

¹³C NMR Investigation of the Reaction in Water of UF Resins With Blocked Emulsifiable Isocyanates

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ABSTRACT: A solid state ¹³C NMR study of hardened networks obtained by the reaction of blocked and non-blocked isocyanates (pMDI) with urea-formaldehyde (UF) resins in water showed different results according to the temperature of the reaction. At high temperature, in water, both a nonblocked or an emulsifiable, blocked isocyanate, appear to crosslink with UF resins through the formation both of traditional methylene bridges connecting urea to urea and of urethane bridges. The latter have been confirmed by ¹³C NMR to form in water by reaction of the isocyanate $-N=C=O$ group with the hydroxymethyl groups of the UF resin. At ambient temperature, UF/pMDI

resins where the pMDI is a emulsifiable blocked isocyanate, do not appear to form urethanes to any great extent but rather to crosslink through the usual UF resin urea to urea methylene bridges. Even in this case, when urethane bridges appear to be absent, evidence of crosslinking in water through reaction of the isocyanate with the $-NH_2$ and $-NH$ -amide of the UF resin has not been observed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 589–596, 2006

Key words: blocked isocyanates; NMR; reactions; resins; structure; urea-formaldehyde; urethanes

INTRODUCTION

PF resins have been clearly shown to copolymerize readily in water with pMDI (polymeric 4,4'-diphenylmethane diisocyanate), and the type of linkages and compounds formed have been isolated, analyzed, and clearly determined by several techniques and by several research groups.^{1–7} While reaction of the isocyanate group with water to form polyurea networks always occurs to a greater or lesser extent, in water the dominant reaction of the system is the reaction of the PF resin methylol group ($-CH_2OH$) with the isocyanate group to form urethane bridges,^{1,2,6} other reputed reactions only having been tested in the absence of water. The final hardened resin network presents then both urethane bridges and methylene bridges pertaining to a normal PF resin network, as well as polyureas all covalently linked in the same network.^{1–7}

A similar type of resin system and reactions has been developed for the reaction between UF resins and pMDI.^{6,8,9} The strength of a joint bonded with UF/pMDI glue-mixes is improved by coreaction between isocyanate groups and UF resin methylol groups to form a certain number of urethane crosslinks. This does occur in the presence of water and under the predominantly acid hardening condi-

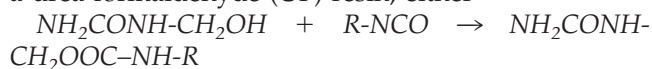
tions characteristic of aminoplastic resins (thus, in the presence of a hardener). The system was tried with very encouraging results for moisture resistant plywood,⁸ and it is now proposed as being of some interest and as giving encouraging results in the bonding of straw-based particleboard.^{10,11}

The use of emulsified blocked isocyanate in PF resins mixed as a single stable resin, according to the PF/pMDI technology described above, have been commercialized since the year 2000.^{4,12,13} The technology described in one of these references¹³ describes the use of a pMDI easily deblocked by just the temperature in the panel press, and thus not needing a deblocking agent. A pressing temperature of 204°C was used, which corresponds to a panel core temperature comprised between 100°C and 120°C, generally for industrially significant press times of a maximum of 102 to 115°C.¹⁴ Recently, an adhesive company has also developed the use of blocked isocyanates as latent crosslinking agents for UF resins¹⁵ according to the same coreaction approach described above. However, among the many interesting technological results reported, it was remarked that the reaction of the isocyanate group, once deblocked, appeared to occur mainly with the UF resin's $-NH_2$ and $-NH$ -amide groups of urea, in water. No structural NMR analysis proof, or other direct proof, was reported for this conclusion. The model compound reactions that were used were carried out in an organic solvent, dimethylformamide, and not in water, as is supposed to be in

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the industrial application of these systems. This latter difference could markedly slant the route the reaction could take, and doubts can be expressed to the compounds formed when the reactions take place in water. This article deals with the comparison of the reaction of commercial emulsifiable blocked isocyanate and nonblocked isocyanate with UF resins in water and with identifying the crosslinking bridges generated by the different UF/pMDI systems in water.

Thus, on top of the standard crosslinking of UF resin through urea to urea methylene bridges, this article deals with testing two hypotheses for the reaction in water of an emulsified blocked isocyanate with a urea-formaldehyde (UF) resin, either



or



EXPERIMENTAL

To a urea-formaldehyde (UF) resin of F/U molar ratio of 1.2, 60% solids content in water, were added two types of commercial polymeric isocyanates, one of which was a blocked emulsified isocyanate. Thus:

1. To 10g nonblocked polymeric 4,4'-diphenylmethane diisocyanate (pMDI) (Bayer Desmodur 44V20) were added 10 g water. The mixture was cured to hardening under continuous mechanical stirring at a temperature of 80°C.
2. 10 g of the same liquid UF resin was used as a control and hardened at 103°C overnight.
3. To 7.57 g liquid UF resin were added 1.075 g nonblocked polymeric diphenylmethane diisocyanate (pMDI) (Bayer Desmodur 44V20), for a total of 19% by weight of pMDI on total resin solids. The reaction mixture was left to react in an oven at 103°C overnight (14 h) to make sure the reaction had reached completion and to study the heat hardening of the resin, as heat hardening is used in its application as an adhesive for particleboard.
4. To 7.57 g liquid UF resin were added 1.075 g emulsifiable blocked polymeric diphenylmethane diisocyanate (pMDI) (Bayer Mondur 1441). The reaction mixture was left to react in an oven at 103°C overnight (14 h) to make sure the reaction had reached completion and to study the heat hardening of the resin, as heat hardening is used in its application as an adhesive for particleboard.
5. To 7.57 g liquid UF resin were added 1.075 g emulsifiable blocked polymeric diphenylmethane diisocyanate (pMDI) (Bayer Mondur 1441).

The reaction mixture was left to react at ambient temperature (23°C) up to hardening.

The solid state ^{13}C NMR spectra of the three hardened UF/pMDI resin systems used, of the UF resin control, and of the hardened water/pMDI product were obtained on a Bruker MSL 300 FT-NMR spectrometer at a frequency of 75.47 MHz and at sample spin of 4.0 kHz. The impulse duration at 90° was 4.2 μ s, contact time was 1 ms, number of transients was about 1000, and the decoupling field was 59.5 kHz. Chemical shifts were determined relative to tetramethyl silane (TMS) used as the control. The spectra obtained are shown in Figures 1–4. The calculation of the different shifts possible of the different structures possible was done by ChemWindows 6.5 Spectroscopy.¹⁶

RESULTS AND DISCUSSION

The reactions where blocked emulsifiable polymeric isocyanate was involved were carried out in the minimum range of temperature where the isocyanate used is capable of deblocking and reacting.^{12,14} The solid phase ^{13}C NMR spectrum of the hardened reaction products of a non blocked polymeric MDI (pMDI) with water shown in Figure 1 correspond to the shifts in Table I. Thus, the peak at 137.2 ppm belongs to the aromatic carbon (Fig. 1, Table I: C1) of pMDI attached to the secondary amide group of urea derived by the reaction of pMDI with water. The peak at 129.7 ppm belongs to the aromatic carbon (Fig. 1, Table I: C2, C6) of the amine in ortho to the methylene bridges internal to the pMDI structure (Table I) derived by the reaction of MDI with water. The 129.10 ppm peak (undetectable, as covered by the 129.7 ppm peak) and 118.78 ppm (Table I, polyureas: C2, C6) pertain, respectively, to the carbons in meta and ortho to the 137.2 carbon and in ortho and meta to the methylene bridges internal to the pMDI structure (Table I). The 118.78 peak has the same shift in the case of carbamic acid (Table I: C3,C5). The internal methylene bridge of the MDI structure is observed at 40.8 ppm. This signal is very wide (35–47 ppm range) and presents several smaller peaks and shoulders. The shifts expected by calculation for different MDI structures should be at 41.06 ppm for the MDI+water-derived amine, and 40.60 ppm for the reaction intermediate carbamic acid, generally unstable. Noticeable as a shoulder at 144.5 ppm is the C4 of the amine (Fig. 1, Table I). Of more interest are the peaks in the 151–165 ppm range: the peaks of the carbonyl groups of substituted polyureas at 152.8 ppm, of biuret at 153.2 ppm, and the carboxyl groups of carbamic acid at 155.55 (expected theoretical = 155.87 ppm) are all present, with the latter being the dominant peak. The series of peaks observed in Figure 1 indicates then that the main reaction products

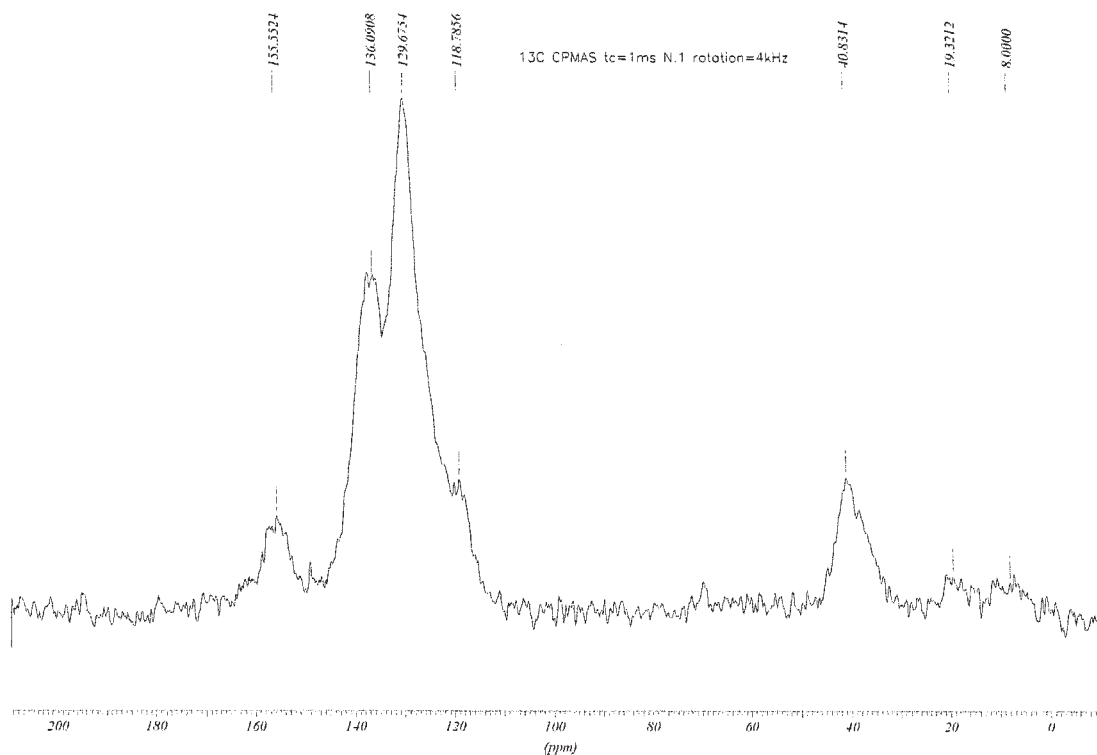


Figure 1 Solid state CP-MAS ^{13}C NMR spectrum of the hardened product obtained by the reaction of pMDI with water at 103°C .

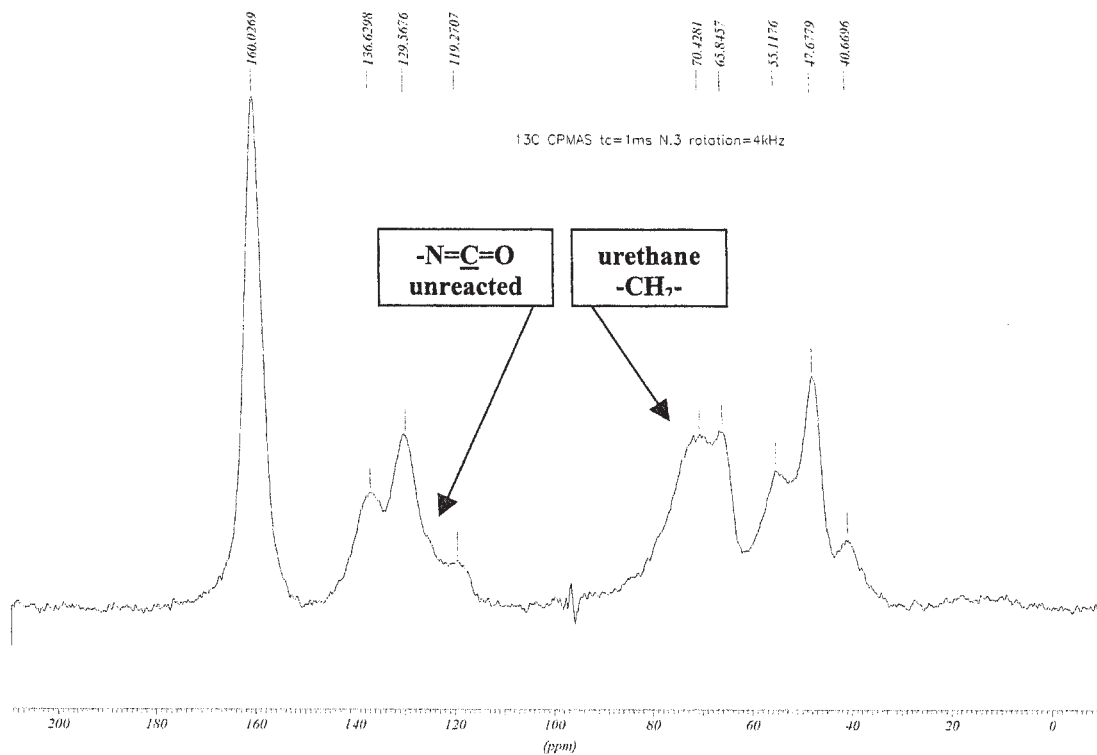


Figure 2 Solid state CP-MAS ^{13}C NMR spectrum of the hardened product obtained by the reaction at 103°C of nonblocked pMDI with UF resin in water. Note the urethane $-\text{CH}_2-$ bridge and the small amount of still unreacted $-\text{N}=\text{C}=\text{O}$ group.

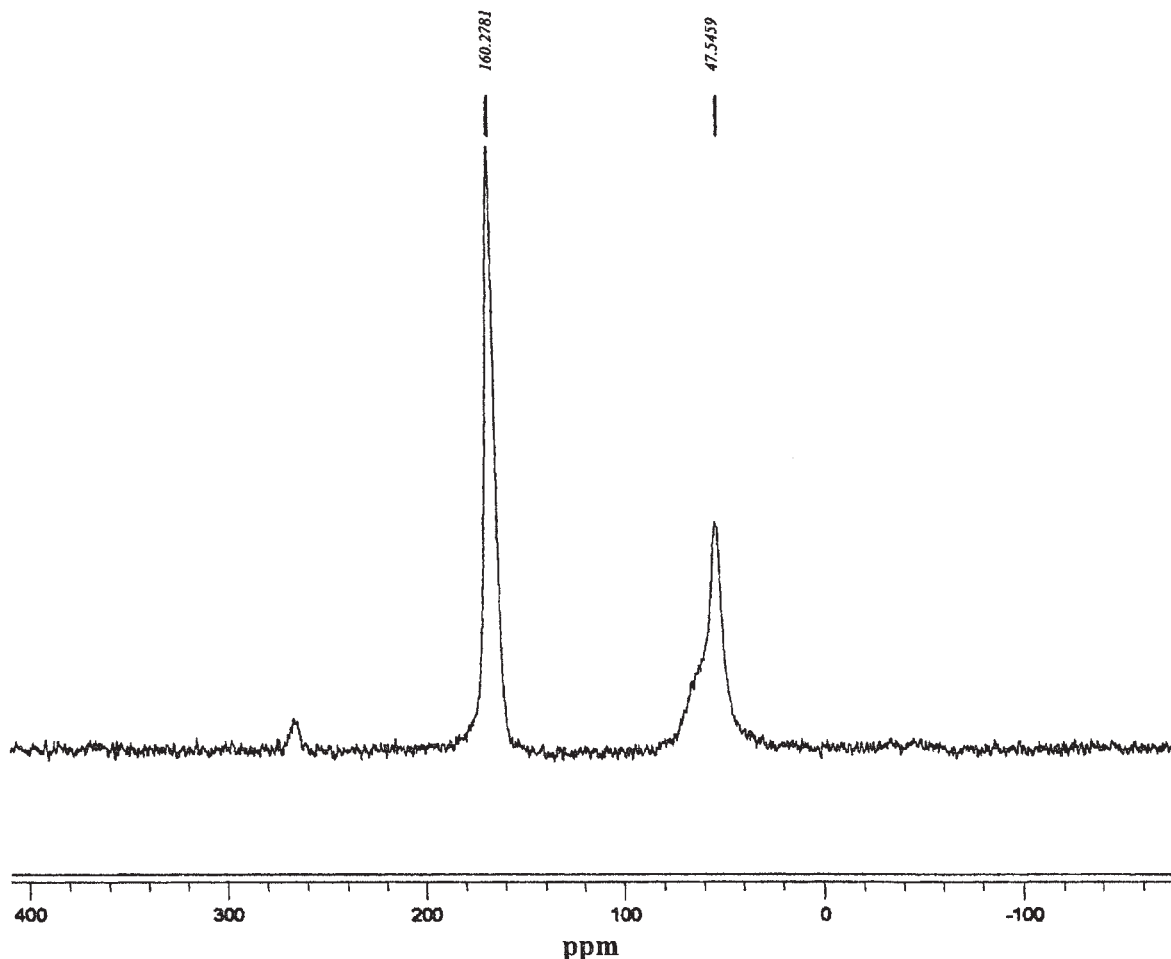


Figure 3 Control solid state CP-MAS ^{13}C NMR spectrum of the UF resin alone hardened at 103°C under the same conditions as those of the resin in Figure 2.

of pMDI with water that can be detected are polyureas, biuret, amine, and carbamic acid. While the first three are expected, the shifts at 155.55 ppm, 118.78 ppm, and 40.60–40.8 ppm clearly identifying the presence of the relatively unstable carbamic acid are relatively unexpected. The presence of carbamic acid can only be due to the high rate of formation of the hardened network leading to its early immobilization, and to groups still reactive as well as of reactive intermediates, such as carbamic acid being left unreacted but part of the network. The broad peaks of the spectra mask or are composed of the majority of the shifts that are not directly visible.

Figure 2 shows the solid phase ^{13}C NMR spectra of the reaction of the UF resin with nonblocked pMDI. Two main possible structures can 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 $-\text{NH}_2$ and $-\text{NH}-$ amide groups of the UF resin. The shifts of both are shown in Table II. The similarity of the shifts in Table II with what is observed in Figure 2

at first does not render it possible to distinguish which of the two structures is present. However, the main and only marked, detectable difference in the shifts of the two structures is the presence of the $-\text{CH}_2-$ bridge (Table II: $-\text{CH}_2-$ b) connecting the urethane with urea. Calculation¹⁶ forecasts that this should appear at 72.7 ppm for the urethane structure and be absent for the polyurea structure. In Figure 2(a) marked, strong peak in the range 69.5–74 ppm, with three points at 70.0 ppm, 70.4 ppm, and 72 ppm, can only belong to different positional isomerides of the $-\text{CH}_2-$ bridge of the polyurethane structure. This confirms what was found earlier,^{1,8,9} namely, that with nonblocked pMDI it is indeed the hydroxymethyl group of urea that reacts with the isocyanate group. The spectra in Figure 3 of the same UF resin when hardened alone confirms such an interpretation. The shifts observed in the spectra of this simple commercial UF resin are confirmed by the results observed by other authors.¹⁷ Thus, in Figure 3, in the absence of isocyanate, the only methylene groups present are those connecting two urea residues, which appear as a main band at 47.5 ppm, as in

TABLE II
Calculated¹³ Shifts Forecast for ¹³C NMR of Urethane and Polyurea Linkages for the Reaction of Blocked and Non-Blocked pMDI with UF Resin in Water

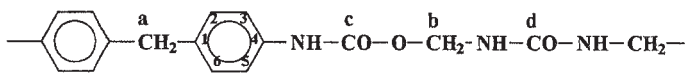
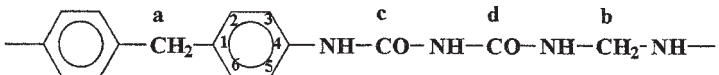
C=O		C1	C2	C3	C4	C5	C6	-CH ₂ -		
c	d							a	b	
urethane linkage										
										
	164.6	158.1	134.5	128.8	118.8	135.9	118.8	128.8	40.6	72.7
polyurea linkage										
										
	164.8	155.1	139.95	128.0	119.2	137.5	119.2	128.0	40.6	59.9

Figure 2. In Figure 3, the small shoulders at 55 and 65 ppm are those pertaining, respectively, to the methylene ether bridges ($-\text{CH}_2\text{-O-CH}_2-$) between ureas and to the still unreacted hydroxymethyl group ($-\text{CH}_2\text{OH}$) of the UF resin. To be noted in Figure 2 is the shoulder at 125.66 ppm, which is the shift of the carbon of the $-\text{N}=\text{C}=\text{O}$ isocyanate group. This is also visible in Figure 4, but not in Figure 3. This shoulder means that, notwithstanding the high proportion of water and of UF reactive groups, unreacted isocyanate groups survive in small proportion and remain in the hardened network. This is possibly due to early immobilization of the network during hardening and attests to the fast rate of hardening of the system UF/pMDI.

The interpretation of the other peaks in Figure 2 is as follows: 40.7 ppm, internal $-\text{CH}_2-$ bridge of pMDI; 47.68 ppm, $-\text{CH}_2-$ bridge connecting two ureas; 55.1 ppm, methylene ether bridges ($-\text{CH}_2\text{-O-CH}_2-$) between ureas; 65.8 ppm, hydroxymethyl group $-\text{CH}_2\text{OH}$ of UF resin. 119.27 ppm and 129.67 ppm are the shifts of aromatic carbons in the pMDI structure, respectively, of the sites ortho and meta to the carbon to which the isocyanate is linked. The 136.63 ppm shift corresponds to the aromatic carbon to which the isocyanate group is linked.

Figure 4 shows the solid phase ¹³C NMR spectra of the reaction of the UF resin with a commercial, emulsifiable, blocked pMDI when hardening is carried out at 103°C. The pattern of shifts observed is very similar to that of a nonblocked isocyanate in Figure 2. Also in Figure 4, one can notice the same marked, strong peak in the range 69.5–74 ppm, here with three points at 69.8 ppm, 70.4 ppm, and 72 ppm, that belongs to the different positional isomerides of the $-\text{CH}_2-$ bridge of the polyurethane structure formed. The intensity of this broad peak appears to be even greater in Figure 4 than in Figure 2. Thus, when reacted at higher temperature, in water, a blocked isocyanate also appears to react preferentially with the hydroxymethyl groups

of the UF resin, and not with its $-\text{NH}_2$ and $-\text{NH-}$ amide groups.

Furthermore, comparing Figure 4 with Figure 2, the relative decrease of the peak at 47 ppm coupled with the increase of both the peaks at 69.5–74 ppm and 65 ppm indicates in the blocked isocyanate case a relative decrease of resin crosslinking through methylene bridges connecting urea resins ($-\text{NH-CH}_2\text{-NH-}$). It also indicates a proportional increase in crosslinking through urethane bridges, accompanied by a higher relative proportion of still unreacted UF hydroxymethyl groups. The resin then appears slightly less crosslinked, with a different relative proportion of different crosslinks and more capable of viscoelastic dispersion of energy on testing. The shoulder at 125.66 ppm, which is the shift of the small proportion of carbons of the unreacted $-\text{N}=\text{C}=\text{O}$ isocyanate group, unreacted due to early immobilization of the network, is visible in Figure 4, too. A further difference is the relative decrease of the three main peaks at 136–138 ppm, 129.5–131 ppm, and 118–119 ppm indicating a relatively small decrease of unsubstituted aromatic carbon rings in the pMDI structure. This appears to confirm that the hydroxymethyl groups of the formaldehyde resin are to a modest extent also capable of reacting on the aromatic rings of pMDI, as shown previously for nonblocked isocyanates.^{1,9} The last difference is the marked decrease in Figure 4 of the proportion of methylene ether bridges ($-\text{CH}_2\text{-O-CH}_2-$) observed by comparing the signal at 54.8–55.1 ppm in Figure 4 with that observed for the nonblocked isocyanate case in Figure 2.

Figure 5 shows the solid phase ¹³C NMR spectra of the reaction of the UF resin with the same commercial, emulsifiable, blocked pMDI of Figure 4, but when hardening is carried out at ambient temperature (25°C). On top of the differences already remarked between blocked and nonblocked isocyanates described above, in Figure 5 the crosslinking pattern

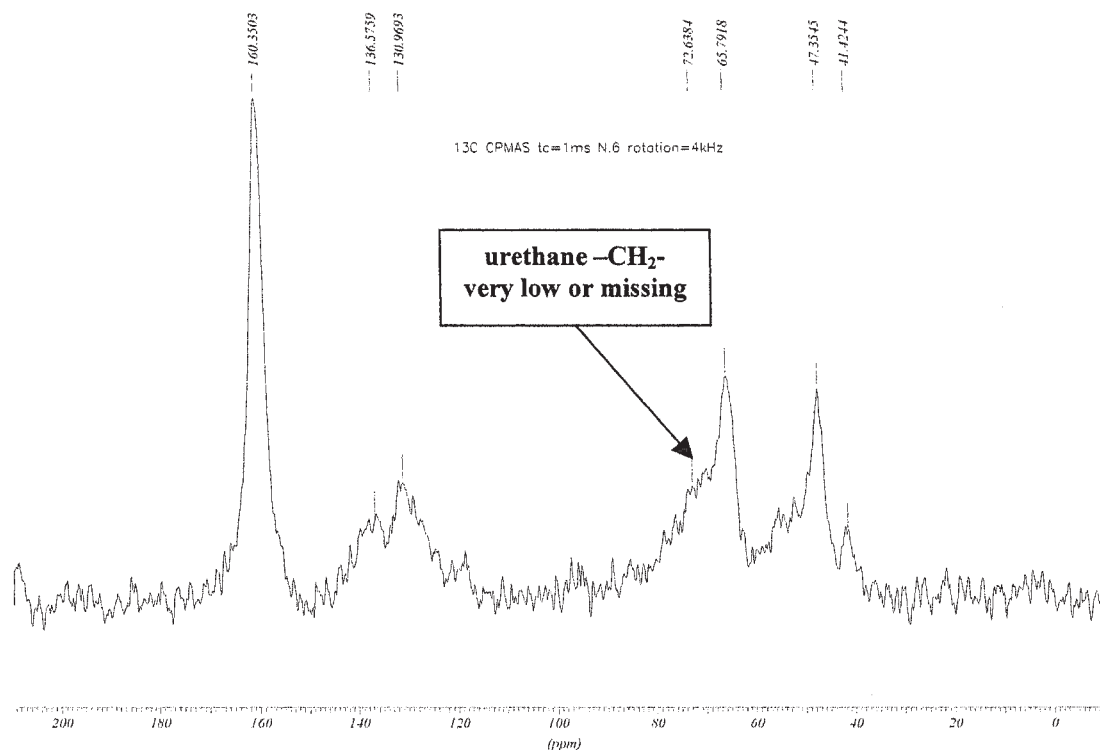


Figure 5 Solid state CP-MAS ^{13}C NMR spectrum of the hardened product obtained by the reaction at ambient temperature (23°C) of a commercial, emulsifiable, blocked pMDI with UF resin in water. Note the very low proportion/absence of the urethane $-\text{CH}_2-$ bridge.

differs even from the previous one. The main difference is that the peak of the $-\text{CH}_2-$ of the urethane bridge at 69.5–72 ppm is very low, practically missing. This means that the proportion of urethane linkages is very low or that they are even absent. Second, the UF hydroxymethyl group peak at 65 ppm is relatively stronger even than that in Figure 4, confirming lower reaction of the $-\text{CH}_2\text{OH}$ group with either the isocyanate or the amide groups of urea. The 47 ppm peak of the methylene bridges connecting urea resins ($-\text{NH}-\text{CH}_2-\text{NH}-$) does not seem to be affected, indicating that UF crosslinking through methylene bridges is not the reason for the decrease in crosslinking. From all this, the lower crosslinking level can only be ascribed to the marked decrease or even absence of formation of urethane bridges under ambient temperature reaction conditions. Notwithstanding the evident absence of crosslinking through urethanes, crosslinking through reaction of the isocyanate with the $-\text{NH}_2$ and $-\text{NH}-$ amide is not evident, confirming that the behavior observed by other groups in DMF cannot reproduce for these hybrid resins the reactions that occur in water.

CONCLUSIONS

At high temperature, both water-carried mixed UF/pMDI resins where the pMDI is nonblocked or an

emulsifiable, blocked pMDI isocyanate, appear to crosslink through the formation of both traditional methylene bridges connecting urea to urea and of urethane bridges. The latter have been confirmed, again, to have been obtained by reaction of the isocyanate $-\text{N}=\text{C}=\text{O}$ group with the hydroxymethyl groups of the UF resin. At ambient temperature, UF/pMDI resins where the pMDI is a emulsifiable blocked isocyanate, do not appear to form urethanes to any great extent but rather to crosslink mainly through the usual UF urea to urea methylene bridges. Even in this case, when urethanes appear to be absent, evidence of crosslinking through reaction of the isocyanate with the $-\text{NH}_2$ and $-\text{NH}-$ amide of the UF resin has not been obtained.

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