

Etherification Versus Amine Addition During Epoxy Resin/Amine Cure: An *In Situ* Study Using Near-Infrared Spectroscopy

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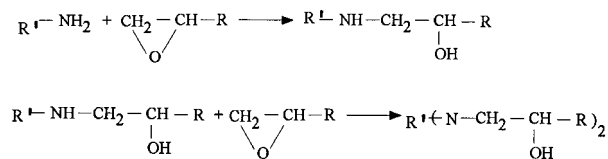
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ABSTRACT: The reactions between a multifunctional epoxy resin, tetraglycidyl 4,4'-diaminodiphenylmethane (TGDDM) and a monofunctional amine, methylaniline (mAnil) are studied. Due to the existence of a tertiary amine catalytic center within the TGDDM molecule, the etherification reaction during cure of TGDDM is usually more significant than in other epoxide systems. The importance of this reaction relative to the amine addition reactions is investigated. *In situ* near-infrared spectroscopy is used to obtain kinetic data during the cure reactions. The reaction rate constants are calculated from linear regression analysis for both amine addition and etherification reactions based on the reaction mechanisms proposed. Arrhenius relationships are observed for all the reaction rate constants involved. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 895–901, 1998

Key words: epoxy resin; cure; etherification; near-infrared spectroscopy; kinetics

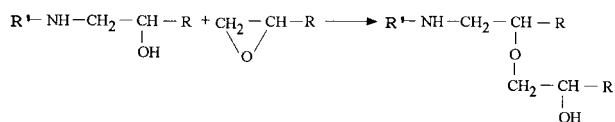
INTRODUCTION

During epoxy resin/amine cure, amine addition reactions shown below are usually the main reactions involved and have been studied extensively.^{1,2}



Etherification during epoxy resin cure refers to the reaction between an epoxide ring and a

hydroxyl group, thus resulting in the formation of an ether link.



This reaction is significant only at certain reaction conditions (high cure temperatures, for example) and for certain epoxy resin/amine cure systems. The importance of this reaction in terms of its effect on the network structure has been studied by Bokare and Ghandi,³ Dusek,⁴ and Riccardi and Williams.⁵ It has been generally agreed that the occurrence of etherification in a curing system may vary the structure and the associated macroscopic properties of the cured product, thereby modifying the glass transition temperature, the elastic modulus in the rubbery state, and so on. This is a result of an increase in the number of possible branches due to etherification. It has

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been found that, during epoxide cure, etherification retards the conversion of finite and pendant branches into crosslinked elastic material.⁵ The presence of etherification also results in gelation at lower epoxide conversion.⁶

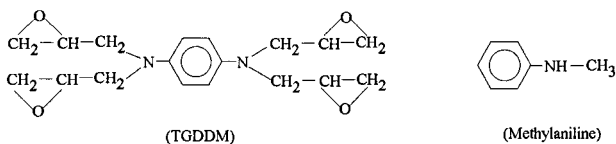
Recently, extensive studies have been carried out on epoxy resin/amine cure reactions involving diglycidylamine derivatives, especially those of TGDDM.⁷⁻¹⁰ The existence of tertiary amine groups in the epoxide molecules and the steric proximity of the two epoxy groups are unique features of these systems. The tertiary amine groups have been found to have a catalytic effect on the etherification reaction^{6,11} (see reaction mechanism in Fig. 1). The presence of such catalytic centers in the epoxide itself greatly enhances the tendency toward etherification even with aromatic amines as curing agents.^{8,9,12} The steric proximity of the epoxy groups also increases the probability of forming cyclic species as a result of intramolecular etherification reactions.^{10,12,13}

The reactions between TGDDM and methylamine (mAnil) are studied herein to examine the importance of etherification reaction. Kinetic parameters for the amine addition reactions are obtained from previously proposed mechanistic models.^{1,2} The etherification reaction is modeled by assuming a reaction mechanism similar to that of the amine addition reactions.

EXPERIMENTAL

Materials

A commercial TGDDM resin, MY 721, was supplied by Ciba Geigy Corporation. The resin contains about 92% pure TGDDM with the balance being impurities. Reagent grade mAnil (99% purity) was purchased from Aldrich Chemical Co.



Instrumentation

The near-infrared spectroscopic data were acquired with a Mattson Nova Cygni 120 FTIR spectrometer. A SpectraTechTM high temperature transmission cell (ATI Instruments North America, Madi-

son, WI) was used to obtain *in situ* spectroscopic data at elevated temperatures. At each time interval, 16 spectra at 8 cm⁻¹ resolution were coadded.

Procedures

The samples were prepared by directly mixing TGDDM with mAnil. The mixture was then stirred until a clear liquid was obtained. Two equivalent ratios (1 : 1 and 2 : 1, epoxy group/secondary amine group) were studied over a temperature range from 413 to 453 K.

The uncured mixture was placed in the high temperature transmission cell at room temperature. One spectrum was obtained prior to heating the sample cell. The cell then was heated to the desired temperature as rapidly as possible and the NIR spectra of the reacting mixture were obtained *in situ* at equal time intervals during isothermal cure.

KINETIC MODELING

Rate Equation for the Amine Addition Reaction

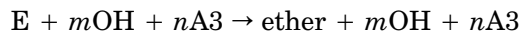
For the TGDDM/mAnil system, the kinetic equation for the amine addition reaction can be obtained using the approach published earlier.^{1,2} The reactions are assumed to proceed via two reaction paths, one noncatalytic and the other catalytic. The formation of a termolecular intermediate in both reaction paths is considered the rate determining step. Under these conditions, the kinetic equation of amine addition for the TGDDM/mAnil system can be written as

$$-\frac{d[A2]}{dt} = k'[E][A2]^2 + k[E][A2][OH] \quad (1)$$

where [A2], [E], and [OH] are the concentrations of secondary amine, epoxide, and hydroxyl groups at time *t*, respectively, and *k'* and *k* are the reaction rate constants for the noncatalytic and catalytic reaction paths, respectively.

Rate Equation for the Etherification Reaction

Possible reaction mechanisms involving etherification have been proposed by Cole and coworkers.^{8,9} The general reaction is expressed as



The corresponding rate equation for etherification can be written as

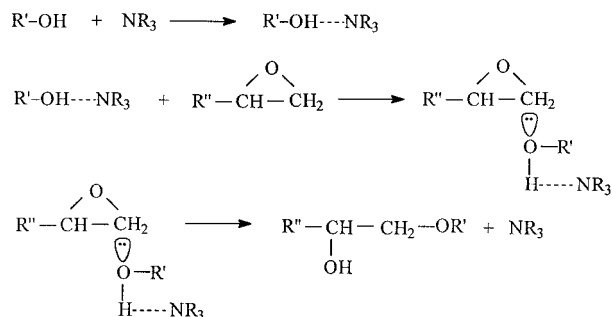
$$\frac{d[\text{ET}]}{dt} = k_e[\text{E}][\text{OH}]^m[\text{A3}]^n \quad (2)$$

where $[\text{ET}]$ and $[\text{A3}]$ are the concentrations of ether linkages and tertiary amine groups at time t , respectively, and k_e is the rate constant of the etherification reaction.

According to Cole, $m = 0$ represents homopolymerization of the epoxide groups without the assistance of hydroxyl groups. The homopolymerization reaction may be catalyzed either by tertiary amine groups ($n = 1$) or uncatalyzed ($n = 0$). The etherification of the epoxide with the hydroxyl group may be represented by $m = 1$ and the reaction may also be catalyzed by tertiary amine groups ($n = 1$) or hydroxyl groups ($m = 2$), or uncatalyzed $n = 0$. Nevertheless, it has been well established that both hydroxyl and tertiary amine groups accelerate the etherification reaction.^{14,15} Therefore, mechanisms that do not involve the tertiary amine ($n = 0$) or hydroxyl group ($m = 0$) are considered to be negligible when considering the overall reaction rate and are excluded from further consideration.

The reaction mechanism corresponding to epoxide-hydroxyl etherification was proposed by Tanaka, Tomio, and Kakuichi¹⁵ and is shown in Figure 1, scheme 1. The homopolymerization of epoxide is considered to proceed through an anionic polymerization mechanism with the formation of active propagating sites as the first step^{13,16} (see Fig. 1, scheme 2). The propagation of this reaction, however, has been found to be severely limited by steric hindrance.¹⁷ Considering the bulky molecular structure of the TGDDM, the tertiary amine is sterically hindered; therefore, the propagation reactions of the anionic polymerization mechanism will be considered negligible in this case.¹⁸ Therefore, epoxide-hydroxyl etherification is considered the main reaction leading to the formation of ether links in this system. By fitting experimental data obtained from DSC experiments into the rate equations derived from a proposed mechanistic model, Cole, Hechler, and Noel⁹ have found that the experimental data best conform to the mechanistic model in the case when $m = n = 1$, in agreement with the above analysis. According to scheme 1 in Figure 1, eq. (2) becomes

SCHEME 1:



SCHEME 2:

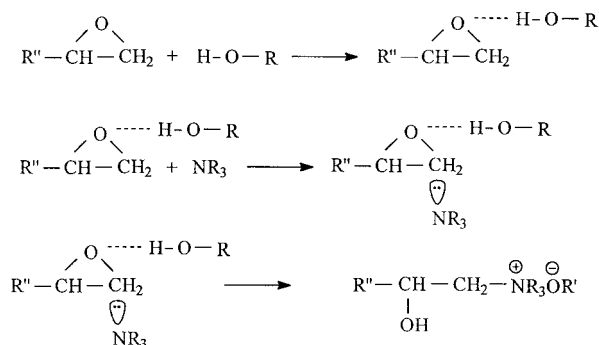


Figure 1 Etherification reaction mechanisms.

$$\frac{d[\text{ET}]}{dt} = k_e[\text{E}][\text{OH}][\text{A3}] \quad (3)$$

Since the etherification reaction usually is significant only in epoxy-rich systems and during the later stages of the cure reactions,¹¹ it will be studied only after conversion of the amine groups is complete. Since the etherification reaction does not contribute to the net change in hydroxyl concentration, both $[\text{OH}]$ and $[\text{A3}]$ will remain constant after complete reaction of the secondary amine groups. At this stage of the reaction, the kinetic equation for the etherification [eq. (3)] can be greatly simplified to

$$-\frac{d[\text{ET}]}{dt} = k'_e[\text{E}] \quad (4)$$

where $k'_e = k_e[\text{OH}][\text{A3}]$. Integration of this expression gives

$$k'_e = \frac{[\text{ET}]_2 - [\text{ET}]_1}{\int_{t_1}^{t_2} [\text{E}] dt} \quad (5)$$

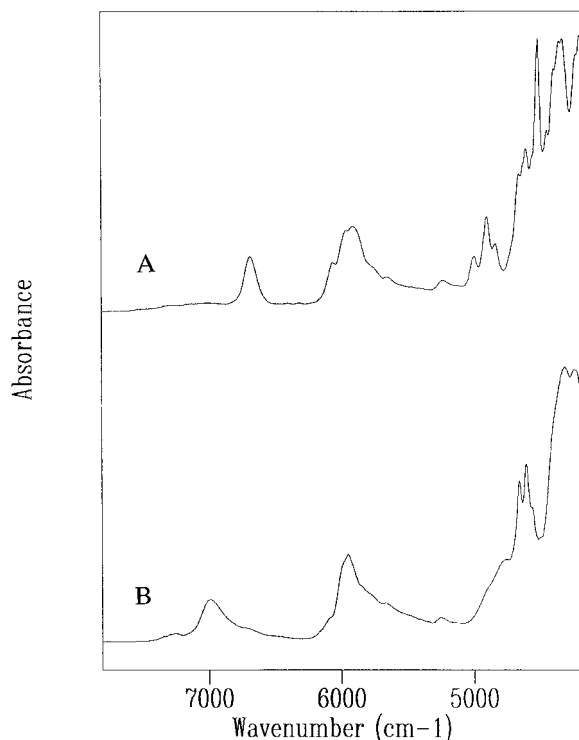


Figure 2 NIR spectra of the TGDDM/mAnil system having a 1 : 1 equivalent ratio (epoxide/amine). (A) unreacted; (B) following reaction at 443 K for 70 min.

where $[ET]_2$ and $[ET]_1$ are the concentrations of ether links at t_2 and t_1 , respectively.

RESULTS AND DISCUSSION

General Spectral Features

The NIR spectra of the TGDDM/mAnil systems before and after cure at 443 K are shown in Figure 2 [1 : 1 (epoxide/amine) equivalent ratio] and Figure 3 [2 : 1 (epoxide/amine) equivalent ratio]. The general spectral features are similar to those reported earlier^{1,2,19} and will only be summarized here briefly (see Table I). The absorption bands centered at 4518 cm^{-1} and 6683 cm^{-1} are characteristic of the terminal epoxide ring combination band and secondary amine overtone band, respectively. Both of them have been successfully employed for quantitative analysis in the previous studies. The absorption band at 6993 cm^{-1} represents the overtone absorption band of hydroxyl groups. The utility of this band for quantitative analysis has been questioned due to the formation of hydrogen bonds in the system.¹⁰ The continuing

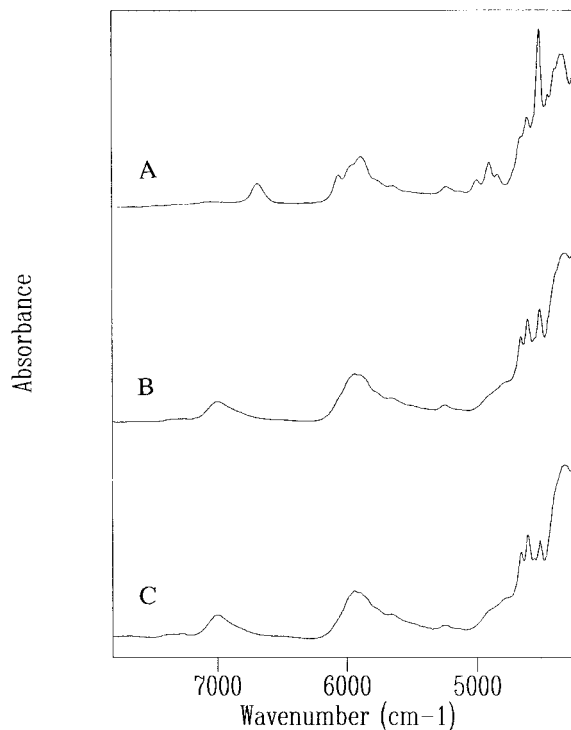


Figure 3 NIR spectra of the TGDDM/mAnil system having a 2 : 1 equivalent ratio (epoxide/amine). (A) unreacted; (B) following reaction at 443 K for 45 min; (C) following reaction at 443 K for 225 min.

decrease in intensity of the epoxide absorption band after depletion of the secondary amine groups in the 2 : 1 (epoxide/amine) system is a clear indication that etherification reaction occurs in this system [see Fig. 3(B,C)].

Reaction Kinetics

The integrated peak intensities of both the terminal epoxide and secondary amine group absorption bands were calculated. These quantities were then ratioed against the aromatic ring C—H band

Table I Assignment of NIR Characteristic Absorption Bands for the TGDDM/mAnil System

Absorption Band	Peak Position (cm^{-1})
Terminal epoxide combination	4518
Secondary amine N—H overtone	6683
Hydroxyl group overtone	6993
Aromatic ring C—H combination	5967

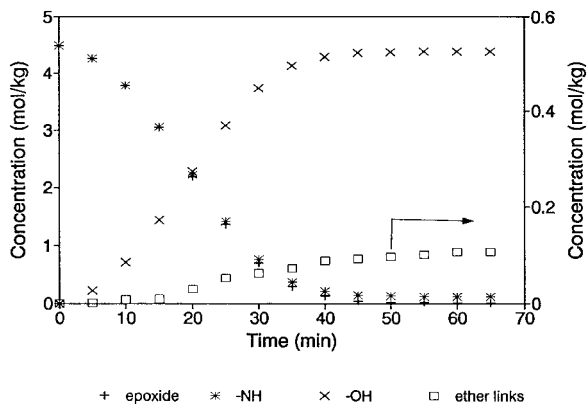


Figure 4 Concentration profiles for the TGDDM/mAnil system having a 1 : 1 equivalent ratio (epoxide/amine) at 443 K.

at 5967 cm^{-1} , thus providing an internal reference. These absorption ratios were correlated with the concentrations through Beer's law. The extinction coefficients were determined from the initial concentrations. The concentrations of the hydroxyl groups, tertiary amine groups, and ether linkages were calculated from material balance equations as follows

$$[\text{OH}] = [\text{A3}] = [\text{A2}]_0 - [\text{A2}] \quad (6)$$

where $[\text{A2}]_0$ is the concentration of secondary amine at $t = 0$.

$$[\text{ET}] = [\text{E}]_0 - [\text{E}] - [\text{OH}] \quad (7)$$

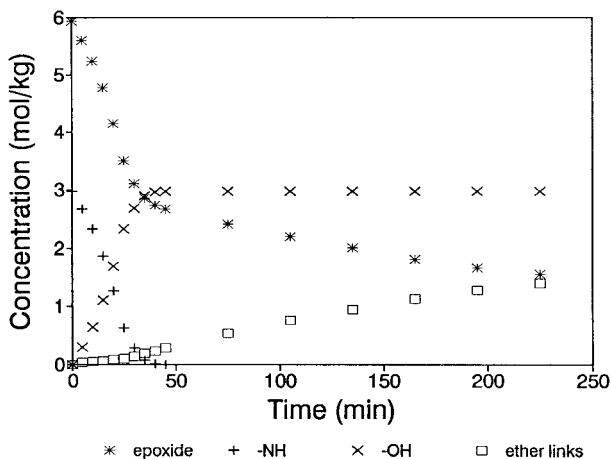


Figure 5 Concentration profiles for the TGDDM/mAnil system having a 2 : 1 equivalent ratio (epoxide/amine) at 443 K.

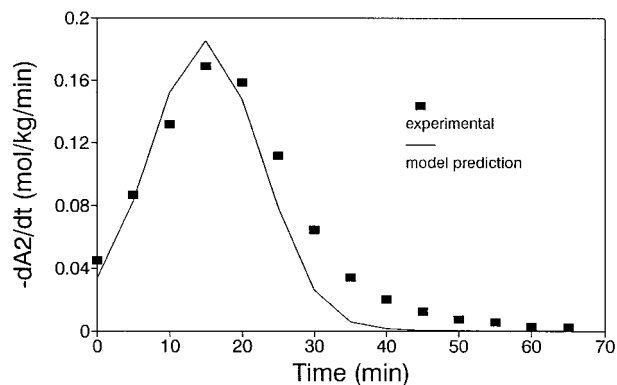


Figure 6 Comparison of experimental and predicted reaction rate data for the TGDDM/mAnil system having a 1 : 1 equivalent ratio (epoxide/amine) at 443 K.

where $[\text{E}]_0$ is the concentration of epoxide groups at $t = 0$.

Typical concentration profiles for both 1 : 1 and 2 : 1 equivalent ratios (epoxide/amine) during reaction at 443 K are shown in Figures 4 and 5, respectively. As evidenced by the calculated ether linkage concentrations in the two systems, the etherification reaction was far more significant when epoxide was in excess (2 : 1) than when stoichiometric quantities were used (1 : 1). Ether linkages form only after the reaction involving secondary amine groups are essentially complete.

For the amine addition reaction, the experimental data were fit to eq. (1) using a multiple linear regression analysis. As shown in Figures 6 and 7, the rate equation derived described the experimental data for the 2 : 1 (epoxide/amine) equivalent ratio system well during the entire

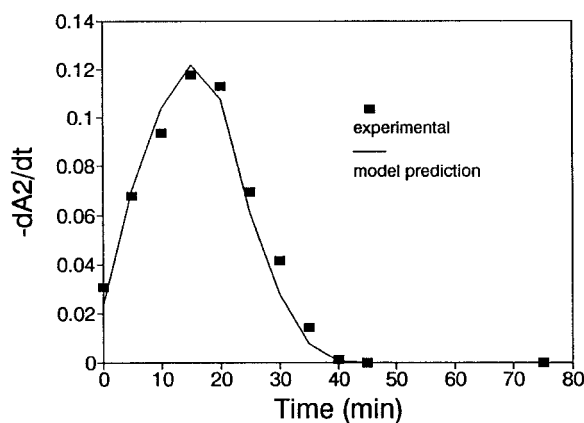


Figure 7 Comparison of experimental and predicted reaction rate data for the TGDDM/mAnil system having a 2 : 1 equivalent ratio (epoxide/amine) at 443 K.

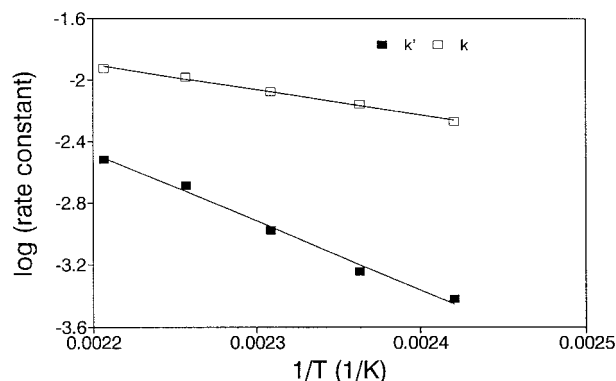


Figure 8 Arrhenius plots of k' and k for the TGDDM/mAnil system having a 2 : 1 equivalent ratio (epoxide/amine).

course of reaction. There are, however, some deviations of the model predictions from the experimental data for the 1 : 1 (epoxide/amine) system at the later stages of the reactions. This is most probably due to the effect of diffusion limitations. It has been noticed that after cure, the viscosity of the 1 : 1 (epoxide/amine) system increases significantly.

The Arrhenius temperature dependence of the reaction rate constants for both noncatalytic and catalytic reaction paths is shown in Figure 8 in a temperature range from 413 to 453 K. Etherification reaction was studied only for the system having 2 : 1 (epoxide/amine) equivalent ratio due to insignificant etherification for the system having 1 : 1 (epoxide/amine) equivalent ratio. The reaction rate constant, k_e , can be calculated directly from eq. (5) by obtaining the area under the $[E] - t$ curve from t_1 to t_2 . An Arrhenius plot for k_e over a temperature range from 413 to 453 K is shown in Figure 9. A summary of the reaction rate constants at the temperatures studied is provided in Table II.

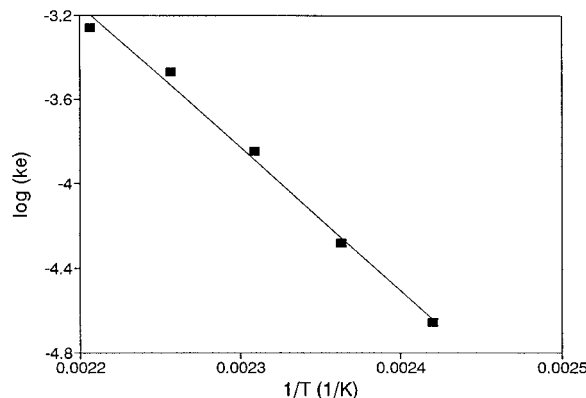


Figure 9 Arrhenius plot of k_e for the TGDDM/mAnil system having a 2 : 1 equivalent ratio (epoxide/amine).

DISCUSSION

It is evident from the experimental results that even in the 2 : 1 system where epoxide groups are in excess, the etherification reaction is still much slower than the noncatalytic amine addition reaction over the temperature range studied. The ratio of the rate constant of noncatalytic amine addition (k') to that of etherification (k_e) is plotted as a function of temperature in Figure 10. Obviously, the etherification reaction only becomes significant at high reaction temperatures. This is consistent with data reported in the literature.^{20,21} The values of k_e obtained in this study are comparable with those reported by Mijovic and Wijaya for the PGE/DDS system.²² Based on the data reported by Morgan and Mones,¹² Chiao⁷ studied the etherification of a TGDDM/DDS cure system. The values of k_e obtained by Chiao were about one order of magnitude larger than the ones obtained in this study, which most likely is a consequence of utilizing $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$ as a catalyst in that study.

Table II Values of Rate Constants and Activation Energies for the TGDDM/mAnil Reactions

Reaction Constant	413 K	423 K	433 K	443 K	453 K	E^a	k_0^b
$k_e'^b$	0.00038	0.000577	0.001056	0.002066	0.003037	20.20 ± 1.09	1.72×10^7
k^b	0.005374	0.006952	0.008367	0.010443	0.011805	7.39 ± 0.37	44.45
k_e^b	2.2×10^{-5}	5.25×10^{-5}	0.000143	0.000342	0.000551	30.97 ± 1.62	5.47×10^{11}

^a In kcal/mol.

^b In $\text{kg}^2 \text{mol}^{-2} \text{min}^{-1}$.

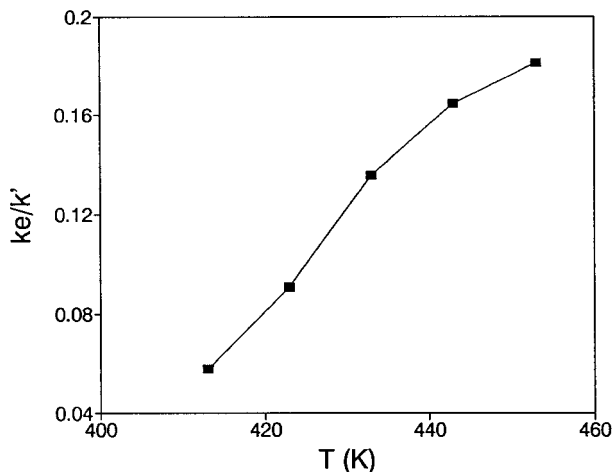


Figure 10 k_e/k' versus time.

CONCLUSION

The cure reactions between TGDDM and mAnil were studied. Due to the existence of tertiary amine groups within the TGDDM molecules, TGDDM/mAnil systems are more likely to exhibit significant etherification reaction as compared to other epoxy resin systems without intramolecular tertiary amine groups. From *in situ* NIR FTIR experiments, it was found that the etherification reaction occurs in both systems having 2 : 1 and 1 : 1 equivalent ratios (epoxide/amine). When the epoxide is in excess, the etherification reaction is much more significant.

The previously proposed mechanistic model fits well the NIR data for the amine addition reaction. The differences between the experimental and predicted rate data observed at the later stages of reaction in the system having 1 : 1 (epoxide/amine) equivalent ratio are attributed to the effect of diffusion limitations. The etherification reaction was assumed to be catalyzed by the tertiary amine groups. Arrhenius temperature dependence is observed for all three reaction rate constants, k' , k , and k_e , measured over the temperature range studied (413 to 453 K). It has been found that the etherification reaction is several times slower than the noncatalytic amine addition

reaction, even with a 2 : 1 (epoxide/amine) equivalent ratio.

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REFERENCES

1. L. Xu, J. H. Fu, and J. R. Schlup, *J. Am. Chem. Soc.*, **116**, 2821 (1994).
2. L. Xu, J. H. Fu, and J. R. Schlup, *Ind. Eng. Chem. Res.*, **35**, 963 (1996).
3. U. M. Bokare and S. K. Ghandi, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 857 (1980).
4. K. Dusek, *Polym. Bull.*, **13**, 321 (1985).
5. C. C. Riccardi and R. J. J. Williams, in *Crosslinked Epoxies, Proc. 9th Discuss. Conf.*, B. Sedlacek and J. Kahovec, Eds., Walter de Gruyter, Berlin, 1987, p. 291.
6. K. Fryauf, V. Strehmel, and M. Fedtke, *Polymer*, **34**, 327 (1993).
7. L. Chiao, *Macromolecules*, **23**, 1286 (1990).
8. K. C. Cole, *Macromolecules*, **24**, 3093 (1991).
9. K. C. Cole, J.-J. Hechler, and D. Noel, *Macromolecules*, **24**, 3098 (1991).
10. N. A. St. John and G. A. George, *Polymer*, **33**, 2679 (1992).
11. L. Matejka and K. Dusek, *Macromolecules*, **22**, 2902 (1989).
12. R. J. Morgan and E. T. Mones, *J. Appl. Polym. Sci.*, **33**, 999 (1987).
13. B. A. Rozenberg, *Adv. Polym. Sci.*, **75**, 113 (1986).
14. I. T. Smith, *Polymer*, **2**, 95 (1961).
15. Y. Tanaka, N. Tomio, and H. Kakuichi, *J. Macromol. Sci.*, **A1**, 471 (1967).
16. A. M. Eastman, B. de B. Darwent, and P. E. Beaubien, *Can. J. Chem.*, **29**, 575 (1951).
17. W. G. Potter, *Epoxide Resins*, The Plastic Institute, Iliffe Books, London, 1970, p. 37.
18. L. Shechter, J. Wynstra, and R. P. Kurkky, *Ind. Eng. Chem.*, **48**, 94 (1956).
19. J. H. Fu and J. R. Schlup, *J. Appl. Polym. Sci.*, **49**, 219 (1993).
20. W. X. Zukas, N. S. Schneider, and W. J. Macknight, *Polym. Mater. Sci. Eng.*, **49**, 588 (1983).
21. C. C. Riccardi and R. J. J. Williams, *J. Appl. Polym. Sci.*, **32**, 3445 (1986).
22. J. Mijovic and J. Wijaya, *Polymer*, **35**, 2683 (1994).