Studies on Curing Urethane Prepolymers with Aniline–Formaldehyde Resins

JANUSZ KOZAKIEWICZ,* ANDRZEJ ORZECHOWSKI, ALINA RASZCZUK, MICHAŁ H. JAMRÓZ, and JAN CZ. DOBROWOLSKI

Industrial Chemistry Research Institute, 8 Rydygiera Street, 01-793 Warsaw, Poland

SYNOPSIS

Commercial aniline–cresol–formaldehyde resin, two model aniline–formaldehyde and aniline–cresol–formaldehyde resins, and methylenedianiline have been used as curatives for NCO-terminated urethane prepolymer prepared from polyoxypropylenediol and toluenediisocyanate. Based on viscoelastic behavior of the investigated systems and changes in their IR spectra, it has been concluded that phenolic OH groups present in aniline–cresol–formaldehyde resin do not play an important role in the curing process carried out at RT despite earlier suggestions to the contrary. The explanation for specific behavior of systems where urethane prepolymers have been cured with commercial aniline–cresol–formaldehyde resin is presumably the presence of small amount of solvent (benzyl alcohol) in that resin, which may influence the reaction kinetics.

INTRODUCTION

Aromatic polyamines are well-known curing agents for urethane prepolymers, especially in the field of polyurethane elastomers,[1] MOCA (3,3′-dichloro-4,4′-diaminodiphenylmethane) being the most frequently used. Both modification of MOCA[2–5] and introduction of new grades of aromatic polyamines[6–10] have been suggested to improve curing characteristics of the system or to lower its toxicity.

In our earlier reports,[11,12] we discussed the possibility of using aniline–cresol–formaldehyde resin (ACF) as a curative for filled, NCO-terminated urethane prepolymers (UP) to produce elastic polyurethane–ureas useful as sealants. We also studied the effect of curing temperature and curing agent concentration on the viscoelastic properties of such a two-component system.[13]

The purpose of the present study is to explain the role of phenolic OH groups in ACF in its reaction with UP. It has been suggested earlier that the presence of these groups in ACF is responsible for its delayed action as curative for filled UP.[11]

For the present study, curatives were made of two grades of ACF (a commercial grade that had been used in the previous investigations, and a special grade synthesized without addition of solvents), aniline–formaldehyde oligomer (AF), and methylenedianiline (MDA) and used to cure the same batch of UP containing ca. 1% of free NCO groups. This UP was prepared at the same NCO/OH ratio as the filled UP investigated in our previous studies.[11–13]

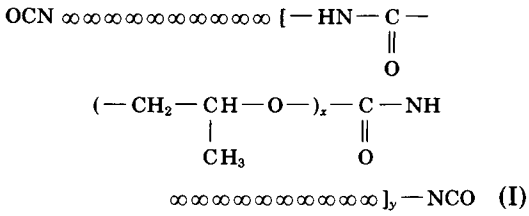
EXPERIMENTAL

Materials

1. Urethane prepolymer (UP) prepared from polyoxypropylenediol (mol weight $\approx$ 2000) and toluenediisocyanate (80/20 mixture of 2, 4 and 2, 6 isomers). NCO content = 1.25%; viscosity = 13 Pa s (25°C Rheoviscometer); $M_n = 5.4 \times 10^3$, $M_w = 1.06 \times 10^4$, and $M_w/M_n = 1.97$ (from GPC measurements). Simplified structure of UP:

* To whom correspondence should be addressed.

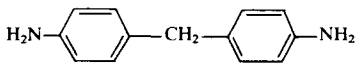
Journal of Applied Polymer Science, Vol. 44, 1349–1353 (1992)
© 1992 John Wiley & Sons, Inc. CCC 0021-8995/92/081349-05$04.00



(I)

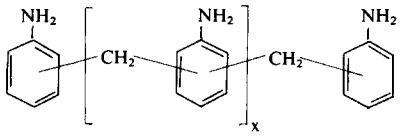
Some allophanate and (or) biuret branching and crosslinks can also be expected. Here ∞∞∞∞∞∞∞∞∞∞∞∞∞∞ = diisocyanate chain, $x \approx 34$, and $y \approx 3$.

2. Methylenedianiline (4,4'-diaminodiphenylmethane, lab. reagent, BASF) (MDA); amine number = 560.9; H_2O content (%) = 0.62:



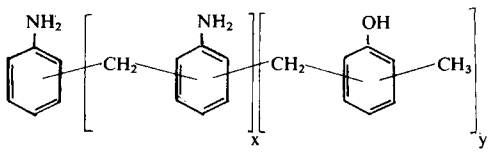
(II)

3. Aniline–formaldehyde resin (AF); amine number = 496.4; H_2O (%) = 0.62; formaldehyde (%) = not detected; aniline (%) = 2.9; dimers (MDA) (%) = 67.2 (from GPC measurements); $M_n = 3 \times 10^2$; $M_w = 3.5 \times 10^2$; $M_w/M_n = 1.16$ (without dimers):

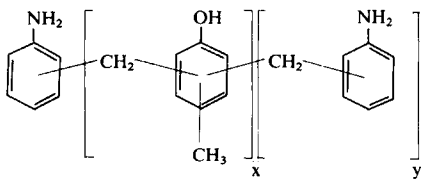


x = 2, 1 or 0 (dimers) (III)

4. Aniline–cresol–formaldehyde resin (ACF) (aniline/cresol = 2/1 mol/mol):



x = 2, 1 or 0 (dimers)
y = 1 or 0 (dimers) (IVa)



x = 1 or 0 (dimers)
y = 2, 1 or 0 (dimers) (IVb)

Table I

	Commercial Grade, ACF-1	Prepared Without Solvent Addition, ACF-2
Aniline number	422.5	414.9
Salicylic acid (%)	3.0	3.0
H_2O (%)	0.38	0.21
Aniline (%)	3.4	3.5
Formaldehyde (%)	Not detected	Not detected
Cresol (%)	Not detected	Not detected
Butanol (%)	Not detected	Not detected
Benzyl alcohol (%)	2.1	Not detected
Dimers (%)	53.7	51.4
$M_n \times 10^2$ (without dimers)	3.0	2.9
$M_w \times 10^2$ (without dimers)	3.6	3.3
M_w/M_n (without dimers)	1.19	1.15

Four curatives based on MDA, AF, and ACF were prepared for the reaction with UP and designated respectively CMDA, CAF, CACF-1, and CACF-2. CAF, CACF-1, and CACF-2 were solutions of AF, ACF-1, and ACF-2 in dibutylphthalate and CMDA was a solution of MDA in CCl_4. The curatives and UP were used in equimolar amounts (regarding NCO and NH_2 groups).

Methods

Rheological Measurements

Dynamic storage modulus (G') and dynamic viscosity (η') were calculated using Walters formulae[14] based on the results of dynamic mechanical measurements performed at 32°C in a dried air atmosphere in a Model R-17 Weissenberg Rheogoniometer. Details concerning preparation of samples for such measurements have been given in our earlier report[13] presenting the detailed study on viscoelastic properties of filled UP cured with ACF.

Infrared Studies

For infrared (IR) studies, a Perkin-Elmer 580 spectrophotometer was used. Spectra recorded for the range 4000–400 cm^{-1} were made for films between KBr windows. Relative changes in intensity of the following bands were measured with respect to ca. 2980 cm^{-1} band in UP spectrum corresponding to $-CH_3$ (stretching, asym) that remained constant during curing:

$\approx 2280\ cm^{-1}$	$-N=C=O$ (stretching)
$\approx 1540\ cm^{-1}$	secondary amides A-II band (combined) NH deformation and $=C-N=$ stretching)
$\approx 3450\ cm^{-1}$	NH_2, NH (stretching) overlapping with H_2O stretching vib. band
$\approx 1600\ cm^{-1}$	aromatic $-C=C-$ (stretching) and $-NH_2$ or $=NH$ (deformation)
$\approx 2340\ cm^{-1}$	CO_2 (asymmetric, stretching)

In this paper, only the results obtained for 2280 cm^{-1} band are given since they seemed to be the most significant for the systems studied.

Both rheological measurements and IR studies were carried out under a 32°C dried air atmosphere, preventing the side reaction of NCO with moisture.

RESULTS AND DISCUSSION

Changes in viscoelastic properties of four different UP–amine curing agent systems can be observed in Figures 1 and 2, where dynamic storage modulus (G') and dynamic viscosity (η') are plotted against curing time. Delayed curing in the case of CACF-1 as compared to both CACF-2 and CAF is clearly proved here. It can be also noticed that the curing rate of CACF-2/UP and CAF/UP systems is approximately the same despite the fact that the former has phenolic OH groups. Thus, since both CACF-1 and CACF-2 have phenolic OH and contain approximately the same amounts of salicylic acid, aniline, water, and dimers (see Experimental), the only reason for slower curing with CACF-1 seems to be the presence of a small amount of reactive solvent (benzyl alcohol) in this curative.

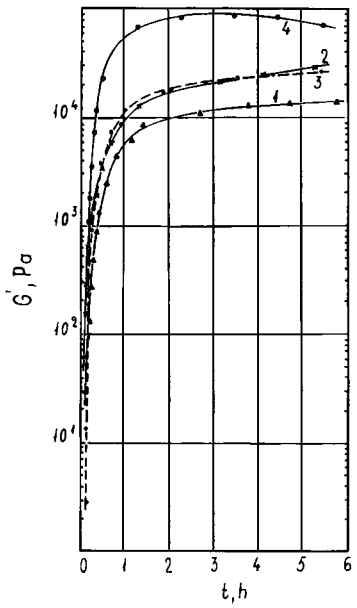


Figure 1 Dynamic storage modulus (G') vs. time at the early stages of curing urethane prepolymer with amine curatives. Frequency = 1 rad/s. (1) UP/CACF-1; (2) UP/CACF-2; (3) UP/CAF; (4) UP/CMDA.

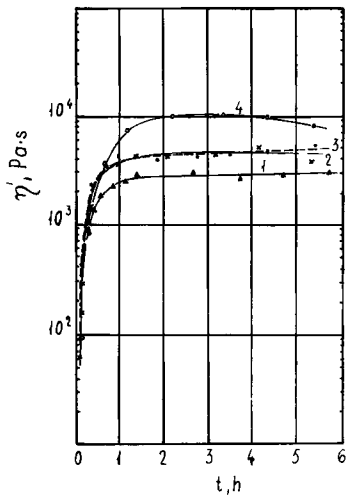


Figure 2 Dynamic viscosity (η') vs. time at the early stages of curing urethane prepolymer with amine curatives: (1) UP/CACF-1; (2) UP/CACF-2; (3) UP/CAF; (4) UP/CMDA.

The plots of dynamic storage modulus (G') for all systems studied after 24 h of curing vs. frequency are presented in Figure 3. The curves seem to be typical for chemically crosslinked polymers. The highest G' values (i.e., high crosslinking density) can be observed for UP/CACF-2 and the lowest (i.e., low crosslinking density) for UP/CACF-1 system, which suggests blocking of some part of active NCO

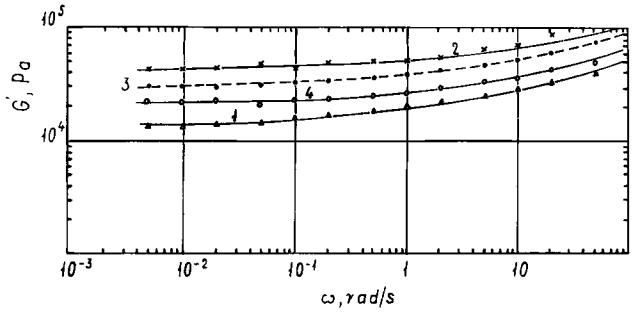


Figure 3 Dynamic storage modulus (G') vs. frequency after 24 h of curing urethane prepolymer with amine curatives: (1) UP/CACF-1; (2) UP/CACF-2; (3) UP/CAF; (4) UP/CMDA.

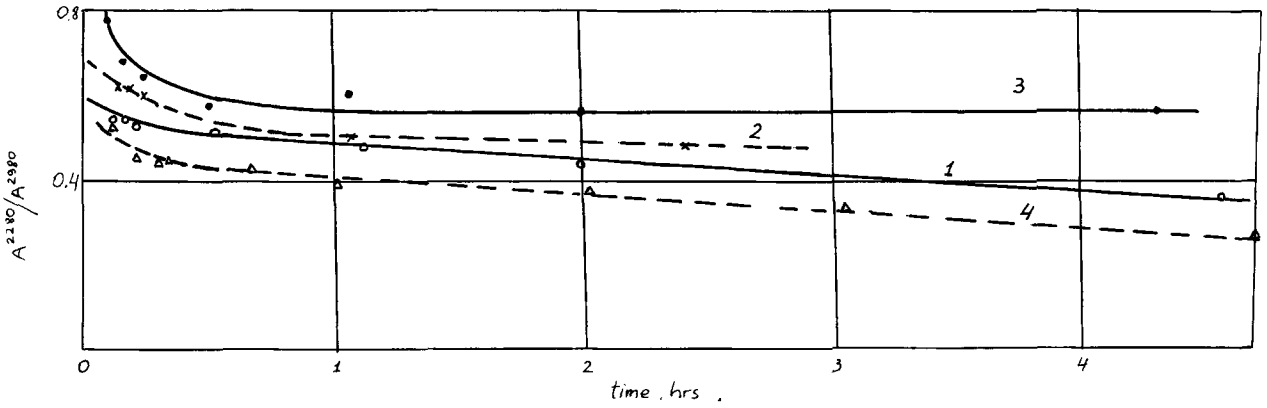


Figure 4 Changes in relative intensity of NCO band (2280 cm^{-1}) in IR spectrum at the early stages of curing urethane prepolymer with amine curatives: (1) UP/CACF-1; (2) UP/CACF-2; (3) UP/CAF; (4) UP/CMDA.

groups with benzyl alcohol in the latter. The other possible reason for a delayed increase in G' and y' observed for UP/CACF-1 system can be just from diluting the reaction mixture with benzyl alcohol; although the amount of solvent is very small (ca. 2%), it can be relevant in a totally solventless system.

A scheme of the process of curing urethane prepolymers with aniline–formaldehyde resins can be presumed after comparing the results of rheological properties of the investigated systems (presented above) with the results of IR studies (Figs. 4 and 5). From these figures, showing changes in NCO band intensity during curing, it can be concluded that although the UP/CACF-1 system appears slower than, for example, UP/CACF-2 because the increase in viscosity and modulus is delayed, it is actually much faster from the chemical point of view since the rate of diminishing NCO band intensity is much greater. It appears then that two factors may affect the unusual behavior of the UP/CACF-1 system:

—"solvent effect" of benzyl alcohol on kinetics of NCO/NH_2 reaction
—side reaction of NCO with benzyl alcohol

Based on these results, it seems that generally three stages are involved in the process of curing urethane prepolymers with aniline–formaldehyde resins at room temperature and in the absence of atmospheric moisture:

Stage I (0–0.5 h). Fast reaction of NCO groups of prepolymer with aromatic NH_2 groups of resin leading to chain lengthening and to a very fast increase of modulus and viscosity. If the system contains some amount of reactive solvent (benzyl alcohol in the UP/CACF-1 system), the reaction of

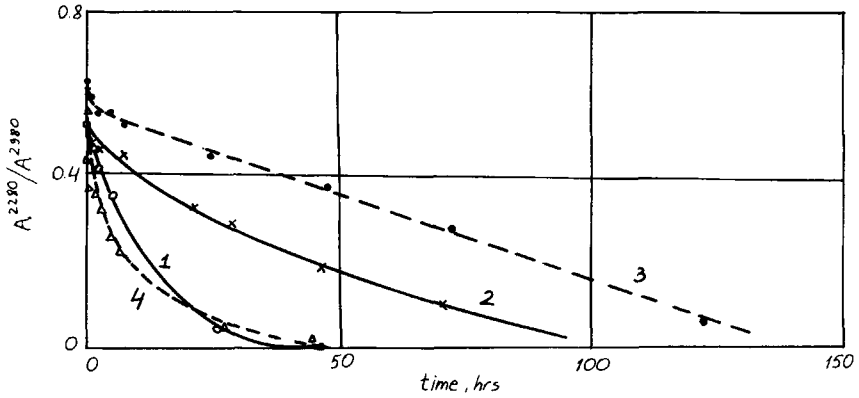


Figure 5 Changes in relative intensity of NCO band (2280 cm^{-1}) in IR spectrum at the late stages of curing urethane prepolymer with amine curatives: (1) UP/CACF-1; (2) UP/CACF-2; (3) UP/CAF; (4) UP/CMDA.

NCO with reactive groups of the solvent can compete with NCO/aromatic NH_2 reaction, especially after some time, when the system becomes more viscous, because the mobility of small molecules of solvent is much greater than that of resin molecules.

Stage II (0.5–5 h). Continuation of NCO–NH_2 (and NCO-reactive solvent) reactions but at a much slower rate because of the high viscosity of the system. Much slower reactions of NCO with water (present in the resins) as well as with urea and urethane groups leading to biuret and allophanate crosslinks can also start at this stage.

Stage III (5–150 h). All reactions of NCO proceed, but very slowly because the system solidifies. After ca. 20–50 h a small CO_2 peak can be clearly observed in the IR spectrum, which is the evidence that the reaction with water proceeds at this stage (its start at stage II cannot be detected because of too low an intensity of the presumed peak). Even after 150 h, tiny peaks of NCO and primary NH_2 could be detected in the reaction products. In our studies, the reaction rate at this stage was relatively high for UP/CMDA system (see Fig. 5) since the mobility of shorter MDA molecules was greater than that of AF or ACF. The reaction rate was also high for UP/CACF-1 system since its lower crosslinking density enabled greater mobility of the molecules.

In practical applications, stages II and III are shortened because of the reaction of NCO with atmospheric moisture.

CONCLUSIONS

Reactions of curing NCO-terminated urethane prepolymers with aniline–formaldehyde and aniline–cresol–formaldehyde resins proceed in a very similar way, which means that phenolic OH groups in the latter do not play an important role in this process. When a small amount of a reactive solvent (benzyl alcohol) is used as a component of aniline–cresol–formaldehyde resin, viscosity of the reaction mixture increases during curing at a lower rate, which is the advantage of such a system in practical field applications. Moreover, in this case the reaction is completed in a shorter time.

Generally, curing NCO-terminated urethane prepolymers with aniline–formaldehyde resins at room temperature is a three-stage process, the first stage being much faster than the other two, which is rather typical behavior of many reactive polymer systems. However, it has been postulated here, that even small changes in the structure or composition of the curative can result in a different reaction rate at a particular stage of the process mainly because of different mobility of the reacting molecules.

REFERENCES

1. E. N. Doyle, *The Development and Use of Polyurethane Products,* McGraw-Hill, New York, 1971.
2. E. F. Cassidy, H. L. Frisch, H. X. Xiao, and K. C. Frisch, *J. Elast. Plast.*, **16,** 84 (1984).
3. U.S. Pat. 3,265,669 (1966).
4. Ger. Pat. Appl. 2,107,360 (1971).
5. L. P. Negrobova, E. V. Olejnikova, S. Y. Zaitsev, and Sa. M. Ustinova, *Plast. Massy,* **9,** 59 (1983).
6. J. Blahak, W. Meckel, and E. Muller, *Angew. Makromol. Chem.*, **26,** 29 (1972).
7. J. H. Simon, C. J. Nalepa, and W. R. Brown, in *Proc. of "UTECH 88" Conference,* The Hague, October 1988, p. 207.
8. P. Knaub and Y. Camberlin, *J. Appl. Polym. Sci.*, **32,** 5627 (1986).
9. Th. Voelker, H. Althaus, and A. Schmidt, *J. Elast. Plast.*, **20**(1), 36 (1988).
10. W. Brown and C. J. Nalepa, *Proc. of "UTECH '90" Conference,* The Hague, April 1990, p. 237.
11. A. Orzechowski, J. Kozakiewicz, A. Lendzion, A. Raszczuk, and M. Jamróz, *Proc. of International Conference "Rubber 84",* Moscow, June 1984, Preprint A-105.
12. J. Kozakiewicz, A. Orzechowski, and A. Raszczuk, *Proc. of 30th IUPAC International Symposium on Macromolecules,* The Hague, August 1985, p. 411.
13. A. Raszczuk, J. Kozakiewicz, and A. Orzechowski, *J. Appl. Polym. Sci.*, **31,** 135 (1986).
14. K. Walters, *Basic Concepts and Formulae for the Rheogoniometer,* Sangamo Controls, Bognor Regis, 1968.

Received July 15, 1991
Accepted May 14, 1991