# Copolymerization in UF/pMDI Adhesives Networks

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**ABSTRACT:** Kinetic evidence in thermomechanical analysis experiments and carbon-13 nuclear magnetic resonance spectroscopy ($^{13}$C NMR) evidence indicates that the strength of a joint bonded with UF (urea–formaldehyde)/polymeric 4,4'-diphenylmethane diisocyanate (pMDI) glue mixes is improved by coreaction of the methylol groups of UF resins with pMDI to form a certain number of methylene cross-links. The formation of these methylene cross-links is predominant, rather than formation of urethane bridges which still appear to form but which are in great minority. This reaction occurs in presence of water and under the predominantly acid hardening conditions, which is characteristic of aminoplastic resins (thus, in presence of a hardener). Coreaction occurs to a much lesser extent under alkaline conditions (hence, without UF resins hardeners). The predominant reaction is then different in UF/pMDI adhesive systems than that observed in phenol-formaldehyde (PF)/pMDI adhesive systems. The same reaction observed for UF/pMDI system at higher temperatures has also been observed in PF/pMDI systems, but only at lower temperatures. The water introduced in the UF/pMDI mix by addition of the UF resin solution has been shown not to react with pMDI to an extent such as to contribute much, if at all, to the increase in strength of the hardened adhesive. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3681–3688, 2002

**Key words:** wood adhesives; thermomechanical analysis; mechanical properties; copolymerization; urea–formaldehyde; Isocyanates

## 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.[1–5] In diisocyanate and urethane chemistry it had long been held that in mixed PF/pMDI resins in water, the isocyanate group can react almost exclusively with water. Although reaction of the isocyanate group with water to form polyureas networks always occurs to a greater or lesser extent, and so does PF resin cross-linking by classical means, it has been proven that the dominant reaction of the system is the reaction of the PF resol methylol group (—CH$_2$OH) with the isocyanate group to form urethane bridges. Therefore, the final hardened resin network presents both urethane bridges, the methylene bridges pertaining to a normal PF resin network as well as polyureas all covalently linked in the same network.[1–5]

A similar type of resin system has been proposed for the reaction between UF (urea–formaldehyde) resins and pMDI to attain similar bonding results as those obtained with melamine–urea–formaldehyde resins but by a different chemical approach and route.[6,7] The system was tried with very encouraging results for moisture-resistant plywood,[6] and it is now proposed as being of some interest and as giving encouraging results in the bonding of straw-based particleboard.[8] Contrary to the PF/pMDI case, what is not clear in the UF/pMDI case, because it has only been deduced from the applied panel bonding results, is if UF resins do react with pMDI in the same manner as do PF resins and if they are capable of giving equally mixed, copolymerized hardened networks. The only direct experimental evidence other than improved panels strength that has been presented up to now is a dynamic mechanical analysis study that the authors[8] claim indicates that UF/pMDI copolymerization is not the preferred reaction and that it may be insignificant. The evidence they presented instead appears to indicate that some sort of copolymerization occurs that contributes, and not insignificantly, to hardened network formation. The analysis was incomplete, by the words of the same authors of the study, because reactions of pMDI alone with water were not followed and, thus, it could not be ascertained if the positive results obtained resulted from the increased availability of water coming from the UF resin rather than from copolymerization.

The study in this paper presents additional thermomechanical analysis (TMA) evidence, according to now established TMA techniques, and carbon-13 nuclear magnetic resonance spectroscopy ($^{13}$C NMR) evidence to indicate that copolymerization does indeed

occur, and to indicate the extent of its contribution to the final strength of the network.

## EXPERIMENTAL

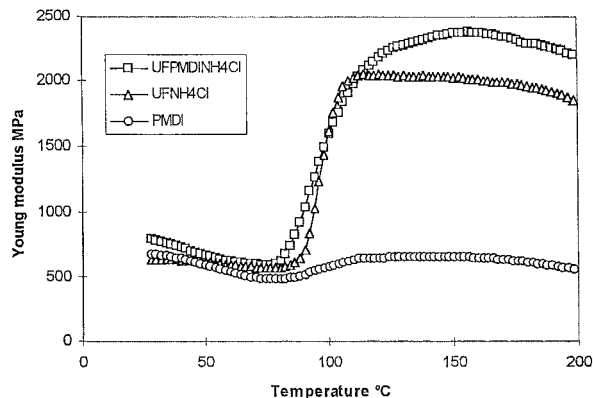### Thermomechanical analysis (TMA)

Glue mixes composed of a commercial UF resin of molar ratio F/U 1.2 added on resin solids of 2% $NH_4Cl$ as a 20% water solution and with 30% pMDI (type 44V20 ex Bayer) added or not added on total resin solids (UF+pMDI) were tested dynamically by TMA. pMDI alone, pMDI alone in water to reproduce the same amount of water as added with the UF, and pMDI on to wood on which had been previously added the same amount of water to increase the percentage moisture content of the substrate have also been tested to ascertain what is the contribution of the water of the UF resin water solution to the curing and reactions of the pMDI. Samples of UF resin and UF/pMDI mixes in the same proportions but without any addition of $NH_4Cl$ hardener were also tested. Triplicate samples of beech wood alone, and of two beech wood layers bonded with the resins+salts as a layer of 350 $\mu$m , for a total samples dimension of 21 $\times$ 6 $\times$ 1.1 mm, were tested with a Mettler 40 TMA apparatus in three points bending on a span of 18 mm and exercising a force of 0.1/0.5 N on the specimens with each force cycle of 12 s (6 s/6 s). The classical mechanics relation between force and deflection, $Y = [L^3/(4bh^3)][\Delta F/(\Delta f_{wood} - \Delta f_{adhesive})]$ would allow the calculation of the Young's modulus $Y$ for each of the cases tested, although this is not the objective of the exercise. Because the deflections $\Delta f$ obtained were proven to be constant and reproducible,[9, 10] and they are proportional to the flexibility of the assembly, the relative flexibility as expressed by the Young's modulus of the different adhesive systems can generally be calculated through the relationship $E_1/E_2 = \Delta f_2/\Delta f_1$. This relationship has been used recently to derive a phenomenological equation describing the average number of degrees of freedom of the polymer segments between cross-linking nodes in a hardened polycondensate network on a wood substrate.[9, 10] The phenomenological equation was then simplified, by the use of experimental data on all the currently used wood adhesives, to a regression equation of easier applied use. The experiments with this approach can be carried out both isothermally and non-isothermally, with the latter yielding considerably more information on the network at any moment of his formation and hardening, as well as the possibility of calculating in a easier manner the kinetics of network formation and tightening, and reproducing closely the kinetics of hardening and the increase of temperature in the curing of a wood panel.

### Solid-state cross-polarization magic-angle sample spinning (CP-MAS) $^{13}$C NMR

Spectra were obtained on a Bruker MSL 300 FT-NMR spectrometer. The solid-state CP-MAS $^{13}$C NMR spectrum of UF/pMDI of resin solids weight proportions 70/30 and of UF/pMDI/$NH_4CL$ of solids weight proportions 70/30/1.4, hardened and dried at a temperature of 70 °C, were obtained at a frequency of 75.45 MHz and at sample spin of 3.5 kHz. Chemical shifts were calculated relative to TMS for NMR control. Acquisition time was 0.026 s, with number of transients of ~1000. The spectra were accurate to 1 ppm. Typical spin-lattice relaxation times for the types of compounds analyzed, as well as peak shifts interpretation for UF, MDI, and PF resins, were taken from the literature.[11–27]
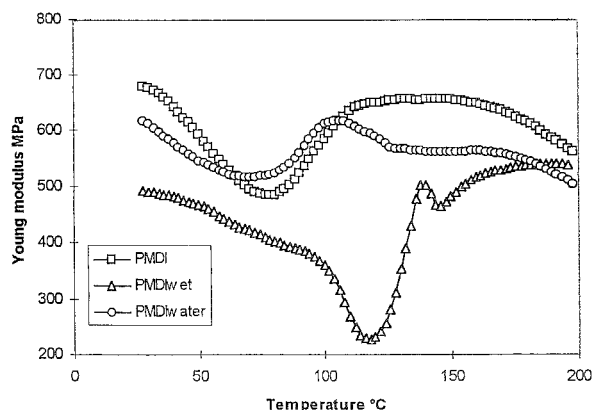
## DISCUSSION

The main difference between an aminoplastic resin/pMDI wood adhesive system and a PF/pMDI system is that the latter hardens under alkaline rather than the preferred acid conditions of the former. Thus, notwithstanding that good bonding results are also obtained with the former,[4, 7] important differences on the causes, type, and extent of the reactions involved might well occur. In this regard, although the PF/pMDI system reactions are rather well defined at molecular level,[4] this is not the case for the pMDI/aminoplastic (UF or MUF) system. In Figure 1 are shown the TMA average results of the increase in modulus as a function of the temperature at a constant heating rate of 10 °C/min for beech wood joints bonded with pMDI alone, with UF alone + 2% ammonium chloride hardener, and of 30% pMDI+70% UF (with 2% ammonium chloride hardener on UF resin solids), where the beech wood used was at an equilibrium moisture content (EMC) of 12%. It is noticeable that whereas the UF curve reaches a maximum value of the modulus of 2000 MPa, the pMDI/UF 30/70 mix reaches a maximum value of the modulus of 2400 MPa, which is an increase of 20%. In contrast, the pMDI/water alone reaction, because of the 12% EMC of the substrate, gives an increase of modulus of only 180 MPa up to 660 MPa. This low increase in strength in the pMDI alone case is due to the well-known behavior on heating, on plywood, of the standard commercial, non-emusified raw pMDI (of which the one used here is one of the most common in industrial use) with relative rapid disappearance of the material within the wood,[7,28] and it is not anomalous for the commercial material used in this work. What is anomalous however, if MDI and UF do not react together, is the 20% (400 MPa) increase in strength of the bond of the UF/pMDI system over the UF alone system (Figure 1). This is so because if no reaction occurred between the
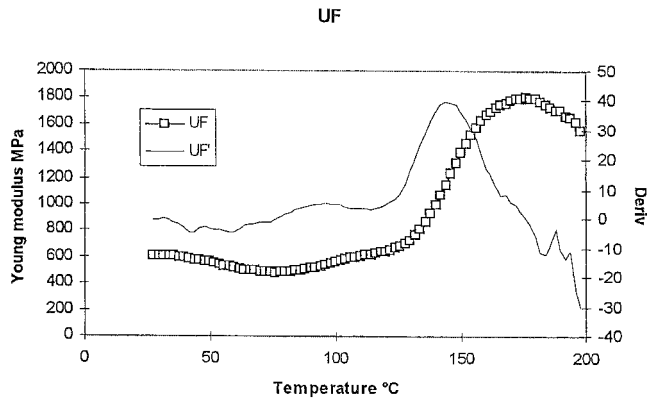
**Figure 1** Average curve of the variation in thermomechanical analysis (TMA) testing of the Young's modulus of a beech wood joint as a function of adhesive hardening due to increasing temperature and curing time when bonded with (○) pMDI alone; (△) UF+2% ammonium chloride and (□) 70% UF solids + 30% pMDI + 1.4% ammonium chloride (2% on UF resin solids).



**Figure 3** Average curve and its first derivative of the variation in thermomechanical analysis (TMA) testing of the Young's modulus of a beech wood joint as a function of adhesive hardening due to increasing temperature and curing time when bonded with (□) 100% UF solids without any UF resin hardener.

two resins, the pMDI type used would rapidly disappear into the wood and would then only be able to contribute at the most 180 MPa × 0.30 = 54 MPa (as in the UF/MDI mix the total proportion of MDI on wood is only 30% of the MDI alone case) to the maximum modulus of the UF/pMDI mix. Instead, this pMDI contributes to a much greater increase in strength, which is an indication that coreaction does occur, at least to a certain extent, under mildly acidic curing conditions between UF and pMDI in water solution.

In Figure 2 are shown the increases in modulus for the beech wood joints bonded with MDI, MDI+water (in the same proportion as for the UF case), and MDI on a substrate in which the water was added on the substrate first and equilibrated at a much higher moisture content. It can be noted that the difference be-
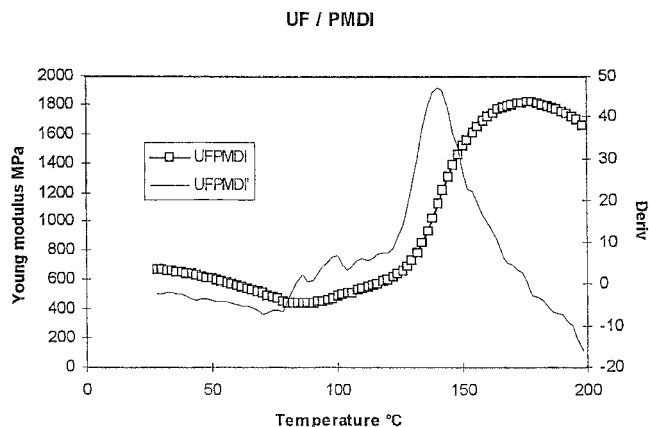


**Figure 2** Average curve of the variation in thermomechanical analysis (TMA) testing of the Young's modulus of a beech wood joint as a function of adhesive hardening due to increasing temperature and curing time when bonded with (□) pMDI alone, (△) pMDI on pre-wetted and conditioned wood substrate, and (○) pMDI pre-mixed with water.
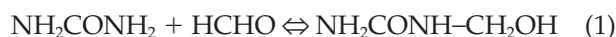
tween MDI and MDI+water is rather small and not very significant, the main difference being a lower maximum value of the modulus in the case of MDI+water, but this value was reached earlier than the MDI alone. This result indicates that (i) the quantity of water introduced with the resin (hence similar to the addition of UF case) does not seem to improve the strength of the bond but only the rate at which it is reached; (ii) the 12% EMC of the substrate alone is more than sufficient to start MDI cross-linking; (iii) at higher moisture content, faster also means early immobilization of the forming tridimensional network and hence a slightly lower strength,[29] and (iv) consistently higher amounts of MDI on UF resins (than on PFs) have to be added to have a clear positive result, a fact that has already been clearly shown from the relative proportions of UF and MDI that had to be used in plywood manufacture.[6] The curve of MDI alone on a substrate at much higher EMC gives instead a better strength improvement (namely, an increase of 300 MPa), but the final strength in reality is not much different than for the other two cases and it is reached later, indicating that heat and mass transfer, physicochemical transport, and diffusion phenomena induced by a higher EMC substrate have a greater influence on the system than the water itself. The conclusion is then that the water introduced in the mix by addition of the UF resin water solution does not react with MDI to an extent such as to contribute much, if at all, to the increase in strength of the hardened system.

The TMA results of joints bonded with UF alone and UF+pMDI in the same proportions as in Figure 1, but where no UF hardener was added (hence under mildly alkaline conditions) are shown in Figures 3 and 4, respectively. Here the situation appears to be different than what was observed under slightly acid
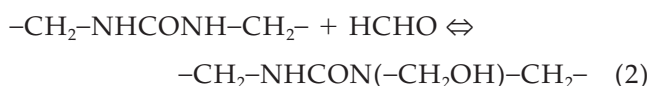
**Figure 4** Average curve and its first derivative of the variation in thermomechanical analysis (TMA) testing of the Young's modulus of a beech wood joint as a function of adhesive hardening due to increasing temperature and curing time when bonded with (□) 70% UF solids + 30% pMDI without any UF resin hardener.
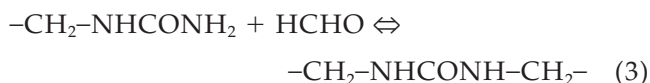
conditions (industrial plywood UF/MDI bonding was carried out under slightly acid conditions,[6] although it is not known what conditions were used for the straw boards[8] where the use of a UF hardener is not mentioned). Here it appears that the two resins harden separately and do not substantially coreact, if at all. The two curves are very similar to the superposition of the increase in modulus of UF alone and of MDI alone. This result can be seen with ease from the UF/MDI first-derivative curve where the small but clear peak at ~100 °C is characteristic of the reaction and networking of MDI under the influence of water, whereas the very pronounced later peak is exclusively due to UF networking (higher temperature and lower modulus maximum value because no hardener is included). This situation is of interest because the PF/MDI system, where coreaction occurs to a great extent, is under alkaline conditions. The reason for this blatant difference and interesting behavior could be ascribed to the relative instability of UF resins methylol groups, and any type of methylene bridge derived from them, that at alkaline pH are in equilibrium with the reagents (formaldehyde and urea or UF oligomers).

$$NH_2CONH_2 + HCHO \Leftrightarrow NH_2CONH–CH_2OH \quad (1)$$

And equally

$$-CH_2–NHCONH–CH_2– + HCHO \Leftrightarrow$$
$$-CH_2–NHCON(–CH_2OH)–CH_2– \quad (2)$$

and

$$-CH_2–NHCONH_2 + HCHO \Leftrightarrow$$
$$-CH_2–NHCONH–CH_2– \quad (3)$$

It is estimated that even with the subsequent condensation reaction, the best conversion in urea and urea oligomers methylolation is of not more than 50%.[13] Thus, even if substantial reaction of the UF methylol group with MDI occurred, a noticeable part of the methylol groups and of the methylene bridges of the urethanes so formed would detach from the UF resin in a reverse of equilibrium, and part of the two systems are likely to harden in part as a separate resin blend.

$$NH_2CONH–CH_2OH + R–NCO \rightarrow$$
$$NH_2CONH–CH_2OOC—NH–R \Leftrightarrow$$
$$NH_2CONH_2 + HCHO + CO_2 + H_2NR \quad (4)$$

Evidence that the aforementioned might be the case is seen by the much longer time and much higher temperature needed to harden a UF resin without hardener in an alkaline environment (Figures 3 and 4). This is not the case for PF resins where methylene and methylol groups are stable and do not decompose down to the original reagents.

However, solid-state CP-MAS $^{13}$C NMR spectra of the UF/pMDI system indicate that the system hardened both with 2% ammonium chloride UF hardener under mildly acid conditions (Figure 5) and without hardener under alkaline conditions (Figure 6). By comparison, the spectra of ammonium chloride-hardened UF resin (Figure 7) and water-hardened pMDI alone (Figure 8) appear to only partly confirm what was already deduced, but appear to be in agreement with a partly different explanation for what was observed. Condensation and copolymerization do indeed appear to occur, but by a different reaction; that is, a reaction that has been reported previously for PF/pMDI but which in that system only predominated at low reaction temperatures.[4]
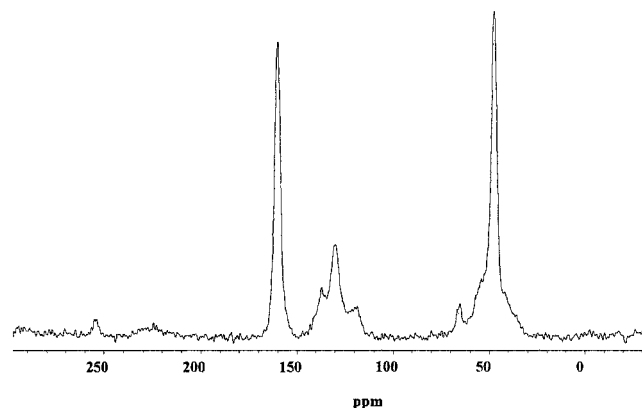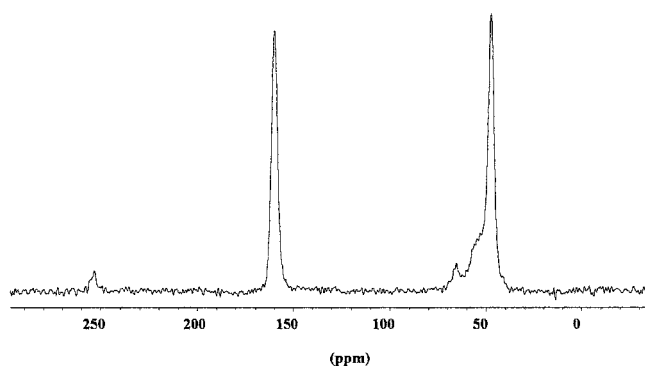


**Figure 5** Solid-state CP-MAS $^{13}$C NMR of a UF/pMDI/NH$_4$Cl resin system of weight proportions 70/30/1.4, hardened under mild acid conditions.
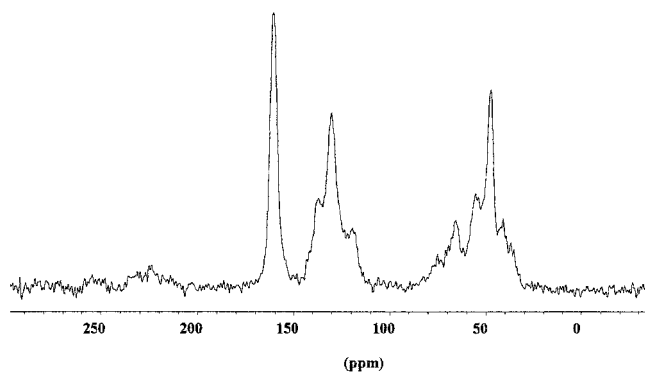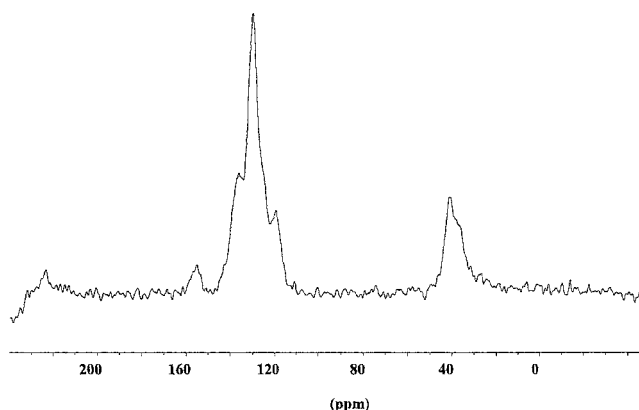
**Figure 6** Solid-state CP-MAS $^{13}$C NMR of a UF/pMDI resin system of weight proportions 70/30, hardened under mild alkaline conditions.

Thus, the CP-MAS $^{13}$C NMR bands visible in Figures 5–8 are assigned to a series of carbon groups, as shown in Table I. Thus, at 40 and 46 ppm are shown two different types of methylene bridges, the 40 ppm one belonging to the methylene bridge connecting the two aromatic rings within the pMDI, whereas the 46–47 ppm one is the methylene bridge linking two urea molecules. The methylene bridge linking urea to aromatic rings (hence, Φ-$\underline{C}$H$_2$-NHCONH-) is also found at the same shift value.[13,22] Thus, this signal alone cannot by itself confirm the coreaction of the UF resin with the pMDI, and additional confirmation is needed. The signal at 54–55 ppm can belong either to a methylene bridge connected to a branched urea amido group,[12,16–18,21] such as -N(-CH$_2$-)$\underline{C}$H$_2$NH-, or to a Φ-N(–$\underline{C}$H$_2$-NH-)-COO-CH$_2$–NH- of a branched N belonging to a urethane bridge.[31] This peak is very weak, just a shoulder in UF resins (compare Figure 7 with Figure 6), indicating that the signal observed in Figure 6 is indeed contributed by the urethane. This peak is very much pronounced under alkaline conditions (Figure 6) but almost absent under acid-setting conditions (just reduced to a shoulder). This result is an important additional clue to the question of which



**Figure 7** Solid-state CP-MAS $^{13}$C NMR of a UF/NH$_4$Cl resin system of weight proportions 100/2, hardened under mild acid conditions.



**Figure 8** Solid-state CP-MAS $^{13}$C NMR of a hardened pMDI resin system.

of the two possible groups the peak belongs. Because methylene bridges between ureas are not formed or formed to a much lesser extent under alkaline conditions, whereas they are formed to a much greater extent under acid conditions,[13,28] the predominance of this peak under alkaline conditions and its almost disappearance under acid conditions indicates clearly that it cannot belong to -N(-CH$_2$-)$\underline{C}$H$_2$NH- (the inverse would otherwise be true) and that it belongs then to Φ-N(–$\underline{C}$H$_2$-NH-)-COO-CH$_2$–NH- . The band at 64 ppm can equally well belong to a urea-linked methylol group, -NH-$\underline{C}$H$_2$OH,[12–14,17,18] or to the methylene group of a urethane, Φ-NH-COO-$\underline{C}$H$_2$–NH-.[31] However, in this work, it would not be possible to definitely determine to which of the two groups it belongs because the signal is more noticeable under alkaline conditions and the conditions used maximize the formation of both groups. However, under alkaline UF/pMDI reaction conditions, this signal is much more pronounced (Figure 6) than with UF alone (Figure 7) and is absent with pMDI alone (Figure 8). These results indicate that either the main contribution to this signal in Figure 6 corresponds to the urethane rather than the methylol group or that, under alkaline conditions, a higher relative proportion of methylol groups are formed. Both situations can present themselves because a greater proportion of the -CH$_2$OH methylol groups of UF would form in line with the expected lack of or marked slow-down of the subsequent UF condensation reaction to methylene bridges (-CH$_2$-).[13, 28] The 73–75 ppm signal belongs to a series of branched species –NH(-X-)-$\underline{C}$H$_2$–(Y-), where X = -CH$_2$– or >C═O, and Y = -OH or –NH-.[12,16,17,21] The following series of three bands in both figures belongs, respectively, to the aromatic unsubstituted carbons of the aromatic nuclei of pMDI (119–120 ppm),[31] to the carbon of the –N═$\underline{C}$═O isocyanate group (128 ppm),[31] and to the –NCO-carrying or urethane-carrying aromatic carbons of the aromatic nuclei of pMDI (136 ppm).[31] The remaining dominant

**TABLE I**
$^{13}$**C NMR Shifts of Hardened UF/pMDI Adhesive Resin Systems**

| Group | Shift (ppm) | Reference |
|---|---|---|
| $\phi$—CH$_2$–$\phi$ (pMDI) | 40 | 31 |
| –NHCONH—CH$_2$–NHCONH– | 46 | |
| $\phi$—CH$_2$—NHCONH– | 46 | 13, 22, 27 |
| > (*ortho*)N–$\phi$—CH$_2$–N–CO–NH– | | |
| (CH$_2$—) | 46 | 13, 22, 27 |
| Branched urethane $\phi$–N(–CH$_2$–NH–)–COO–CH$_2$–NH– | 54 | 31 |
| —N(–CH$_2$–)CH$_2$NH– | 54 | 12, 13, 16–18, 21 |
| —NH–CH$_2$OH | 64 | 12–14, 17, 18 |
| Urethane $\phi$–NH–COO–CH$_2$–NH– | 64 | 31 |
| —NH(–X–)–CH$_2$–(Y–) where X = –CH$_2$– or > C = O, | | |
| and Y = –OH or –NH– | 73–75 | 12, 13, 16, 17, 21 |
| (Ar)*C*–H | 119–120 | 4, 19, 20, 22–27, 31 |
| —N—*C*—O | 128 | 31 |
| (Ar)*C*—N=C=O | 136 | 31 |
| –CH$_2$–NHCON(–CH$_2$–)$_2$–R–NHCON(–R$_1$–)R$_2$ | | |
| $\phi$–N(–CH$_2$–NH–)–COO–CH$_2$–NH– | 161–162 | 12–14, 16–27, 31–33 |

peak at 161–162 ppm belongs to the carbonyl group of multisubstituted ureas, which could both be generated from (i) the hardened UF network [hence, -CH$_2$-NH*C*ON(-CH$_2$-)$_2$] as well as from (ii) the polyureas generated by the MDI reaction with the –CH$_2$OH, –NH$_2$, and -NH- groups of UF, both observed at 159–162 ppm,[12,13,17,22–27] or could belong to (iii) the >C=O group of the urethane bridges formed by the reaction between –N=C=O and -CH$_2$OH groups, which under some conditions is also observed at 159–160 ppm.[31–33] The shift of this peak renders possible then all three the explanations. The only way to see which among these possibilities is correct is to observe the change in relative intensities of the various bands when changing from acid to alkaline pH. It appears first of all that under mildly alkaline conditions a much greater proportion of the isocyanate group is not reacted, which appears to confirm the lack in strength increase when comparing UF alone and UF/pMDI in Figures 3 and 4. Also under alkaline conditions, a greater proportion of the -CH$_2$OH methylol groups of UF appear to form in line with the expected lack, or marked slow-down of the subsequent UF condensation reaction to methylene bridges (-CH$_2$-).[13,28] This also leads to a marked increase of the relative proportion of the urethanes formed by reaction of the -NCO groups of the pMDI with the abundant methylol groups of the UF resin. Under acid conditions, because the condensation of the UF methylol groups to yield in-between-ureas methylene bridges is rapid, the proportion relative to other species of both UF methylol groups and urethane bridges is drastically reduced. The reaction product that predominates is also a copolymer but of a different type; namely, that formed by the reaction of the UF methylol groups to yield methylene bridges linking the UF resin to the aromatic rings of the isocyanate. The isocyanate group

itself reacts also to form urethanes, but these are in the minority, and the reaction with the water in the system to form polyureas and biuret becomes relatively more important. The series of reactions occurring under mildly acid reaction conditions (Figure 5) is shown in Scheme 1. The reaction in Scheme 1 is the predominant reaction, whereas urethanes are still formed but in the minority and some noticeable amounts of the isocyanate groups form polyureas. It is then mainly the reaction in Scheme 1 that appears to contribute to the increase in strength observed for the UF/pMDI system in Figure 1.

In contrast, under alkaline conditions, a great amount of isocyanate groups and of UF methylol groups is not able to react (due to the immobilization of the network), some urethane is formed, and the same product that predominates under acid conditions is formed but to a lesser extent. It is the formation of the methylene bridges cross-linked network by this product (Figure 4) that counterbalances to an almost equal extent the loss of the methylene bridges cross-linked pure UF network (Figure 3). What is obtained is just a substitution of a network with a similar
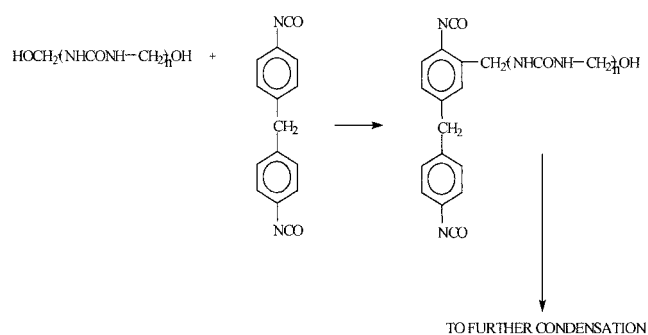


**Scheme 1**

one of comparable cross-linking density and hence no gain in strength.

All these results indicate that although urethanes form, they are not as important a product in the case of the UF/pMDI reaction as they are in the PF/pMDI reaction.[4]

As regards the work reported by previous authors on dynamic mechanical analysis (DMA) and straw particleboard, as good as this work was on several aspects, several features that were used and that are likely to have negatively influenced the result should also be noted:[8] (i) the use of emulsifiable MDI is known to adversely affect the result because the emulsifier remains in the hardened glue-line and tends to adversely and markedly affect water resistance;[4, 7] (ii) the use that was made of an extended high-temperature press schedule that is well known to induce degradation in most aminoplastic resins hardened networks[28–30] without evaluation of internal bond (IB) strength after boil testing; and (iii) the separate application on the wood particles of MDI and of the formaldehyde-based resin is well known to minimize the possibilities of coreaction between MDI and formaldehyde-based resins in wood panels and to decrease the maximum value of the strength of the joint. No information on the type of UF used (high or low molar ratio, which influences the capacity of coreaction with MDI) or of the use of UF hardeners was reported, so it is not possible to say under which reaction conditions, acid or alkaline, the results were obtained. Notwithstanding this, the authors obtained encouraging results.[8] However, what is even more evident from their DMA figures depicting the tan δ results is the clear presence of peaks and shoulders that do not correspond to those of UF resins or to those of pMDI, which indicates that some extent of coreaction between the two occurred also in their study.[8] The authors could not conclude if it was coreaction or reaction of MDI with the water added to the system by the UF resin because an experiment like that reported in Figure 2 was not done. The results in Figure 2, by denying this possibility, confirm also their results that coreaction of UF with pMDI indeed occurs to a greater or smaller extent, even under the conditions they used for their experiments,[8] but leads to a network formed by a main product different than what was previously thought.[4, 7]

## CONCLUSIONS

Kinetic evidence from TMA experiments and $^{13}$C NMR measurements indicated that the strength of a joint bonded with UF/pMDI glue-mixes is improved by coreaction between pMDI and UF resins methylol groups to form a certain number of methylene cross-links. These methylene cross-links predominate compared with formation of urethane bridges, which still appear to form but are in great minority. The formation of methylene cross-links occurs in the presence of water and under the predominantly acid hardening conditions characteristic of aminoplastic resins (thus, in presence of a hardener). Coreaction occurs to a much lesser extent under alkaline conditions (i.e., without UF resins hardeners). The predominant reaction is then different in UF/pMDI adhesive systems than that observed in PF/pMDI adhesive systems. The same reaction observed for the UF/pMDI system at higher temperatures has also been observed in PF/pMDI systems, but only at lower temperatures. The water introduced in the UF/pMDI mix by addition of the UF resin solution has been shown not to react with pMDI to an extent such as to contribute much, if at all, to the increase in strength of the hardened adhesive.

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