Cross-Linked Coatings by Co-Reaction of Isocyanate–Methoxymethyl Melamine Systems

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SYNOPSIS

Two-components methoxymethyl melamine/isocyanate and three-components methoxymethyl melamine/isocyanate/polyol coating systems were studied. Methoxymethyl melamine was shown to react with isocyanate groups through the carbocation formed by splitting within the methoxymethyl group. In three-components systems, methoxymethyl melamine/polyol and methoxymethyl melamine/isocyanate reactions appear to occur, but not isocyanate/polyol reactions. This was ascribed to the release from the methoxymethyl melamine/polyol reaction of methanol which reacts more rapidly than the polyol with the isocyanate group. A blocked isocyanate was then used whereby the methoxymethyl melamine reacts at an earlier stage and urethane formation is delayed. Introducing the blocked isocyanate, however, required significant increases in cure temperature for the isocyanate/polyol reaction, narrowing the cure temperature window of the system. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

High-solids coatings currently used in the automotive industry as top coats are typically thermoset systems which derive most of their physical properties from the formation of highly cross-linked networks.[1] The two systems generally used are based on the reaction of isocyanates with polyols to form urethanes and on methoxymethyl melamine/polyol systems.[1] In the latter, methyl ethers of methylol melamine are generally reacted with acrylic resins to obtain hard, glossy, weather-resistant cross-linked films.[1] Attainment of cross-linking is realized by the formation of methylene ether bonds between melamine and the polyol with elimination of methanol. The mechanisms involved have been studied and reported extensively,[2,3,4] and so have the kinetics of such cross-linking reactions.[5-12]

Isocyanate/polyol systems forming cross-linked urethane coatings are also extensively used and have been extensively studied.[13-16] Recently, the reaction of hydroxymethyl urea and hydroxymethyl melamine with monomeric and polymeric MDI (4,4'-diphenylmethane diisocyanate) have been described[17] for the formation of cross-linked networks used as wood adhesives. As the formation of the final urethane bridges goes through reaction steps very similar to those observed for the methoxymethyl melamine/polyol system[2,3,6,18,19] and for the isocyanate/polyol system, it was of interest to study the formation of cross-linked networks by a two-components methoxymethyl melamine/isocyanate system and three-components methoxymethyl melamine/isocyanate/polyol system. The aim of this paper is to report on this study and to ascertain if combination of the two most often used automotive coating systems can be integrated into one with its own particular characteristics.

EXPERIMENTAL

Preparation of Methoxymethyl Melamines

- Hexamethylol melamine (HMMM): To 0.3 moles of melamine were added 2.4 moles of formaldehyde 37% solution, the pH was ad-

justed to 9.0 with 40% NaOH, and the mixture heated to 50°C for 65 min under mechanical stirring. The product, which proved to be hexamethylol melamine, was cooled to form a thick precipitate which was then filtered and dried. To 27.9 g of the hexamethylol melamine so produced was added 100 g of methanol. The pH was adjusted to 1.0 with HCl and left to react overnight at 25°C. The product, hexamethoxymethyl melamine, was then neutralized and concentrated under vacuum at room temperature.

- Trimethylol melamine (TMMM): To 251.9 g of 37% formaldehyde solution was added 2.0 ml of 0.5 N NaOH and the temperature was maintained at 60°C. 126.1 g of melamine were then added and the pH adjusted to 8.7 with 40% NaOH. Heating at 60°C was maintained for 20 min, after which a buffer of glycine, sodium chloride in 0.5 N NaOH was added. Heating was continued for another 10 min. The clear solution obtained was cooled promptly, filtered, and dried at 50°C for 48 h. A product of melting point 155–160°C, which proved to be trimethylol melamine, was obtained. To 0.1 mole of trimethylol melamine were added 80 g of methanol and the mixture heated to 60°C. 4.0 ml of HCl were added and the mixture reacted for 2 h, during which time all of the trimethylol melamine dissolved. The pH of the trimethoxymethyl melamine so produced was adjusted to 6.8. The product was then dried under vacuum, yielding a clear resin of low solubility in nonpolar solvents.

- Partially methylated hexamethylol melamine (PHMM): 0.04 moles of hexamethylol melamine and 0.13 moles methanol were mixed and sufficient n-hexane added to dissolve all the HMMM 2 ml HCl were added to the mixture and this maintained at 35°C for 1 h. Hexane was then evaporated at 35°C under vacuum.

- Pentamethoxymethyl melamine: The procedure followed was identical to that for trimethoxy methyl melamine already outlined above, to react 55.2 g pentamethoxymethyl melamine with 210 g methanol at pH of 3.25 for 1 h.

- Maprenal[18] MP 900: This is 93% monomeric hexamethoxymethyl melamine with a few methylene ether bridges leading to an average molecular weight of 598, and only a few traces of some free methylol groups. There are only traces of methylene bridges, typical of most commercial melamine resins. It is not a solution but a liquid 100% composed of the product.

- Maprenal[18] MP 915: This is a partially methylolated etherified melamine-formaldehyde co-reaction product. The spectrum shows a high content of secondary nitrogens belonging to methylene ether bridges as well as methylene bridges. The higher methylol and amino group contents are responsible for a larger molecular weight (= 1265), as these groups are susceptible of self-condensation under the given preparation conditions. Maprenal MP 915 contains noticeable amounts of free formaldehyde and is carried in isobutanol to yield a manageable viscosity.

- Kinetics of two-components systems: The different two-components mixtures were reacted at equal weight ratios of reagents. Thus, 2.5 g HMMM in dimethyl formamide was added 2.5 g MDI and reacted under continuous mechanical stirring at the temperatures indicated in Table I. Samples were removed at time zero and subsequently at 5-minute intervals. Urethane formation was monitored by FTIR by following the disappearance of the isocyanate band at 2250 cm^{-1}. The results obtained are shown in Table I.

- Kinetics of three-components systems: (a) In three components systems using non-blocked isocyanate, to 4.0 g of methoxymethyl melamine were added 2.0 g MDI and 5.0 g of DiEG with or without the use of 0.5% of p-toluenesulphonic acid (pTSA) (by weight of melamine). The reactions were monitored by FTIR by following the disappearance of the isocyanate and methoxymethyl bands and the appearance of the urethane band.

(b) Caprolactam-blocked MDI was prepared by adding 0.61 moles of caprolactam to 0.03 moles of MDI and adding this to 50 g xylene at ambient temperature. Five drops of tributyl amine were then added, and the mixture was heated to 80°C and allowed to react for 24 h at reflux. The final product was obtained by precipitation in ether. To a mixture of 3.0 g Maprenal MP900 and 11.0 g of syntacryl SSC 300 (acrylic polyol) in 10.6 g xylene solution were added 3.0 g of blocked MDI. In cases in which p-TSA was used, 0.5% (by weight) of Maprenal was added. In cases in which dibutyltin oxide and dibutyltin diacetate were used, these were added as 0.3% by weight of blocked diisocyanate.

Table I **Reaction of MDI with Polyols and Methoxymethyl Melamines at Different Temperatures**

| Temp. (°C) | k [l/(mole × sec) | | | | | | |
	MDI/ PEG6000	MDI/ DiEG	MDI/ HMMM	MDI/ Mapr900	MDI/ Mapr915	MDI/ TMMM	MDI/ PHMM
120	4.2×10^{-3}	5.2×10^{-4}	5.0×10^{-2}	1.0×10^{-3}	9.8×10^{-3}	9.5×10^{-3}	*
100	2.5×10^{-3}	3.3×10^{-4}	2.3×10^{-2}	6.2×10^{-4}	2.8×10^{-3}	6.6×10^{-3}	*
80	1.5×10^{-3}	2.0×10^{-4}	1.0×10^{-2}	3.6×10^{-4}	7.1×10^{-4}	4.5×10^{-3}	*
60	8.2×10^{-4}	1.1×10^{-4}	3.9×10^{-3}	2.0×10^{-4}	1.5×10^{-4}	2.9×10^{-3}	*
40	4.2×10^{-4}	5.9×10^{-5}	1.4×10^{-3}	1.0×10^{-4}	2.7×10^{-5}	1.8×10^{-3}	*
25	2.4×10^{-4}	3.4×10^{-5}	5.5×10^{-4}	5.9×10^{-5}	6.0×10^{-6}	1.2×10^{-3}	*
r	0.98	0.92	0.94	0.99	0.99	0.93	—
Ea (kcal/mole)	7.0	6.7	11.0	7.0	18.0	5.1	—
ln A	3.53	0.98	11.11	2.01	18.44	1.89	—

* Very high; immediate gelling.

DISCUSSION

Table I reports the rate constants and their dependence from the temperature of the reaction of polymeric MDI (4,4'-diphenylmethane diisocyanate) with a laboratory-prepared hexamethoxymethyl melamine (HMMM), with two different industrial hexamethoxymethyl melamines (Maprenal MP900 and Maprenal MP915), with trimethoxymethyl melamine (TMMM), and with a partially methylated hexamethylol melamine (PHMM). Apparent rate constants of the reaction of polymeric MDI with two polyols, namely polyethylene glycol (PEG 6000) and diethylene glycol (DiEG) are also reported for comparison purposes. It is interesting to compare the results obtained with the different methoxymethyl melamines. In the case of HMMM, where care was taken to minimize the proportion of hydroxymethyl groups (although a small proportion of them still remained: see ^{13}C-NMR,[21] an activation energy (Ea) of 11.0 kcal/mole is obtained. The effect then does not appear to result only from reaction of the isocyanate with methylol groups, as these were present only in traces, but mainly from reaction of newly generated — CH_2OH groups from hydrolysis of NCH_2OCH_3 groups. Such a hydrolysis would also produce CH_3OH which would contribute to inactivating the isocyanate group by reacting with it. Thus the indications are that fully methylated methylol melamines can indeed react with the isocyanate group, this appearing to confirm mechanisms of methoxymethyl decomposition already advanced for methoxymethyl melamine/polyol systems.[5-12]

Regarding the data (Table I) for the two commercial methoxymethyl melamines, the isobutanol contained by Maprenal MP 915 could give confusing results. However, reaction rate studies[20] show that isobutanol has considerably lower reactivity toward — NCO than methylol melamine and thus the melamine/isocyanate reaction is still likely to occur. However, due to the presence of isobutanol, the results for the MDI/Maprenal MP 915 couple must be treated with caution and cannot be taken as evidence of the reaction investigated. More conclusive results are obtained from the MDI/Maprenal MP 900 reaction, as this commercial hexamethoxymethyl melamine contains only one interfering group, N — CH_2OH, and this only in traces. A low activation energy indicates again that reaction between methoxymethyl groups on melamine with the isocyanate group is possible and appears to occur. As the proportion (even if small) of pre-existing hydroxymethyl groups increases, so does the rate of reaction, as expected and as can be seen by the relative values of k for HMMM and Maprenals MP 900 and MP 915 (Table I). Thus, in the case of HMMM where the proportion of — CH_2OH is still very small, an increase in the value of the rate constant is noticed. Even more evident are the results obtained by reaction of MDI with TMMM and PHMM. In PHMM where methylol groups constitute a third of the total melamine groups present, reaction with MDI is instantaneous, even at ambient temperature (Table I). In the case of TMMM in which, due to its preparation, a proportion of methylol groups higher than in HMMM and Maprenals occurs, the value of the rate constant is high and does not vary much with the temperature. All the rate constants in Table I indicate that reaction of isocyanates not only with hydroxymethyl melamines but also with methoxymethyl melamines is com-

parable to and often faster than the reaction of isocyanates with polyols such as polyethylene and diethylene glycols. Thus a cross-linked coating system exclusively based on just a methoxymethyl melamine/isocyanate couple, without any polyol being present, appears to be very feasible. It is also of interest, however, to introduce into this two-components system a polyol to see if the competitive cross-linking reactions isocyanate/polyol and melamine/polyol still occur parallel to the melamine/isocyanate one. The rate constants obtained by other authors for methoxymethyl melamine/polyol reactions[5-12] are comparable to those shown for methoxymethyl melamine/isocyanate and isocyanate/polyol in Table I. A three-components system might then be quite flexible in introducing control of properties of the final finish, just by changing the relative proportions of the components and the conditions under which they are coreacted.

Figure 1, for instance, shows the response of several functional groups under different reaction conditions, relative to the melamine's triazine ring deformation band at 815 cm^{-1}. The significant participation of the NCH_2OCH_3/acrylic couple in the cross-linking is seen from the extent of the methoxymethyl transformation. The low activation energy of the isocyanate/hydroxyl reaction is rather the one responsible for the fast gelling. Noteworthy is that the intensities of the NH deformation band are higher at lower temperature (90°C and 100°C). This is probably because urethane formation occurs at lower temperatures while higher temperatures would also cause activation of the methoxy/acrylic hydroxyl reaction. Of course, the isocyanate can also react with other active hydrogen-containing groups such as $-NH_2$ and $-NHCH_2OCH_3$, fostering further cross-linking. Similar results were also obtained using a penta(methoxymethyl) melamine.
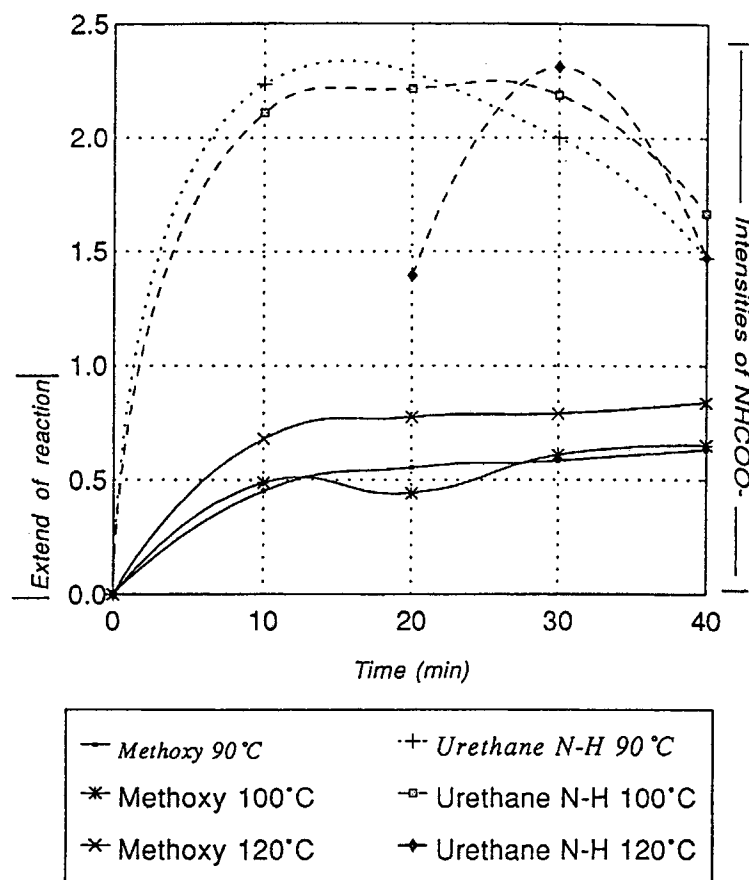

* MF/MDI/acrylic ratio of 20:20:60 by weight

Figure 1   Extent of reaction of methoxymethyl functional groups as a function of time compared to intensities of urethane groups for TMMM/MDI/acrylic system at different temperatures.

However both three-components resins gave films which were quite brittle, indicating that networking is not likely to be extensive. The overall result seems to be that use of high temperatures achieves improved cross-linking. This is probably because high temperatures would promote the acrylic/— NCO reaction prior to any increase in methanol concentration of the system. The fact that there is a wider cure temperature window[1] for —NCO/acrylic reactions means that urethane cross-linking will overlap with the transetherification reaction, resulting in the occurrence of —NCO/CH$_3$OH reactions. Thus it might be difficult to achieve MF-isocyanate reactions when a polyol is present, while at the same time achieving conventional cross-linking (— NCO/acrylic and NCH$_2$OCH$_3$/acrylic) in the same reaction mixture.

An approach to overcome such a problem would be to effect the methoxymethyl transformation at an earlier stage, or to delay urethane formation, thus

overriding premature gelling and thickening because the solvent would evaporate at raised temperatures. The reaction of caprolactam-blocked MDI with various MF resins and acrylic hydroxyls is shown in Figure 2. This shows a slightly slower increase in the extent of reaction with increase in temperature than that seen in corresponding two-components melamine/acrylic films containing an equal amount of p-toluenesulphonic acid.[21] This is not, then, the solution to the problem. In the case of the addition of dibutyltin oxide and dibutyltin acetate as accelerators of urethane formation,[21,22] the extent of reaction of acrylic hydroxyls and other functional groups in the system containing an acrylic/methoxymethyl melamine (Maprenal MP900)/caprolactam-blocked isocyanate is shown in Figure 3. This plot shows that much higher extents of reaction of acrylic hydroxy groups were achieved at relatively low temperatures than in the case of uncatalyzed systems, especially the systems which contained no

— MP900 + MP915 * PNTMXY
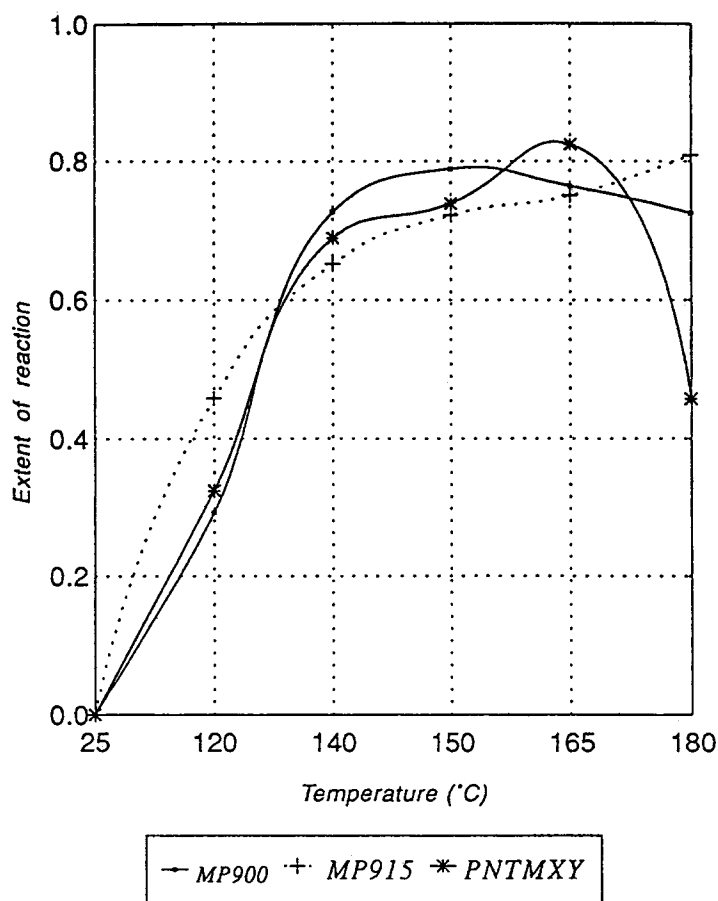
CBL-NCO/MF/acrylic ratio of 17.5:17.5:65 by weight

Figure 2 Extent of reaction as a function of temperature of acrylic hydroxy groups with caprolactam-blocked isocyanate and different methoxymethyl melamines.
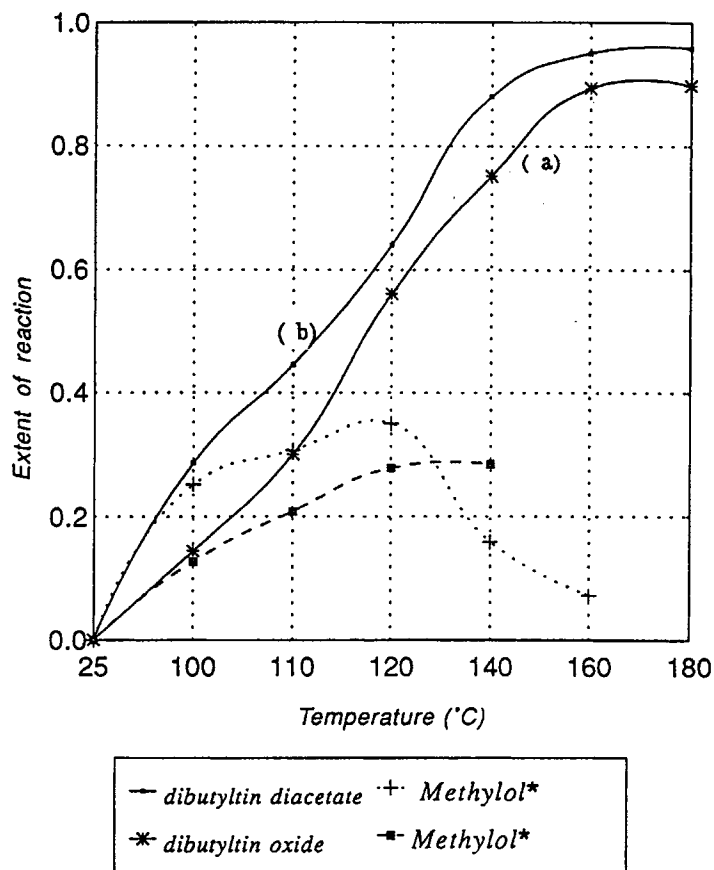
*N.B.: Methylol groups overlap badly with NH of caprolactam
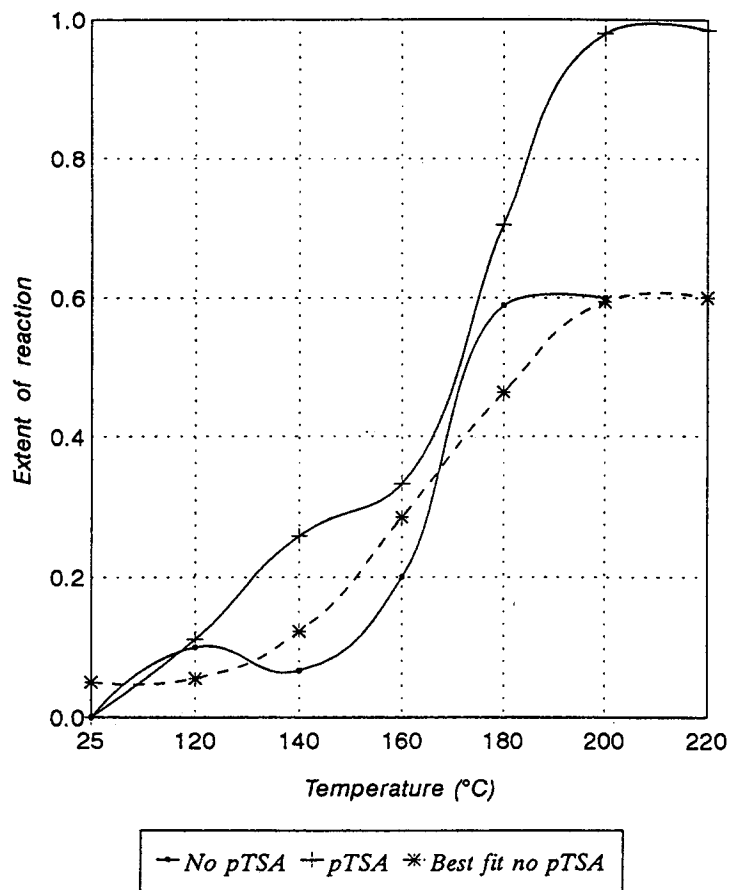CBL-NCO/MF/acrylic ratio of 17.5:17.5:65 by weight

Figure 3 Extent of reaction as a function of temperature for the reaction of acrylic hydroxy groups with caprolactam-blocked isocyanate/Maprenal MP900 system and catalytic amounts of organotin compounds and pTSA.

organotin compounds. The high extent of reaction, which cannot be accounted for by $-NHCH_2OCH_3/$ acrylic reactions alone, suggests participation of blocked diisocyanate in cross-linking at relatively low temperatures, and thus catalysis by the dibutyltin compounds. The cured films obtained in all systems containing blocked $-NCO$ were smooth, glossy and fairly strong. No brittleness was observed. They compared well with two-components melamine/acrylic systems.

Cross-linking in the three-components system can be quantified by using either the $-OH$ band (3500 cm^{-1}) or the methoxymethyl group band at 915 cm^{-1} (Fig. 4). The $-OH$ reaction is common to both urethane formation and methoxymethyl melamine/acrylic cross-linking, whereas the 915 cm^{-1} band is specific to the transformation the methoxymethyl groups undergo. It is difficult to run a conventional infrared analysis of these cured films

because of their brittleness, unless they are cured on a thin glass film. However, it is also difficult to measure the extent of methoxymethyl cross-linking as the glass absorbs in this region of the infrared spectrum. This problem was overcome by the use of Fourier Transform photoacoustic infrared. A major disadvantage of this technique, however, was its inability to measure frequency bands above 3000 cm^{-1}, thus making it difficult to accurately measure the extent of reaction of the acrylic hydroxygroup. Since both acrylic–urethane and acrylic–melamine cross-links occur in this system at elevated temperatures, the analysis of the extent of cross-linking by means of the methoxymethyl transformation gave sufficient insight into the overall cross-linking behavior of the system.

The effect of the acid catalyst on the degree of cross-linking is shown in Figure 4. In the uncatalyzed system, a very low degree of methoxy transformation
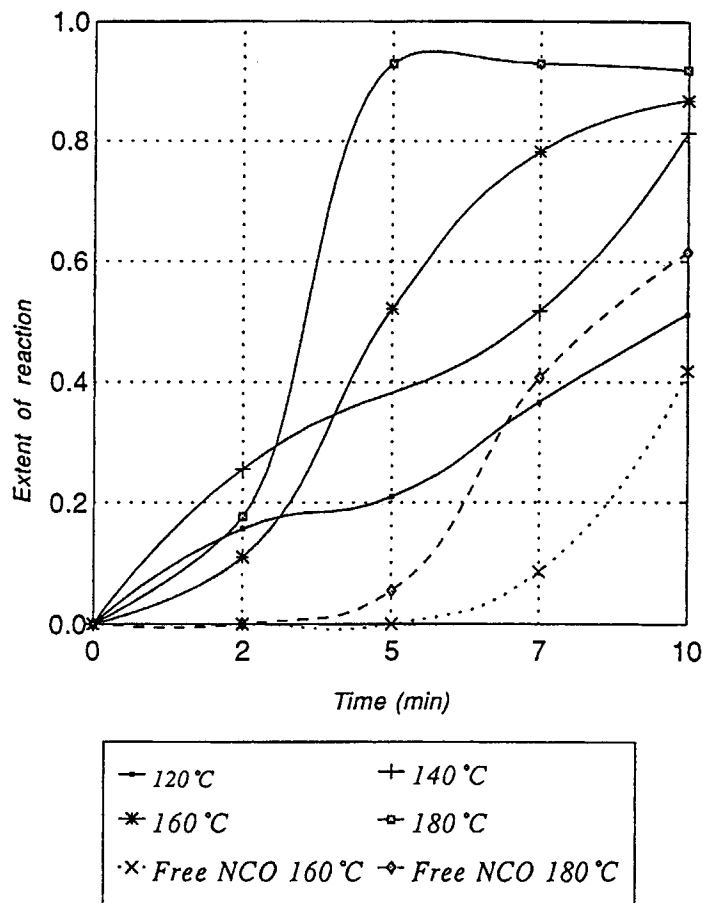
CBL-NCO/acrylic ratio of 35:65 by weight

Figure 4   Extent of reaction as a function of temperature for the reaction of methoxy-methyl groups with caprolactam-blocked isocyanate/acrylic hydroxyls. Effect of pTSA on cross-linking reactions.

is observed: at temperatures as high as 200°C the extent of reaction reaches only 0.6. The extent of reaction at lower temperatures was limited. This is consistent with the poor curing observed for films baked at 120°C and 140°C. On the other hand, coatings cured at higher temperatures showed good film coalescence and were fairly hard. Poor curing at the lower temperatures and good curing at the higher temperatures, despite limited methoxy/acrylic cross-links, are consistent with the formation of urethane cross-links as a result of the dissociation of the caprolactam-blocked MDI. Therefore any cross-linking which occurs at the lower temperature ranges (120–140°C) appears to be a result of the reaction of the acrylic resin with the newly released isocyanate. These temperatures are high enough to cause dissociation of the blocked isocyanate, but not high enough to result in effective melamine/acrylic cross-linking. The absence of isocyanate groups in

the cured films also showed that any free isocyanate that might have been deblocked had sufficient hydroxyl groups with which to react.

The effect of addition of 0.5% p-toluenesulphonic acid (pTSA) on cross-linking in these systems is also shown in Figure 4. Contrary to the case of uncatalyzed systems, when pTSA is added a rather pronounced increase in the degree of methoxymethyl transformation is observed. The reaction clearly goes to completion. The higher extent of reaction at lower temperatures of methoxymethyl functional groups, as well as the good properties of the films now formed at such temperatures, such as improved coalescence, surface hardness, and abrasion resistance,[21] are consistent with the view that both urethane and transetherification cross-links occur. That is, for a film with a low extent of methoxy transformation, good cured properties could only be the result of the combined effect of the two cross-linkers. However,

CBL-NCO/MP900/acrylic ratio of 17.5:17.5:65 by weight

Figure 5 Extent of reaction as a function of time at different temperatures of the reaction of acrylic hydroxy groups with methxymethyl melamine/blocked isocyanate systems.

this view seems inconsistent with the high extent of reaction at 180°C and 200°C, where a very high extent of transformation of methoxymethyl groups is observed. This seems to suggest the exclusion of the isocyanate from the cross-linking process in the film. On the other hand, if such exclusion had occurred, one could observe the formation of free isocyanate without the formation of urethane cross-links. This was not observed and the strong IR band at 1540 cm^{-1} in all the spectra indeed indicates the presence of urethane cross-links. The high degree of methoxymethyl transformation can perhaps be explained by the reaction of the isocyanate secondary products (urethane and polyureas) with the melamine functional groups, as proposed by other authors.[23]

Figure 5 illustrates the extent of reaction of the acrylic hydroxy group with caprolactam-blocked — NCO and methoxymethyl melamine as a function of baking time and temperature in the presence of catalytic amounts of pTSA and tributylamine. The

extent of reaction increases with increasing baking time and temperature. Also shown in Figure 5 is the extent of formation of free isocyanate. The amount of free isocyanate increases with the temperature and it is observed only at higher temperatures. As the splitting temperature of caprolactam-blocked isocyanate is 120°C, the occurrence of free isocyanate only at 160°C and 180°C, coupled with the high extent of acrylic hydroxy groups, implies that the cross-linkers were in excess. This again shows that the observed extents of reaction result from the combined effect of the melamine and of the caprolactam adduct of MDI. Much higher temperatures are thus necessary to achieve faster curing for such a system.

CONCLUSIONS

Both two-components (isocyanate/methoxymethyl melamine) and three-components (isocyanate/

methoxymethyl melamine/polyol) systems were found capable of producing high-solids, high-temperature coatings by cross-linking reactions. The two-components system showed that reactions between methoxymethyl melamine and isocyanate occur. The three-components system showed that all the cross-linking reactions, namely melamine–acrylic, urethane linkages as well as melamine-isocyanate through methylol and hydrolyzed methoxymethyl groups, can occur. However, contrary to expectations, no effective acrylic-isocyanate cross-links were observed in systems containing high methoxy functionality such as hexamethoxymethyl and pentamethoxymethyl melamines, despite the observed methoxy transformation and apparent urethane formation. The isocyanate will react with any free methanol that has been released from the methoxymethyl melamine/acrylic reaction.

An alternative approach was attempted, whereby the methoxymethyl transformation is effected at an earlier stage and the urethane formation is delayed. This was achieved through the use of a blocked isocyanate. Introduction of the blocked isocyanate also requires significant increases in cure temperature of the isocyanate-polyol reaction thus narrowing the cure temperature window for urethane formation. Thus, during cure, the polyols and the cross-linkers react to form a three-components network having in-between properties of the acrylic/urethane and acrylic/melamine systems.

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