little evidence for these in the cured UF resin. This suggests that these bridges are



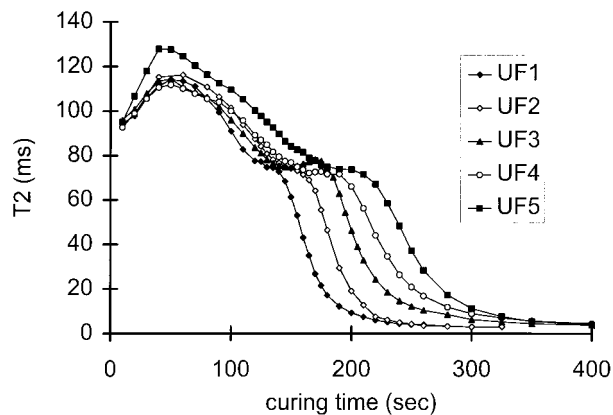
**Figure 5** Plots of  $T_2$  vs. curing time for fresh and aged UF4 (F/U = 1.03) at 80°C.



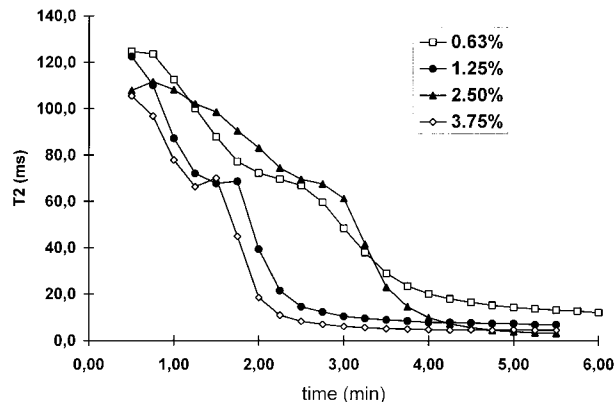
**Figure 6** Plot of  $T_2$  vs. curing time for UF3 ( $F/U = 1.03$ ) at  $80^\circ\text{C}$ .

broken at some point during the curing, probably by hydrolysis, forming two methylol groups that can then react with the free urea. Decomposition of these bridges may also lead to a decrease in viscosity and, thus, an increase in  $T_2$ . This probably occurs early on in the curing process, and may contribute to the initial rise in the  $T_2$  at the beginning of the curing curve. There is some evidence for a small upward curve in the  $T_2$  plots shown in Figures 2 and 6 just before the pronounced hump due to evolution of water.

An important question is which groups in the resin are responsible for the speed with which the resin cures. Figure 7 shows the curing curves obtained for resins UF1–5 at  $80^\circ\text{C}$ . The trend in hardening times from these curves is as follows:  $\text{UF1} < \text{UF2} < \text{UF3} < \text{UF4} < \text{UF5}$ . This agrees reasonably well with the curing times measured by the traditional gel time method also given in Table I. In this case, this trend is not echoed in the total methylol group amount, and also not in the methylene bridge content, although there is a



**Figure 7** Plots of  $T_2$  vs. curing time for UF1–5 (all with  $F/U = 1.03$ ) at  $80^\circ\text{C}$ .

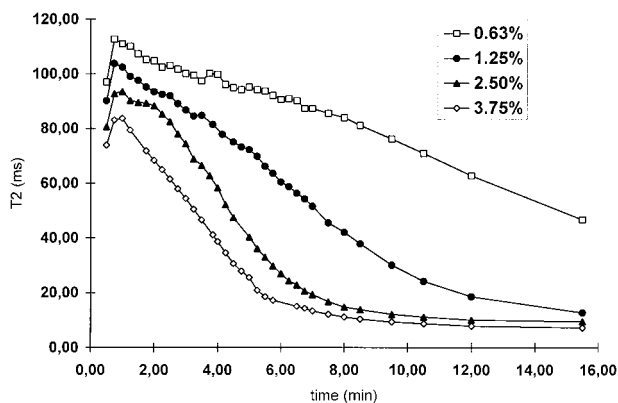


**Figure 8** Plots of  $T_2$  vs. curing time for UF6 ( $F/U = 1.03$ ) at  $80^\circ\text{C}$  using different levels of hardener.

small correlation with the ether bridge content. However, the most striking correlation is with the linear methylol groups, which clearly decrease across the series of resins UF1–5. It is tentatively concluded that these groups are those mostly responsible for the curing speed of the resins. It cannot be said from this data whether these linear methylol groups are at the end of polymer chains or in small monomers such as monomethylol urea (MMU), but from the  $^{13}\text{C}$  carbonyl area of these low mol ratio resins (not shown) it is likely that there are significant amounts of MMU present. These conclusions are probably only valid for these type of resins, i.e., those within this specific low mol ratio area.

#### Hardener Concentration

Figure 8 shows the  $T_2$  vs. curing time curves for UF6 for four different levels of hardener. Figure 9



**Figure 9** Plots of  $T_2$  vs. curing time for MUF1 [ $F/(\text{NH}_2)_2 = 1.12$ ] at  $80^\circ\text{C}$  using different levels of hardener.

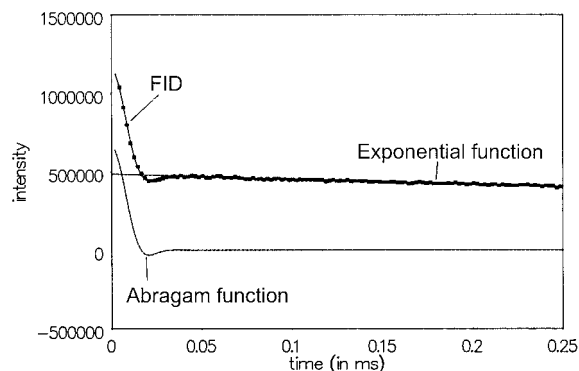
**Table II Concentration of Glue Mix for the Various Hardener Amounts Used**

Hardener Content (%)	Glue Concentration (%)
0.63	66.0
1.25	65.1
2.50	63.4
3.75	61.8

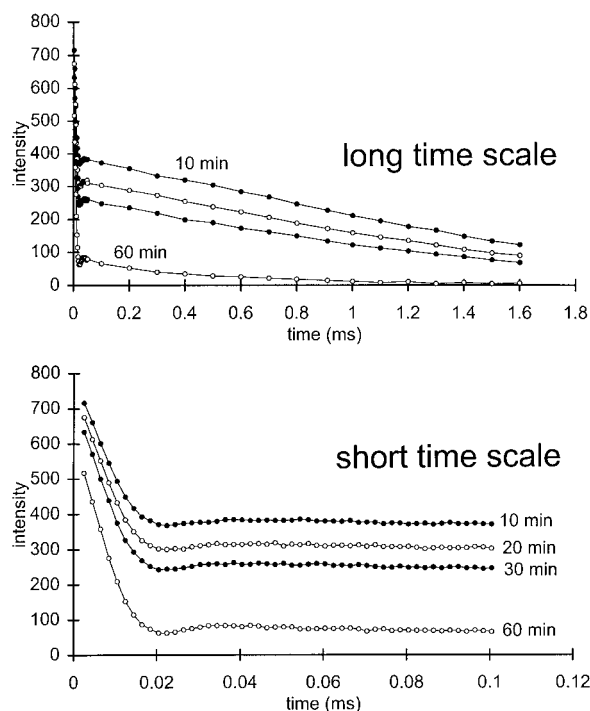
shows the same set of data for MUF1. While figure 9, for the MUF resins, shows the expected decrease in curing time with increasing hardener content, Figure 8 shows quite different behavior. For the UF resin at low hardener content (0.63%) the curing time is long, decreasing when the hardener level increases (1.25%) but then increases again when the level reaches 2.5%. Increasing the hardener content further (3.75%) again shortens the curing time. For the MUF resin, there is a continual decrease in curing time as the level of hardener increases. The reason for this strange behavior for the UF resin is assumed to be due to the dilution effect discussed in the Experimental section. As the hardener content increases, so does the amount of water added in the  $(\text{NH}_4)_2\text{SO}_4$  solution. Table II shows the glue mix concentration for the different hardener levels. Increasing the level of hardener concentration from 0.63 to 1.25 only decreases the glue mix by 0.9%. It is assumed that the increase in hardener content has a bigger influence on the curing time than the dilution effect. When the hardener level is increased to 2.5%, the glue concentration decreases by 1.7%. In this case, the glue concentration presumably has a bigger effect, giving rise to an increase in curing time. The further increase to 3.75% gives a decrease in glue concentration of 1.6%, but in this case the extra hardener added has a bigger effect than the dilution of the glue mix. This phenomenon was also observed with other UF resins with similar mol ratios (not shown). Because these effects are not seen for the MUF resin, it is concluded that the UF resins are much more sensitive to glue mix concentrations than MUF resins.

### Postcuring

Figure 10 shows the  $^1\text{H}$  FID of UF7 cured for 30 min at  $100^\circ\text{C}$  measured on the same day at  $37^\circ\text{C}$ , using the single pulse excitation method. The signal is composed of two components: the long  $T_2$  component, which was observed in the experiments above, and a short  $T_2$  component, due to


**Figure 10**  $^1\text{H}$  FID for UF7 ( $F/U = 1.07$ ) cured for 30 min at  $100^\circ\text{C}$  measured on the day of cure at  $37^\circ\text{C}$ .

the rigid material. This short  $T_2$  component was not observed in the curing experiments above because the CPMG sequence was used to acquire the data. The long  $T_2$  component can be described by an exponential decay, while the short decay can be described by the Abragam function, as shown in Figure 10. From this the values of the short and long  $T_2$  values can be found together with the relative contributions of the two components to the FID. Figure 11 shows the long and


**Figure 11** Long- and short-time behavior of the  $^1\text{H}$  FIDs from UF7 cured at 10, 20, 30, and 60 min recorded on the day of cure.

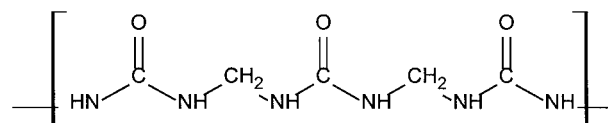


**Table III** Values of  $T_2$  (in  $\mu\text{s}$ ) and Populations of Each Component Obtained for UF7 Cured at 100°C for 10, 20, 30, and 60 min Measured on Days 0, 1, and 6

$T_2/\mu\text{s}$	Time Sample Cured at 100°C			
	10 min	20 min	30 min	60 min
Day 0	19.0 (44%) 2820 (56%)	18.6 (51%) 2132 (49%)	18.0 (57%) 1726 (43%)	15.1 (84%) 500 (16%)
Day 1	17.9 (63%) 1195 (37%)	18.1 (64%) 1210 (36%)	17.1 (64%) 1225 (34%)	16.8 (81%) 500 (19%)
Day 6	16.7 (84%) 274 (16%)	17.0 (81%) 419 (19%)	17.3 (85%) 269 (15%)	16.1 (85%) 308 (15%)

short time behavior of the  $^1\text{H}$  FIDs from the four samples cured at 10, 20, 30, and 60 min on the first day of cure. Table III shows the results of this analysis for the samples cured at 10, 20, 30, and 60 min after 0, 1, and 6 days at room temperature. Table IV shows the results of the quantitative analysis for these resins in terms of the number of Hs/g for each sample as well as the number of rigid Hs/g, calculated by using the percentage of rigid component present.

It is assumed that the polymer matrix is mainly made up of the following type of chains:

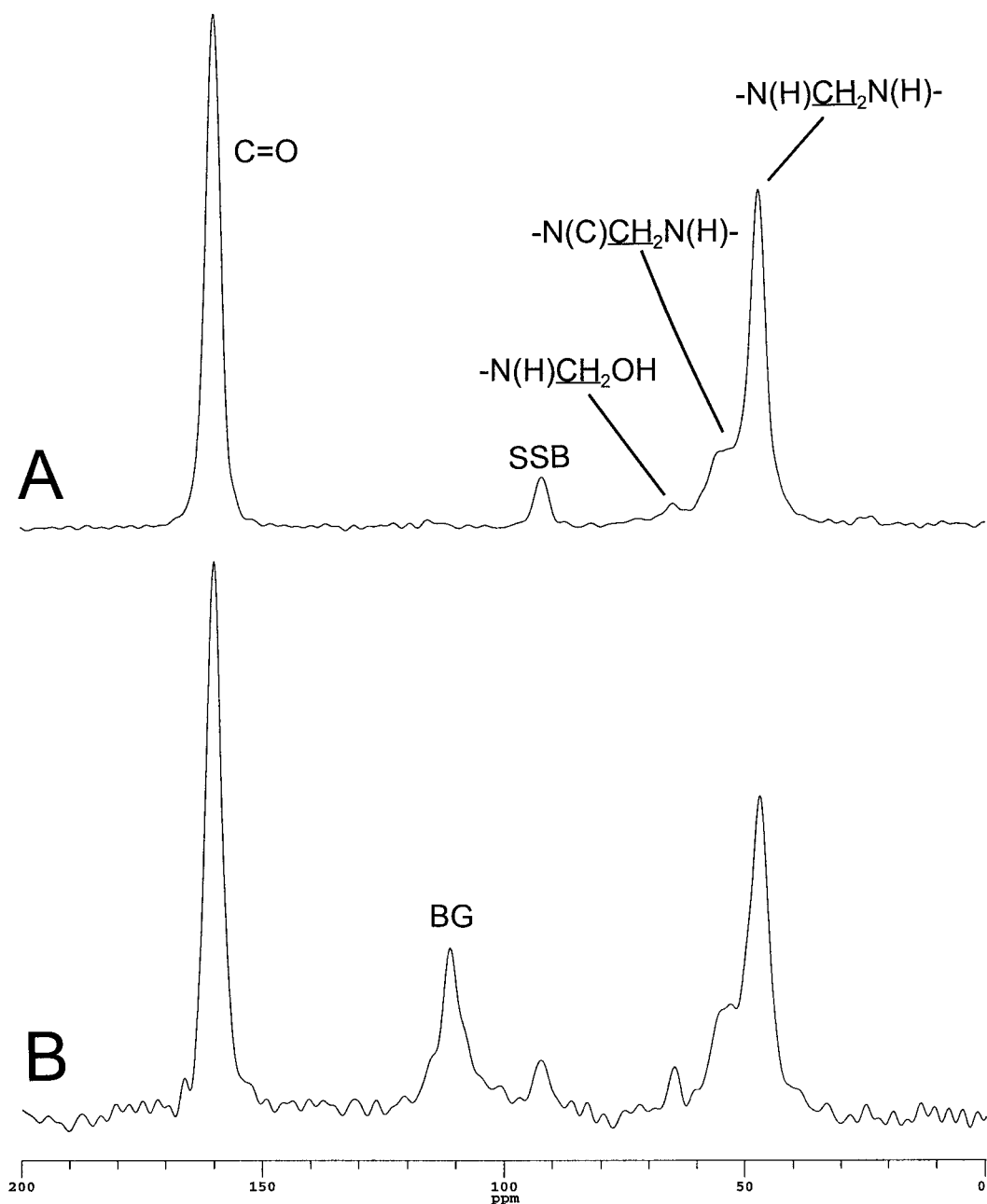
**Table IV** Summary of Total H/g, Rigid H/g, and wt % Water for UF7 Cured at 100°C for 10, 20, 30, and 60 min Measured on Days 0, 1, and 6

	Time Sample Cured at 100°C			
	10 min	20 min	30 min	60 min
Total H/g $\times 10^{20}$				
Day 0	396	372	351	278
Day 1	326	321	329	281
Day 6	270	278	269	275
Rigid H/g $\times 10^{20}$				
Day 0	175	190	201	233
Day 1	206	204	216	226
Day 6	227	226	229	234
wt % Water				
Day 0	31	25	20	1
Day 1	13	12	14	2
Day 6	0	1	0	0

This approximation is based on the presence of mainly  $-\text{N}(\text{H})\text{CH}_2\text{N}(\text{H})-$  groups in the  $^{13}\text{C}$  CP-MAS NMR spectrum of these low mol ratio resins (Fig. 3). The long  $T_2$  component seen in the  $^1\text{H}$ -NMR FIDs in Figure 11 is assumed to be mainly due to water trapped within the polymer matrix during curing. This long  $T_2$  component decreases in intensity with increasing curing time and aging, and is attributed to "postcure." The decrease in this long  $T_2$  component is also associated with a decrease in the total number of Hs within the cured resin. Therefore, there is a loss in some species with increasing curing time and aging. For the data presented here, this is assumed to be due to loss of the trapped water within the resin matrix.

An alternative explanation is that there is real postcuring during aging with some or all of the reaction (1)–(3) occurring, with loss of water or formaldehyde. This seems unlikely, because there are very few methylol groups present even after curing for only 10 min, and the decrease in the number of Hs is so large. This is shown in Figure 12(a), where the  $^{13}\text{C}$  CPMAS NMR spectrum of UF8 (F/U = 1.03) cured at 100°C for 10 min recorded on the same day of cure is shown. The  $^1\text{H}$ -NMR FID (not shown) of this sample is very similar to that of the 10-min sample of UF7 in Table III. The short and long  $T_2$  components have the same populations of 44 and 56%, respectively, with  $T_2$  values of 14.6 and 2380  $\mu\text{s}$ . Even though there is a substantial amount of mobile material in this sample, the number of free  $-\text{N}(\text{H})\text{CH}_2\text{OH}$  groups is very small.

However, because the CPMAS experiment is not strictly quantitative, a normal single pulse experiment was also carried out on the same sample (UF8 measured on the same day after curing



**Figure 12** (A)  $^{13}\text{C}$  CPMAS NMR, and (B)  $^{13}\text{C}$  MAS NMR spectra of UF8 (F/U = 1.03) cured for 10 min at  $100^\circ\text{C}$  measured on the day of cure. BG is due to the background signal of the PTFE plugs.

for 10 min at  $100^\circ\text{C}$ ). In this case, magnetization from the  $^{13}\text{C}$  nuclei was generated by a single  $90^\circ$  pulse, and the  $^{13}\text{C}$  FID collected with  $^1\text{H}$  decoupling. This spectrum is shown in Figure 12(b). Even in this case the 20-s recycle delay is probably not long enough to result in a quantitative spectrum. However, those more mobile parts of the sample probably have a shorter  $T_1$ , and

should be enhanced in intensity. As can be seen, there are slightly more methylol groups evident, but the spectrum is not significantly different to the  $^{13}\text{C}$  CPMAS NMR spectrum. We conclude that this small amount of residual methylol groups is insufficient to account for the large decrease in the number of Hs, by reactions (1)–(3), seen when the sample ages. This loss in Hs is mainly due to

water, produced during curing, gradually emitting from the sample as it ages.

Assuming that the structure of the cured polymer is approximately as shown above, the number of Hs/g can be calculated, assuming no residual water present. This is  $334 \times 10^{20}$  H/g, and is somewhat higher than the completely aged week-old samples. This could be due to the extra crosslinking, which can be seen in the  $^{13}\text{C}$  CP-MAS spectra of the cured resin as peaks due to  $-\text{N}(\text{C})\text{CH}_2\text{N}(\text{H})-$ , and also due to the presence of other inorganic material such as the hardener. If the average of the day 6 values for the Hs/g of the cured samples is taken as the number of Hs/g for the cured sample with no water present ( $273 \times 10^{20}$  H/g), then the wt % water can be calculated for each of the samples. These results are shown in Table IV.

As can be seen, immediately after curing there are substantial amounts of water present in the 10-, 20-, and 30-min samples, and this decreases with increasing curing time. After 1 day the amount of water in these samples is about the same, but still quite high. The 60-min cured sample appears to be fully dehydrated immediately after the cure. The other samples have reached this fully dehydrated level after 1 week, although, due to lack of data after 2–5 days, this may have occurred earlier also. The total amount of rigid Hs/g increases with curing time and aging, but never quite reaches the total amount of Hs/g, even after 1 week. Therefore, at least in the early stages of “postcuring,” some of the resin molecules are present in this mobile phase. It is assumed that the resin is effectively fully cured in terms of the crosslinking in the resin even at the shortest curing time of 10 min. Fully cured here means cured to the same extent as an aged sample. Thus, the large amounts of water present in the matrix in the fresh resins probably act as a solvent for some of the polymer chains, giving rise to a mobile component of mainly water, but also some polymer material. As the sample ages, the water is released from the matrix and these polymer chains become more rigid, contributing more to the rigid part of the  $^1\text{H}$ -NMR FID. After full “postcure” there is still some residual mobile component that is assigned to the more flexible polymer chains in areas where the crosslinking density is not so great. Some part of the process of reduction in mobility with aging may be due to some additional crosslinking, but the main contribution to this seems to come from the loss of water.

Because there is so much water present in the resin after curing and the cured resin is probably

somewhat acidic from the presence of the hardener, it is possible that hydrolysis can take place, releasing formaldehyde. This may be one of the mechanisms of formaldehyde emission from resins in particle board and MDF board. Compared to the emission of water from the matrix, this is small but because formaldehyde emissions have to be very low this has to be considered for commercial purposes.

## CONCLUSIONS

It has been shown that low-resolution  $^1\text{H}$ -NMR can be used to study the curing behavior of wood glues such as UF resins. Although the experiments carried out here were rather time consuming, because each  $T_2$  point had to be analyzed individually, a modern dedicated low-resolution spectrometer could easily be set up to carry out these measurements automatically.

During the curing process it was seen that the spin-spin relaxation time ( $T_2$ ) of the most mobile region of the sample decreased with curing time. For low mol ratio UF resins (F/U 1.00) the rate of decrease can be related to the number of linear methylol groups in the resin; the more linear methylol groups, the faster the cure. During the curing there is usually a pronounced local increase in  $T_2$ , corresponding to a decrease in viscosity. This is taken to be the point at which a large amount of condensation reactions occur, releasing many small molecules that are probably water. This appears to be related to the total number of methylol groups as well as the amount of free urea present in the resin.

It was found that the variation of curing time with hardener content for a UF resin did not follow the expected trend, i.e., a faster cure with more hardener. This was due to the complicating effect of dilution of the glue mix, which tends to slow down the cure when the glue is diluted. This effect was not evident for an MUF resin. It is assumed that MUF resins are not so sensitive to glue mix dilution.

Postcuring effects were studied and showed that initially after the cure there are substantial amounts of water present in the resin. The amount of water left in the resin depends on the time of curing, and decreases with aging. The postcuring effects observed here seemed to be mainly due to loss of water from the resin.

It seems that low-resolution  $^1\text{H}$ -NMR is a very useful tool for studying curing phenomena in UF resins. Even though it is a simple technique, by

studying a range of different samples under different conditions, important conclusions can be reached concerning the parameters affecting the curing behavior, especially when used in combination with high-resolution <sup>13</sup>C-NMR techniques. The quantitative nature of this method also allows important conclusions to be drawn when studying postcuring effects.

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