# The Reaction in Water of UF Resins with Isocyanates at Short Curing Times: A $^{13}$C NMR Investigation

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**ABSTRACT:** CP MAS $^{13}$C NMR spectra of hardened resins have shown that urethane bridges derived from the reaction of the isocyanate group with the hydroxymethyl group of urea do form even at fast curing times comparable to what was used in the wood panels industry, in lower proportions than what was shown earlier. Polyureas and biurets obtained from the reaction of isocyanate with water are the predominant crosslinking reactions of pMDI alone and in UF/pMDI resin systems under fast curing conditions. Residual, unreacted isocyanate groups in the hardened network are consistently observed. Their proportion markedly decreases when the original proportion of urea–formaldehyde (UF) resin is high and that of pMDI is low. Under these fast curing conditions, the UF resin appears to self-condense through an unusually high proportion of methylene ether links rather than methylene bridges alone. A marked proportion of residual, unreacted hydroxymethyl groups is also noticeable, initially, in the UF self-condensation network. Direct NMR tests on thin hardboard bonded under fast pressing conditions with different proportions of UF/pMDI confirmed that crosslinking due to polyureas and biurets formation are predominant in the crosslinking of pMDI when alone and in UF/pMDI resin systems. They confirmed that residual, unreacted isocyanate groups are present in the finished panel. Their proportion is higher when the proportion of pMDI in the system is high. The presence or absence of urethanes could not be confirmed directly on the panels as the relevant peaks are masked by the wood carbohydrates signals of wood cellulose and hemicelluloses. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1624–1632, 2006

**Key words:** NMR; structure; isocyanates; urea–formaldehyde; resins; urethanes; reactions

## INTRODUCTION

Urea–formaldehyde (UF) resins have been clearly shown to copolymerize in water with pMDI (polymeric diphenylmethane diisocyanate), and the type of linkages and compounds formed have been isolated, analyzed, and clearly determined by several techniques and research groups.[1–3] While reaction of the isocyanate group with water to form polyureas networks always occurs to a greater or lesser extent, in water, in the absence of UF hardeners and at long curing times, the reaction that predominates is the reaction of the UF methylol group (—CH$_2$OH) with the isocyanate group to form urethane bridges,[1] other reactions having only been tested in the absence of water.[4] The final hardened resin network presents then in almost equal proportions both urethane bridges, and methylene bridges pertaining to a normal UF resin network, as well as polyureas all covalently linked in the same network.[1] This situation occurs at long curing times and when salts normally used as hardeners of the UF resin are not present.

The strength of a joint bonded with UF/pMDI glue-mixes is much improved, among others due to the coreaction between isocyanate groups and UF resins methylol groups to form a certain number of urethane crosslinks. This also appears to occur in the presence of water and under the predominantly acid hardening conditions characteristic of aminoplastic resins (thus, in the presence of a hardener). The system was tried with very encouraging results for moisture resistant plywood[2] and it is now proposed as being of some interest and as giving encouraging results in the bonding of straw-based particleboard.[5,6]

UF resins are used as the main adhesive in the wood panels manufacturing industry. In about 10% of the cases, a hardener is not used, such as in some types of MDF boards and in HDF boards. However, in about 90%, a hardener/catalyst is used, ammonium sulfate being the most common one. While the reaction products obtained in UF/pMDI adhesive systems to which a hardener has not been added have been described in detail,[1] the UF/pMDI systems in which a hardener has been used have only been scantily investigated.[3] A hardener is necessary because of the fast industrial

**TABLE I**
**Gel Times at 100°C of Glue-Mixes Composed of Different Relative Proportions of UF Resin and pMDI in the Presence of 1% Ammonium Chloride Hardener**

| | Gel time (100°C) (s) | |
|---|---|---|
| UF/pMDI | Nonemulsified pMDI | Emulsified pMDI |
| 100/0 | 100 | — |
| 90/10 | 79 | 80 |
| 70/30 | 72 | 72 |
| 50/50 | 72 | 89 |
| 25/70 | 108 | 175 |
| 10/90 | 179 | 236 |
| 0/100 | 242 | 319 |

curing times used in the wood panels industry, often as short as 3–5 min in the hot press.

This article then deals with the $^{13}$C NMR investigation of the hardened products of the UF/pMDI reaction at industrial significant curing time, thus at short gel times obtained by addition of a hardener, both for the resin alone and for the resin in the finished wood board itself. High-density fiberboards (hardboards) were the panel type used as they lended themselves better to subsequent NMR analysis.

## EXPERIMENTAL

To a commercial UF (Kauritec 305, BASF) resin of F/U molar ratio of 1.2, and 68% solid content in water was added one of two commercial polymeric isocyanate used for binding wood panels (Woodcure 300 and Woodcure 220, Nippon Polyurethane Industry), one of which is an emulsified isocyanate (Woodcure 300).

Gel times at 100°C, according to the standard FESYP test,[7] of the mixed resins containing different proportions of UF resin and pMDI were done. The proportions tested were (based by weight on a resin solids/resin solids ratio) UF/pMDI = 0/100, 10/90, 25/75, 50/50, 70/30, 90/10, and 100/0. To these mixes was added 1% by weight on resin solids of ammonium chloride hardener, added as a water solution of 10% salt concentration. The results obtained are shown in Table I. The gelled/hardened resins obtained by the gel test were air dried at ambient temperature, up to hardening, and then finely ground for NMR analysis.

The same glue mixes earlier were used to prepare duplicate, one-layer laboratory hardboard (high-density fiberboard) of dimension $273 \times 293 \times 4$ mm$^3$. The total resin solids by weight onto the wood fibers was of 12%, at a pressing time of 30 s/mm thickness (120 s total press time) and at a press platens temperature of 193°C. Aimed hardboard (high density fiberboard) density was 875 kg/m$^3$. The panels after testing were finely ground for NMR analysis.

The solid state CP-MAS $^{13}$C NMR spectra of the hardened UF/pMDI resin systems used, of the UF resin control and of the hardened water/pMDI product, were obtained on a Bruker Avance DRX200 FT-NMR spectrometer at a frequency of 50.33 MHz and at a sample spin of 5.0 kHz. The impulse duration at 90° was 5 $\mu$s, contact time, 1 ms; aquisition time, 50 ms; number of transients, 2000; recycle delay, 2.5 ms; and the decoupling program, TPPM 15. Chemical shifts were determined relative to tetramethyl silane used as control. The calculation of the different shifts possible for the different structures was checked according to the shift values already reported in the literature.[1,8]

## RESULTS AND DISCUSSION

The gel-time results shown in Table I show that the samples of hardened resins obtained for NMR analysis by the 100°C gel-time test are obtained in times sufficiently short to be of industrial significance. In fact in wood panels, the core of the board reaches a maximum temperature between 100 and 115°C, generally not higher than that of 105–110°C for no longer than 3 min. This, in the short hot pressing times used in industry for wood panels manufacture and wood adhesives hardening. While coreaction has been shown to occur,[1,3] the concept of short hardening time is of importance in determining whether coreaction occurs and at what level under the industrial application conditions of these resins.

An accurate study of the solid state CP MAS $^{13}$C NMR shifts of the coreaction at a fixed proportion of 20/80 by weight of UF resins with pMDI has already been carried out.[1] The shifts of polyureas, biuret, ammines, carbammic acid, unreacted isocyanate groups trapped in the immobilized hardened network, and urethanes as well as traditional UF networking features were identified. Such study, however, did not take into account the fast rate of hardening, hence, the shortness of the time imposed on use of wood adhesives, nor the relative variation of these groups in relation to the relative proportions of the two resins.

Figures 1–6 show the solid phase $^{13}$C NMR spectra of the reaction of the UF resin with nonblocked pMDI obtained by varying the relative proportion of UF to pMDI. The spectra obtained with emulsifiable isocyanate are not reported here as all cases gave comparable results to what is reported here. The previous work[1] had clearly shown that of the two possible structures that could be formed, namely (i) that obtained by reaction of the isocyanate group with the hydroxymethyl group of the UF resin and (ii) that obtained instead by its reaction directly with the —NH$_2$ and —NH— amide groups of the UF resin, only the first type form, together with the reaction products of the isocyanate with water.

The presence of the —CH$_2$— bridge connecting the urethane with urea (69.5–74 ppm) is separate and well distinct from the shift of the —CH$_2$— bridge connect-
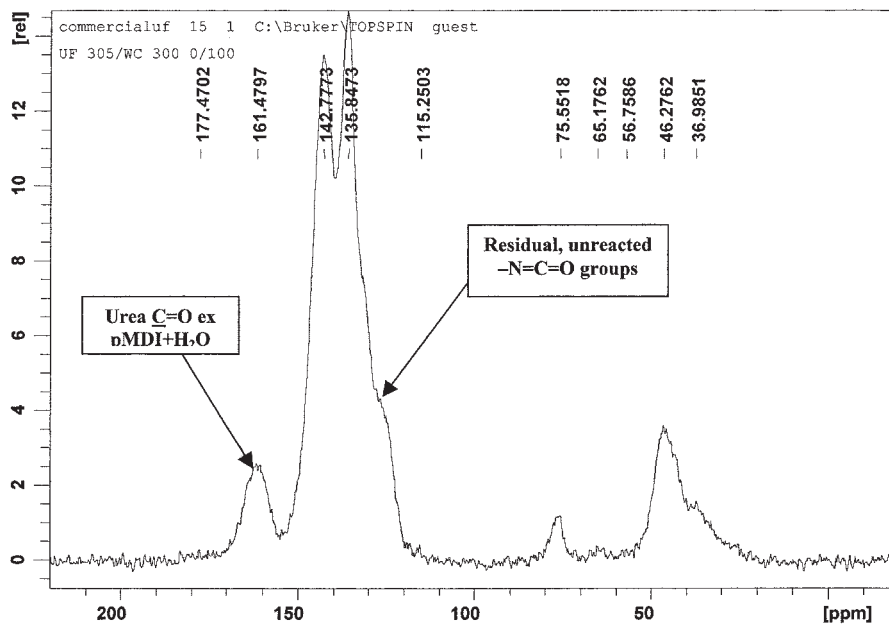
**Figure 1** Control solid state CP-MAS $^{13}$C NMR spectrum of the hardened product obtained by the reaction of nonemulsified pMDI with water at 100°C after gelling in 241 s.

ing two ureas obtained by self-condensation of the UF resin and of the internal —CH$_2$— bridge connecting the aromatic rings within pMDI. Thus, in Figure 1 the reaction of the isocyanate with water shows clearly the peaks at 46.5 and at 37–40 ppm both characteristics of the —CH$_2$— bridges connecting the aromatic rings within pMDI. In Figure 1 too are also visible the peaks at 142.3 ppm assigned to the aromatic carbon of pMDI attached to the amine group obtained by reaction of —NCO with water and decomposition of the carbammic acid formed in amine and CO$_2$. The peak at 135–136 ppm belongs to the aromatic carbon derived from the original pMDI structure and attached to the secondary amide group of urea obtained by the reaction of pMDI with water to produce polyureas and biurets. The internal methylene bridges of the MDI structure
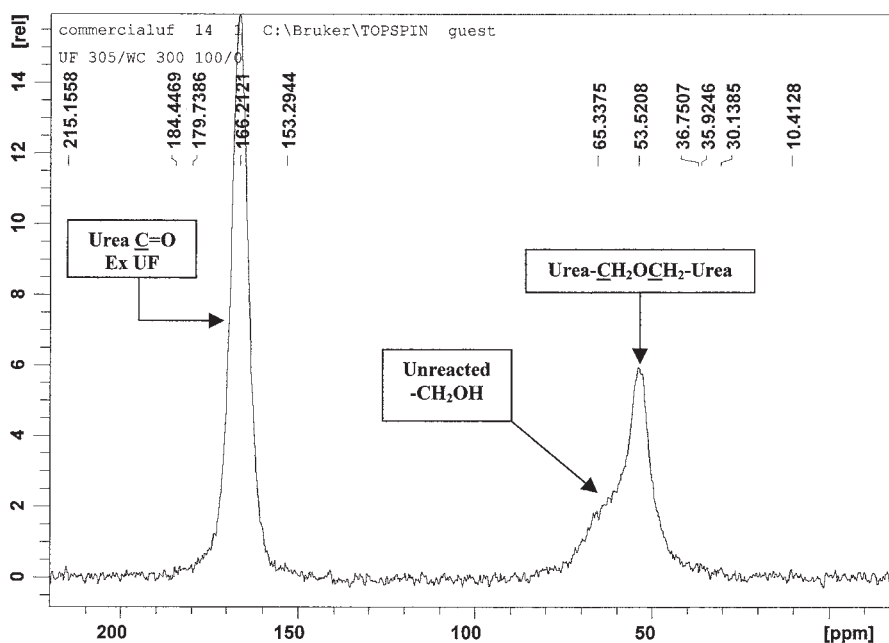


**Figure 2** Control solid state CP-MAS $^{13}$C NMR spectrum of the UF resin + 1% ammonium chloride hardener, hardened at 100°C in 100 s.
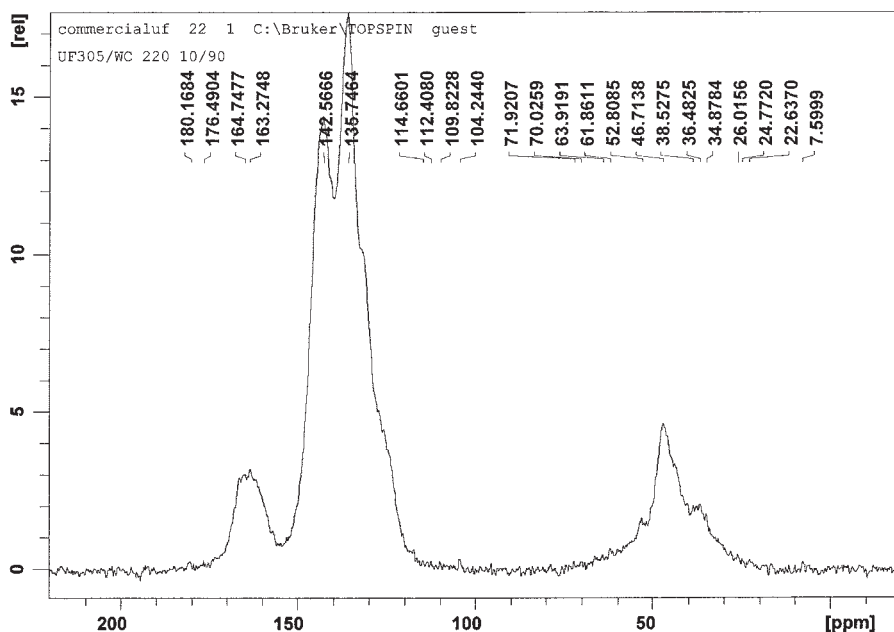
**Figure 3** Solid state CP-MAS $^{13}$C NMR spectrum of the hardened product obtained by the reaction at 100°C in water of UF/pMDI in weight proportions 10/90, +1% ammonium chloride hardener.

are observed in Figure 1 at 46.5 and at 37–40 ppm both characteristic of the —CH$_2$— bridges connecting the aromatic rings within pMDI. This signal is generally very wide (35–47 ppm range) and always presents a major peak and several smaller peaks and shoulders.[1] The shifts expected by calculation for different MDI structures should be at 41.06 ppm for the MDI + water-derived amine, and 40.6 ppm or lower for the reaction intermediate carbammic acid, generally un-

stable.[1] Of interest are the peaks in the 155–170 ppm range, the major ones being at 157 and 160.5 ppm, both belonging to the carbonyl group of differently substituted polyureas and biurets derived from the reaction of the ammine, derived from the original reaction of a isocyanate with water, with another isocyanate group. The peaks of the carbonyl groups of substituted polyureas at 152.8 ppm and of biuret at 153.2 ppm are masked by the broadness of the peak at
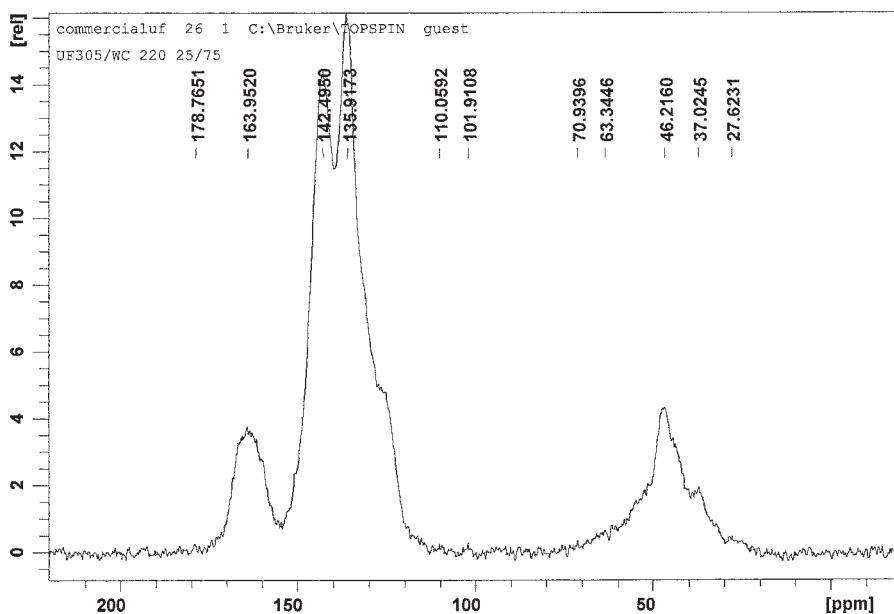


**Figure 4** Solid state CP-MAS $^{13}$C NMR spectrum of the hardened product obtained by the reaction at 100°C in water of UF/pMDI in weight proportions 25/75, +1% ammonium chloride hardener.
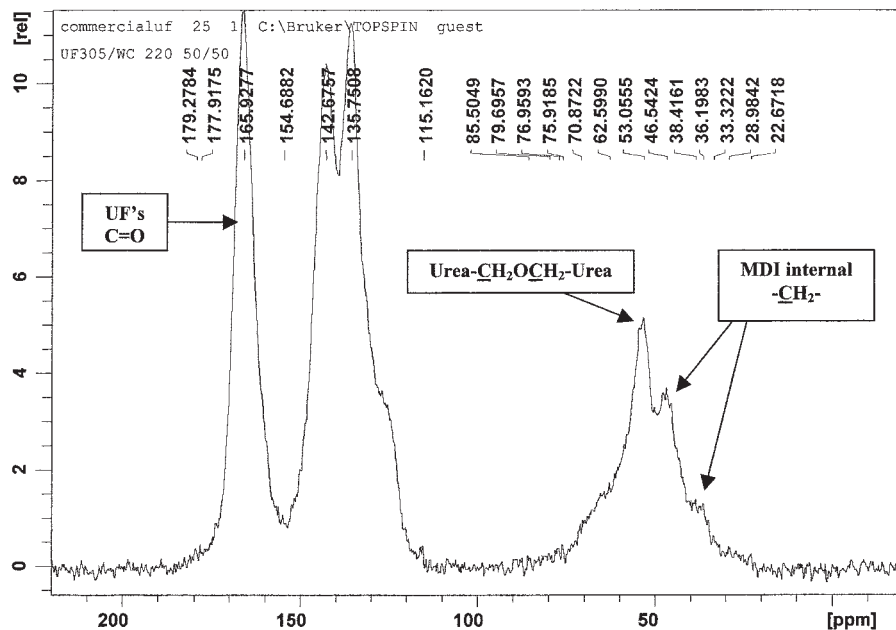
**Figure 5** Solid state CP-MAS $^{13}$C NMR spectrum of the hardened product obtained by the reaction at 100°C in water of UF/pMDI in weight proportions 50/50, +1% ammonium chloride hardener.

142.3 ppm. The small signal of the carboxyl groups of carbammic acid at 155.8 is also visible. The series of peaks observed in Figure 1 indicate then that the main reaction products of pMDI with water which can be detected are polyureas, biuret, amine, and some carbammic acid. The broad peaks of the spectra masks or are composed of the majority of the shifts that are not directly visible. Notwithstanding this the signal at 125–126 ppm of unreacted isocyanate groups immo-

bilized in the network is clearly visible as a shoulder in Figure 1.

In Figure 2 is shown the shifts observed in the spectra of the commercial UF resin used and confirmed by the results observed by other authors.[8] The urea carbonyl group signal is at 165–167 ppm. The only methylene groups present are those connecting two urea residues that appear as a shoulder at 47–48 ppm. It is interesting to note that in fast cured ureas, as
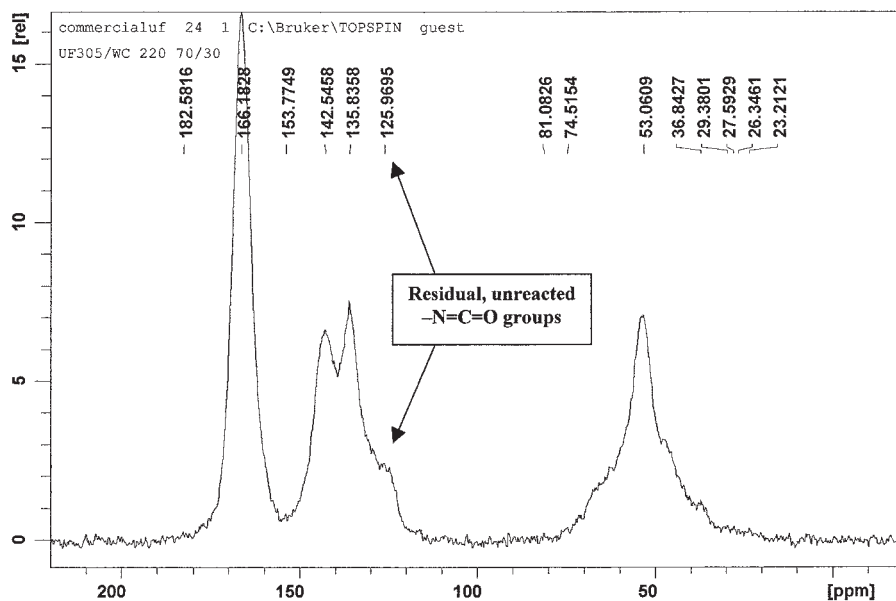


**Figure 6** Solid state CP-MAS $^{13}$C NMR spectrum of the hardened product obtained by the reaction at 100°C in water of UF/pMDI in weight proportions 70/30, +1% ammonium chloride hardener.

**Figure 7** Solid state CP-MAS ^{13}C NMR spectrum of the hardened product obtained by the reaction at 100°C in water of UF/pMDI in weight proportions 90/10, +1% ammonium chloride hardener.
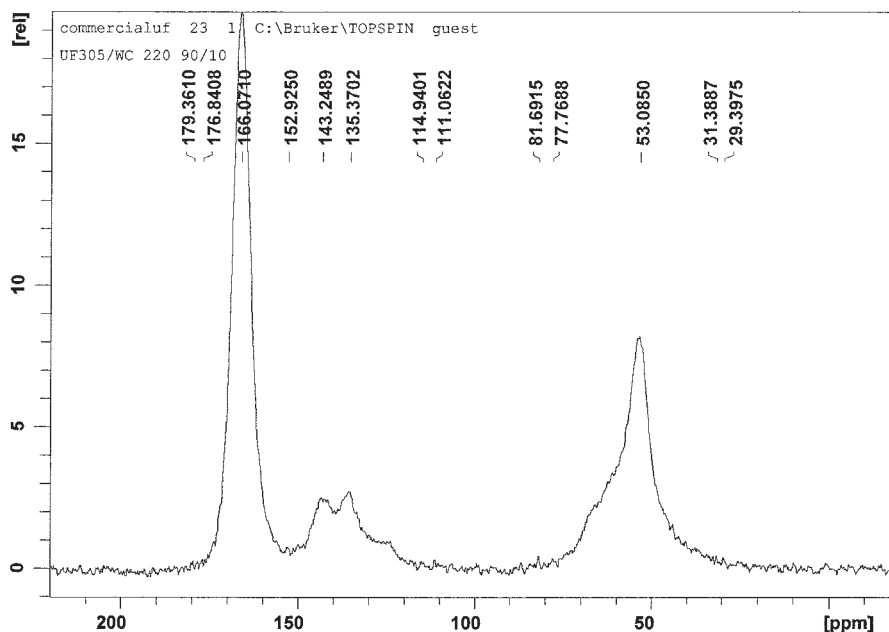
it is the case in Figure 2, the usually small shoulders[1] at 53–55 and 65 ppm, pertaining respectively, to the methylene ether bridges (—CH$_2$—O—CH$_2$—) between ureas and to the still unreacted hydroxymethyl group (—CH$_2$OH) of the UF resin, become the dominant peaks instead. This correctly describes the structure of just cured, fast-gelled UF networks, as is the case here, where methylene ether bridges (—CH$_2$—O—CH$_2$—) are known to dominate,[9,10] and only to rearrange later to methylene bridges with liberation of HCHO. The 65 ppm shoulder is relatively less marked, but still quite intense, indicating that in the initial curing of the resin a noticeable proportion of the UF resin hydroxymethyl group (—CH$_2$OH) remains unreacted in the initially, fast-immobilized network.

In Figures 3–7 are shown the spectra of the reaction mixes UF/pMDI 25/75, 50/50, 70/30, and 90/10 after gelling and air drying. These are marked by the relative increase of the proportion of the methylene ether bridges (—CH$_2$—O—CH$_2$—) at 53 ppm belonging to the pure UF-derived network, and the relative decrease of the 46 ppm and 36–38 ppm signals of the internal methylene (—CH$_2$—) bridges of pMDI as the relative proportion of UF resin in the mix increases. The three peaks are clearly distinct in the 50/50 case in Figure 5. Also passing from the C=O group of MDI-derived polyureas at 157–160 ppm the shift of the C=O shifts to first 163 ppm (Fig. 4) and then to the higher values (165–166 ppm) characteristic of the urea belonging to the UF resin where the UF resin is predominant in the mix (over 50% by weight) (Figs. 5–7). In Figures 3–7 also notable is the marked and progres-

sive decrease in the 135.7 and 142.5 ppm peaks from the isocyanate as the relative proportions of pMDI decrease lower than 50%. Finally, to be noted in all the Figures 3–7 is the shoulder at 125–126 ppm which is the shift of the carbon of the —N=C=O isocyanate group left unreacted.[1] This is visible in Figures 3–7. This shoulder means that, not withstanding the high proportion of water and of UF reactive groups, unreacted isocyanate groups survive in some proportion and remain in the hardened network. Its proportion in the hardened mix is lower the lower is the initial proportion of pMDI, in Figures 6 and 7 being much lower than in the other mixes. However, in relation to the isocyanate present, the percentage of unreacted isocyanate groups appear to remain approximately constant. This is possibly due to early immobilization of the network during hardening and attest of the fast rate of hardening of these systems. Its maximum proportion can be observed in the control case, pMDI alone in Figure 1.

The NMR spectra in Figures 3–7 indicate that core-action of the two resins, hence the formation of urethane bridges involving the isocyanate group and the methylol group of the UF resin, already shown to consistently occur in noticeable proportions at longer curing times,[1] is indeed rather limited at the faster curing times characteristic of the majority of wood panel adhesives, namely, when a UF hardener is present. Thus, in Figure 4, at UF/pMDI 25/75, the proportion of urethane is almost unnoticeable, and only in Figure 5 at UF/pMDI 50/50 the consistent presence of a relatively important shoulder at 69–75 ppm, mainly 70 ppm (—CH$_2$— of the urethane formed
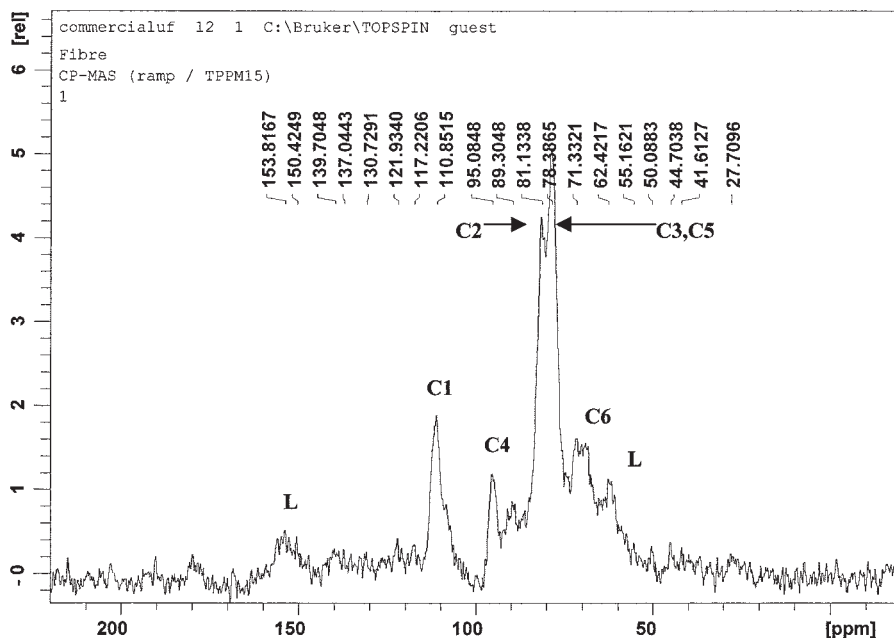
**Figure 8** Control solid state CP-MAS $^{13}$C NMR spectrum of the wood fiber used for hardboard manufacture. The letter C indicates the shifts characteristic of the carbon atoms of wood carbohydrates, and the letter L indicates those visible of wood lignin.

by reaction of —N=C=O and the —CH$_2$OH of the UF resin) can be noticed.

In Figures 8–11, are shown solid state CP MAS $^{13}$C NMR spectra of the wood fiber used to prepare laboratory hardboards (Fig. 8) and of the hardboard made with the UF/pMDI mixes 10/90, 25/75, and 70/30

(Figs. 9–11). Figure 8 shows the classical pattern of wood, with the dominant peaks pattern of cellulose and hemicelluloses. Visible are the C1, C2, C3, and C5 peaks of wood carbohydrates and the C4 and C6 double peaks each identifying amorphous and crystalline state of the wood structural carbohydrates.
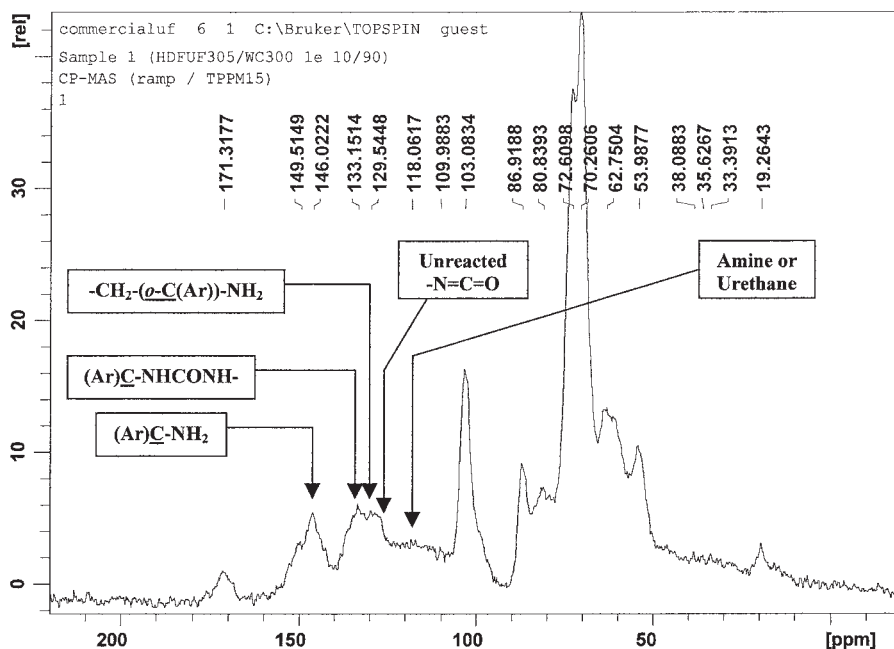


**Figure 9** Solid state CP-MAS $^{13}$C NMR spectrum of a hardboard bonded with of UF/pMDI in weight proportions 10/90, + 1% ammonium chloride hardener.
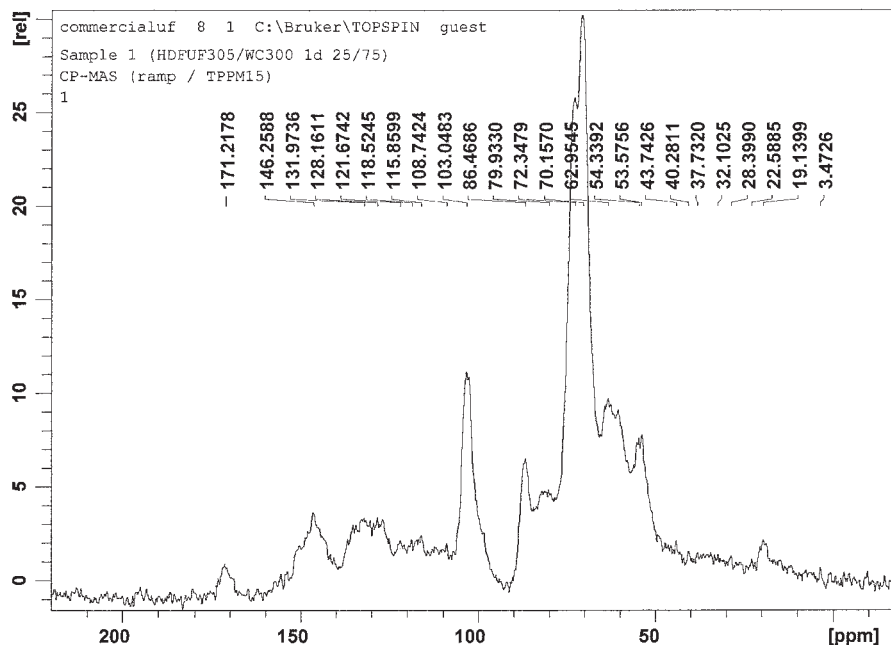
**Figure 10** Solid state CP-MAS $^{13}$C NMR spectrum of a hardboard bonded with of UF/pMDI in weight proportions 25/75, + 1% ammonium chloride hardener.

Peaks characteristic of wood lignin at 150–154 ppm and 60–65 ppm are also visible.

In Figure 9 (UF/pMDI 10/90) the two major peaks of the reaction of pMDI with water are visible. First, the 146 ppm peak masked by its broadness the small 149.5 (this is still slightly visible in Fig. 9) to 154 ppm

peaks from the fiber. The 146 ppm peak corresponds to the 143 ppm peak observed in the pure resins. Secondly, the 133–136 ppm peak of the aromatic carbon of pMDI attached to the secondary amide group of the final urea derived by the reaction of pMDI with water. The peaks at 129.5 ppm belongs to the aromatic
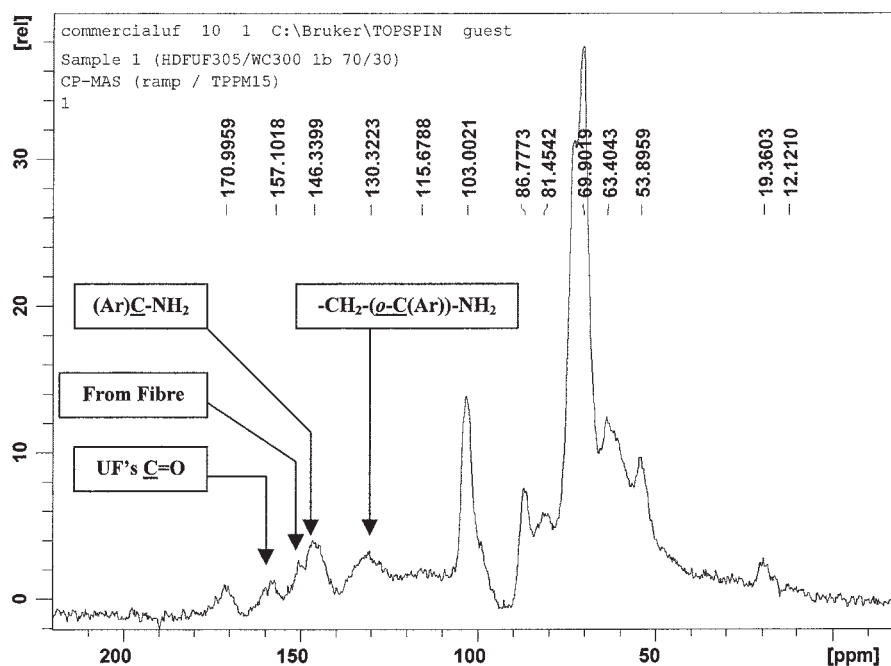


**Figure 11** Solid state CP-MAS $^{13}$C NMR spectrum of a hardboard bonded with of UF/pMDI in weight proportions 70/30, + 1% ammonium chloride hardener.

carbons of the amine in ortho to the methylene bridges internal to the pMDI structure derived by the reaction of MDI with water.[1] The shoulder at 125–126 ppm appears to exist here also, and to be reasonably important, with the proportion of pMDI (90%) rather high. This is of considerable interest as it shows, under the fast pressing conditions pertaining to thin fiber panels that unreacted isocyanate groups remain in the panel. Their proportion decreases markedly as the proportion of UF increases and of pMDI decreases (Figs. 10 and 11). In Figures 9 and 10, a peak at 118 ppm is also visible. This 118 ppm pertains to the aromatic carbons in ortho to the amine groups and to the carbammic acid group of the reaction of pMDI with water, and to the aromatic carbons in ortho to the urethane groups due to coreaction of pMDI with UF.[1] The peak that would prove the coreaction of pMDI with the methylol groups of urea at 70–75 ppm is not visible here as it is masked by the dominant peak pattern due to the wood carbohydrates. The carbonyl group of the urea of the UF resin is particularly visible as a series of peaks at 157–161 ppm in Figure 11 (70% UF). The NMR results on the wood panel themselves do not allow to prove or disprove the presence or not of the urethanes directly in the board itself, but only indirectly from the NMR spectra of the fast-cured resin. The NMR on the board itself allows, nonetheless, seeing the presence of polyureas and biurets, where the reaction is complete, and of amines where the reaction is incomplete. These are due to the reaction of pMDI with water from the fiber and from the UF resin, and appear to be the main crosslinking pattern of the pMDI in the boards, under fast press time conditions significant to industrial application. It also allows demonstrating by direct observation that residual, unreacted isocyanate groups remain in the panel under the condition used for industrial board pressing. The argument could be advanced that in the hot, humid environment inside the panel in the hot press, or later during log-term panel service, moisture in the air would be sufficient to react with the residual, unreacted urethane groups and transform them in amines or ureas. However, some doubts should be expressed on this possibility, as weather- and water-resistant networks of other polycondensates have already been shown to be so water-repellant to protect well from moisture attack even inherently water-sensitive links buried deeply in the hardened network.

## CONCLUSIONS

Reaction at fast curing times comparable to what used in the wood panels industry have shown by NMR analysis of the hardened resins that urethane bridges derived by the reaction of the isocyanate group with the hydroxymethyl group of urea do form. However, they appear to form in lower proportions than what has already been shown to occur at much longer curing times. Crosslinking due to the formations of polyureas and biurets by reaction of the isocyanate group with water are predominant in the crosslinking of pMDI when alone and in UF/pMDI resin systems. Relatively high proportions of residual, unreacted isocyanate groups immobilized in the network that has formed are consistently observed, their proportion markedly decreasing when the original proportion of UF resin is higher and lower than that of pMDI. Under these fast curing conditions the UF resin, even one of low molar ratio as used here, appears to self-condense through an unusually high proportion of methylene ether links rather than methylene bridges alone. A marked proportion of residual, unreacted hydroxymethyl groups is also noticeable in the UF self-condensation network.

Direct NMR tests on hardboard bonded under fast pressing conditions with different proportions of UF/pMDI systems could not confirm the presence or absence of urethanes as the relevant peaks are masked by the relevant wood carbohydrates signals of the board cellulose and hemicelluloses. They confirmed, however, that crosslinking due to the formations of polyureas and biurets by reaction of the isocyanate group with water are predominant in the crosslinking of pMDI when alone and in UF/pMDI resin systems. They confirmed too that residual, unreacted isocyanate groups are consistently present in noticeable amounts in the finished panel. The higher the proportion of pMDI in the system, the higher is their proportion.

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