

Cure kinetics of elementary reactions of a diglycidyl ether of bisphenol A/ diaminodiphenylsulfone epoxy resin: 2. Conversion *versus* time

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The kinetics of the elementary reactions (primary amine-epoxy and secondary amine-epoxy) in addition to the overall reaction have been studied in a diglycidyl ether of bisphenol A (DGEBA) epoxy resin system, cured with diaminodiphenylsulfone (DDS) hardener. The conversion *versus* time data for the elementary reactions and for the overall reaction were obtained by monitoring the changes in concentration of epoxy, primary and secondary amine groups during cure using near-infra-red spectroscopy. The data were evaluated using *n*th-order and autocatalytic kinetic models. The primary amine-epoxy reaction (linear polymerization) was described well by the *n*th-order kinetic model over the whole range of conversion of the primary amine, whereas the secondary amine-epoxy reaction was described by both the *n*th-order kinetic and first-order autocatalytic models in the ranges of initial 30% conversion at 130°C cure, and 80% conversion at 205°C cure. The kinetic parameters for each reaction were also obtained. The reactivity ratio of the secondary amine to the primary amine for a non-catalysed reaction increased with increasing cure temperature, whereas the opposite trend was observed for the autocatalysed reaction.

(Keywords: epoxy resin; elementary reactions; cure kinetics)

INTRODUCTION

Depending on the reactivity characteristics of epoxy systems, various kinetic models have been proposed¹⁻⁴. In general, the kinetic models are either phenomenological or mechanistic, based on the elementary reactions⁵. The existing kinetic models for epoxy systems are mostly based on experimental data obtained from differential scanning calorimetry (d.s.c.), solid-state ¹³C nuclear magnetic resonance (n.m.r.)^{6,7} or Fourier-transform infra-red spectroscopy (FTi.r.)⁸⁻¹¹. However, d.s.c. gives only overall cure kinetics from measuring the heat of the reaction (enthalpy) as a bulk phenomenon and requires assumptions about the enthalpies of elementary reactions. N.m.r. and FTi.r. techniques generally cannot detect the individual conversions of the complex elementary reactions involved in the epoxy systems. In this respect the existing kinetic models are mostly phenomenological models, which represent only the overall conversion as a function of cure time and temperature. But the progress of the elementary reactions may affect the structure and properties of a curing epoxy system in different ways, a phenomenon that we observed in our previous study¹². In order to predict the cure behaviour accurately, and to control the properties of systems by arresting the structure at an appropriate cure time, a mechanistic

kinetic model, based on progress of elementary reactions, is needed.

In previous publications^{12,13} we have established the reaction mechanisms of a diglycidyl ether of bisphenol A/diaminodiphenylsulfone (DGEBA/DDS) epoxy system by measuring the changes in the concentrations of the functional groups (epoxy, primary and secondary amine groups) during the cure. Furthermore, a model, describing T_g as a function of conversions of elementary reactions (primary amine-epoxy reaction \equiv linear polymerization reaction, and secondary amine-epoxy reaction \equiv cross-linking reaction), has been established. Recently, St John and George¹⁴ have modelled the kinetics of the tetraglycidyl-diaminodiphenylmethane / diaminodiphenylsulfone (TGDDM/DDS) epoxy system mechanistically by monitoring the elementary reactions using near-infrared (n.i.r.) spectroscopy. They observed an autocatalytic reaction mechanism for both the primary amine-epoxy and the secondary amine-epoxy reactions. In this study, a mechanistic kinetic model for the DGEBA/DDS epoxy system is described using the conversion *versus* time data for the elementary reactions and includes the calculated kinetic parameters for each reaction.

THEORETICAL BACKGROUND

The isothermal cure kinetics for an *n*th-order reaction is described (in a general form) by the following

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conventional equation:

$$r = \frac{d\alpha}{dt} = k(1-\alpha)^n \quad (1)$$

where r is the rate of the reaction, α is the conversion (fractional), and n is the order of the reaction, which can be obtained from the slope of the plot of $\ln r$ versus $\ln(1-\alpha)$. The apparent rate constant, k , is usually expressed in an Arrhenius form:

$$k = A \exp(-E_a/RT) \quad (2)$$

The kinetic parameters, namely the pre-exponential factor (A), and the apparent activation energy (E_a), can be determined by plotting $\ln(k)$ against the inverse of absolute temperature, $(1/T)$. R is the universal gas constant.

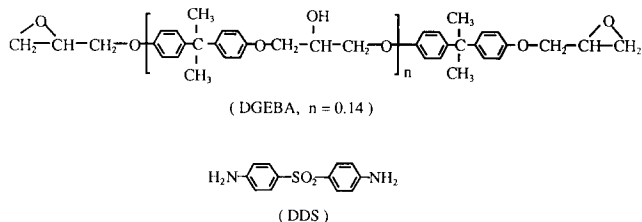
The cure of epoxy resins has been frequently considered as an autocatalytic reaction between the epoxy and amine groups. The general kinetic equation that has been used to describe the autocatalytic reaction is as follows¹:

$$r = (k_1 + k_2\alpha^m)(1-\alpha)^n \quad (3)$$

where k_1 and k_2 are the apparent rate constants for the non-catalysed and the autocatalysed reactions respectively, and m and n are the constants related to the order of the reactions. Horie *et al.*¹ assumed that the reactivities of the primary amine and secondary amine groups are equivalent ($k_2/k_1=0.5$) and they derived the values $m=1$ and $n=2$. Sourour *et al.*^{2,15} used the same equation for their diglycidyl ether of bisphenol A/*m*-phenylenediamine (DGEBA/MPD) system with the values $m=n=1$. Ryan and Dutta¹⁶ proposed the value $m+n=2$. When $m=1$, the kinetic parameters for non-catalysed reaction and autocatalysed reaction can be obtained from the plots of $r/(1-\alpha)^n$ versus α and $\ln(k_1)$ and $\ln(k_2)$ versus inverse absolute temperature, in a similar manner as described above for the n th-order kinetic model.

EXPERIMENTAL

The epoxy resin used in this study was the diglycidyl ether of bisphenol A (DGEBA; Epikote 8283, Shell chemicals, $M_n=380$, liquid) and the amine curing agent was 4,4'-diaminodiphenylsulfone (DDS; Anchor chemicals, $M_n=248$, powder). The chemical structures of these are as follows:



An intimate mixture of DGEBA and DDS in stoichiometric (1:1) ratio, based on the functionality of the two monomers, was prepared in a rotary evaporator under vacuum starting from a temperature of 80°C and finishing at 120°C. In order to minimize chemical reaction between the monomers during the mixing process, the heating time was limited to less than 30 min. The flask was rotated at a constant speed during the process. When the temperature reached 120°C, the mixture became a

clear transparent solution. At that point set volumes of the mixtures were cast into aluminium foil cups to form discs of about 15 mm diameter and 2 mm thickness. The samples were placed in an air oven at two different temperatures, 130 and 205°C, for various intervals so that different degrees of cure were achieved. Samples prepared in this way were used for n.i.r. studies.

The i.r. absorption spectra of the samples with various degrees of conversion were recorded by an Alpha Centauri FTIR Spectrophotometer (Mattson Instruments Inc., USA) in the region from 11 000 to 4000 cm^{-1} . The operating conditions for obtaining the spectra involved 32 scans at a resolution of 8 cm^{-1} . The conversions of epoxy, primary and secondary amine groups were obtained as a function of cure time by quantifying the changes in their concentrations during the cure using the analysis methods reported in our previous paper¹³. The conversion versus time data for epoxy, primary amine and secondary amine groups were individually analysed by both an n th-order kinetic equation and an autocatalytic kinetic equation.

RESULTS AND DISCUSSION

To perform the kinetic analysis, analytical equations that express the conversion in terms of time were derived by applying a fourth-order polynomial fit to the experimental data. The analytical expressions and their differentials were used to obtain the necessary data, such as conversion (α), rate of the reaction (r), $\ln r$, $\ln(1-\alpha)$ and $\ln(1-\alpha)^n$ as a function of time, for calculating the kinetic parameters. The conversion versus time data for epoxy (overall reaction), primary amine (linear polymerization) and secondary amine (crosslinking reaction), at two different cure temperatures (130 and 205°C), are shown in Figure 1. It shows that the primary amine conversion is achieved mainly in the early stages of cure, while that of the secondary amine is achieved at a later stage, regardless of cure temperature. The reaction mechanisms of the present system were reported in detail in our preceding paper¹³. In Figure 2 the rates of reactions are shown comparatively as a function of cure time and also as a function of epoxy conversion (system conversion). The rates at high temperature, shown in Figures 2b and 2d, are noticeably higher compared to those at low temperatures in Figures 2a and 2c. The rate of the reaction for primary amine is relatively high in the early stage of the cure and rapidly decreases as the cure progresses, whereas that for the secondary amine is essentially stable up to 75% epoxy conversion and then rapidly drops (see Figures 2c and 2d). For the high-temperature cure (see Figures 2b and 2d) the stability of the rate of the reaction for secondary amine is slightly lower than for the low-temperature cure, shown in Figures 2a and 2c. The rate of reaction for epoxy group is intermediate, as expected.

The experimental data were first evaluated by the n th-order cure kinetic model described in equation (1). The plots of $\ln r$ versus $\ln(1-\alpha)$ for epoxy, primary amine and secondary amine are presented in Figure 3. For n th-order kinetics the plots should be linear with a slope of n and an intercept of $\ln k$. It can be seen that the plot for primary amine is remarkably linear over the whole range of conversion at both 130 and 205°C. This implies that the primary amine-epoxy reaction is a non-catalysed

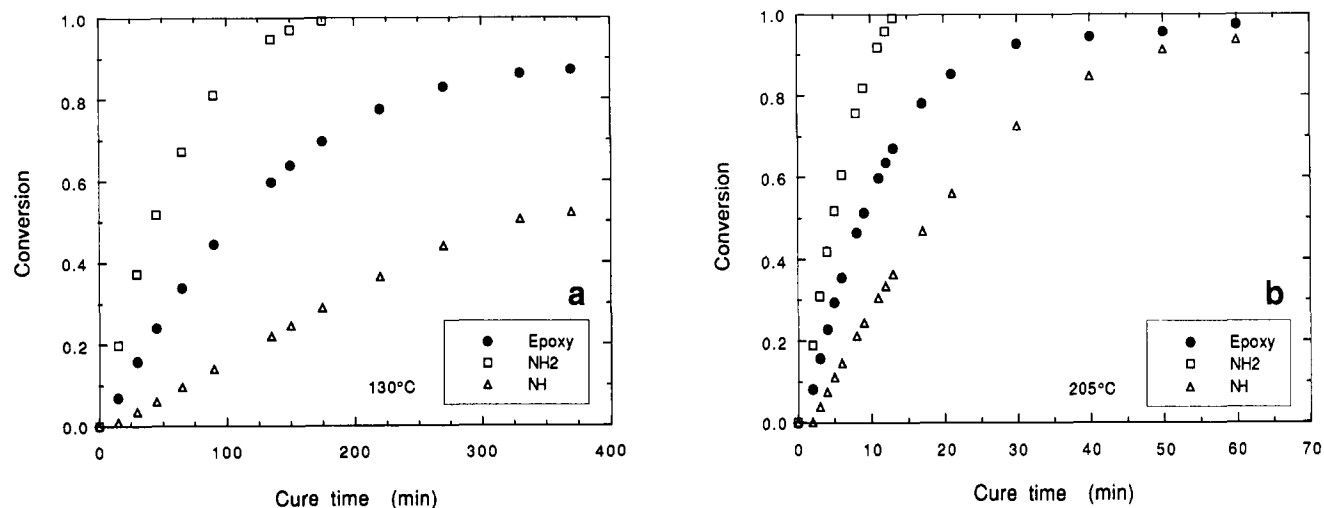


Figure 1 Plot of conversion versus time for overall (epoxy) and elementary (primary and secondary amines) reactions in the DGEBA/DDS epoxy system, cured respectively at (a) 130°C and (b) 205°C

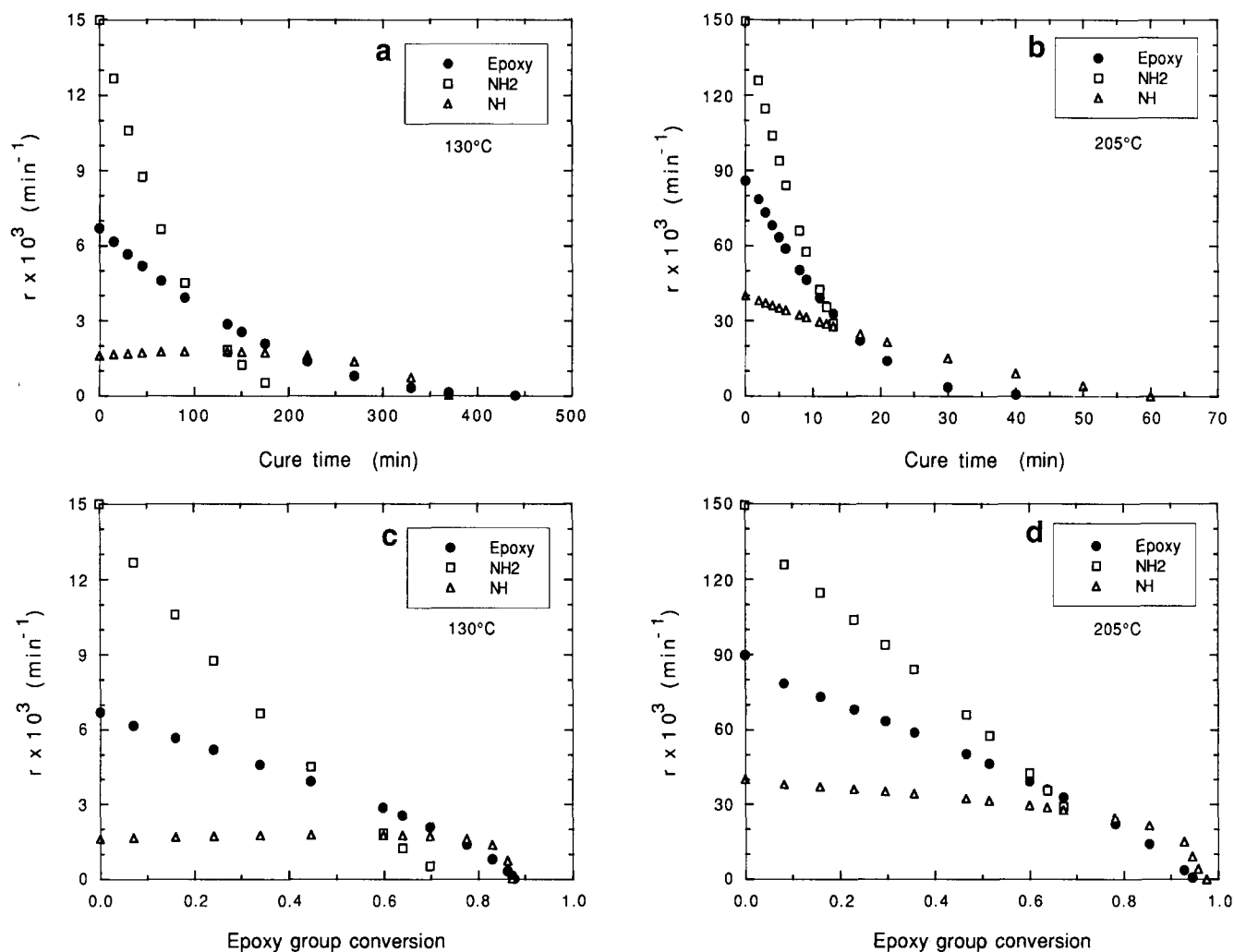


Figure 2 Plot of the reaction rate (r) versus time ((a) and (b)) and versus overall conversion ((c) and (d)) for overall and elementary reactions in the DGEBA/DDS epoxy system. Cure temperature was 130°C for (a) and (c), and 205°C for (b) and (d) respectively

reaction. On the other hand, the plot for the secondary amine reaction is linear only within the initial 30% of the secondary amine conversion at 130°C, and up to 80% at 205°C, implying that the secondary amine-epoxy reaction is not so much a non-catalysed reaction (as observed in the primary amine-epoxy reaction) but is

more nearly an autocatalysed reaction, especially at low temperature. The greater persistence of the linear portion with increasing temperature (see Figure 3b) is also noteworthy, implying that the cure temperature may promote the secondary amine-epoxy reactions, presumably by decreasing the system viscosity. Therefore

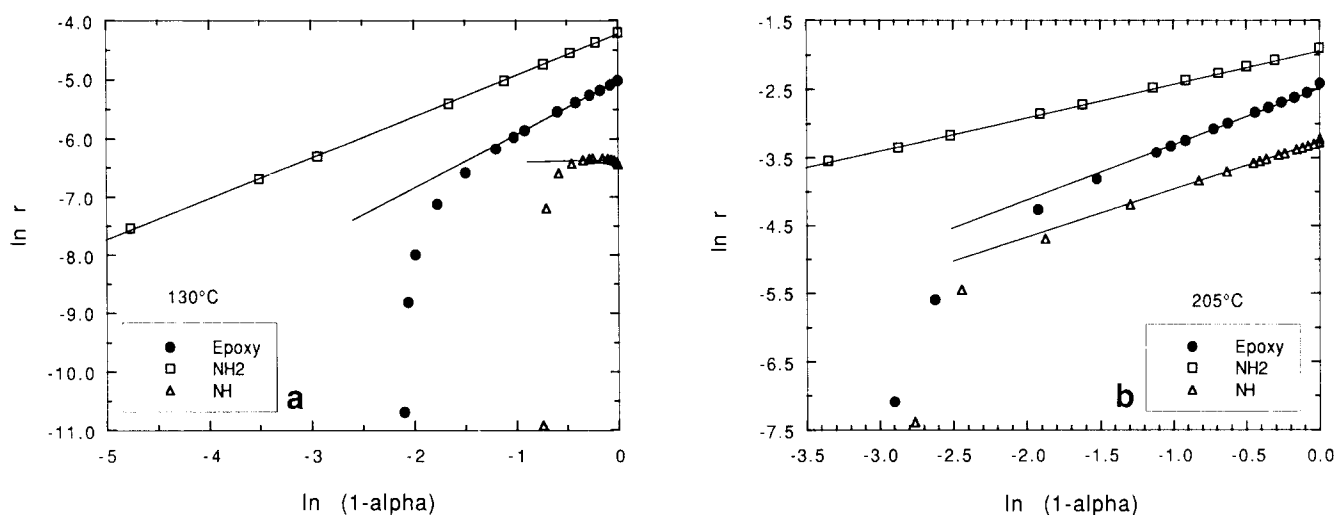


Figure 3 Plot of $\ln r$ versus $\ln(1-\alpha)$ for overall and elementary reactions. Cure temperature was 130°C for (a) and 205°C for (b). The straight line expresses the fit with the n th-order kinetic model. The order of the reaction, n , and $\ln k$ were obtained from the slope and the intercept of the plot respectively

at high temperature the secondary amine becomes more reactive. The plot of $\ln r$ versus $\ln(1-\alpha)$ for epoxy again follows an intermediate pathway. The deviation from linearity in the plot for epoxy is due to the deviation of the plot of secondary amine-epoxy reaction. The order of reaction, n , and the apparent rate constant, k , for each reaction have been obtained from the slope and intercept of the respective plot in Figure 3. The graph of $\ln k$ versus $1/T$, which is used to derive the other kinetic parameters in equation (2), is shown in Figure 4. E_a and $\ln A$ are obtained from the slope ($-E_a/R$) and intercept respectively. The data for the n th-order kinetic parameters for DGEBA/DDS system are given in Table 1. The reactivity ratio of secondary amine to primary amine is 0.12 at the 130°C cure and 0.26 at the 205°C cure. When the reactivities of the primary amine and secondary amine are equivalent, the ratio becomes 0.5¹. Therefore the values obtained indicate that the primary amine is more reactive than the secondary amine, approximately four times at 130°C and two times at 205°C. This result supports our earlier observation that the reactivity of the secondary amine increases more rapidly than that of the primary amine with increasing cure temperature. This results in the reduction of the difference in reactivity between primary and secondary amines. The activation energy, E_a , is higher for the secondary amine-epoxy reaction than for the primary amine reaction (66 vs. 49 kJ mol⁻¹). The overall activation energy of 54.4 kJ mol⁻¹ is considered as the average value.

To analyse the conversion versus time data for epoxy, primary and secondary amine groups, the autocatalytic model in equation (3) was used with $m=1$ and different values of n (1, 2 and 3). The plots of the reduced rate, $r/(1-\alpha)^n$, against α are shown in Figure 5. If the reaction is autocatalytic, then the plot should be linear, with a slope of k_2 and an intercept of k_1 . The best fit is obtained with $n=1$ (see Figures 5a-f). The fit of the data for the secondary amine-epoxy reaction is in similar ranges to that observed in the fit of n th-order kinetics (approximately up to 30% conversion at 130°C in Figure 5e and up to 85% conversion at 205°C in Figure 5f). However, the data for the primary amine-epoxy reaction, which was described well by the

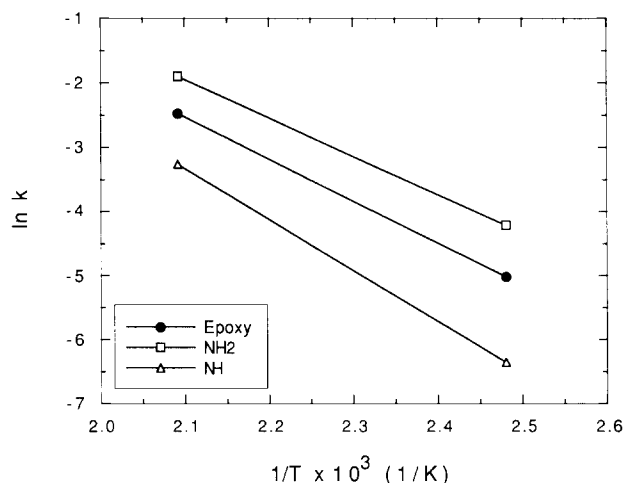


Figure 4 Plot of $\ln k$ versus $1/T$ for overall and elementary reactions. The n th-order kinetic parameters, E and $\ln A$, were obtained from the slope and the intercept of the plot respectively

Table 1 The n th-order kinetic parameters for elementary reactions of a stoichiometric DGEBA/DDS epoxy system

Parameters	n	$k \times 10^3$ (min ⁻¹)	Fit range in α	E_a (kJ mol ⁻¹)	$\ln A$
Epoxy					
130°C	0.914	6.3	0 to 0.70	54	11.2
205°C	0.833	84.6	0 to 0.75		
NH ₂					
130°C	0.703	14.8	0 to 1.00	49	10.5
205°C	0.491	150.1	0 to 1.00		
NH					
130°C	0	1.7	0 to 0.30	66	13.4
205°C	0.703	38.5	0 to 0.80		

n th-order kinetics, can only fit the autocatalytic model in the initial stages of conversion, less than 50% (see Figures 5c and 5d). The apparent rate constants for the non-catalysed reaction and the autocatalysed reaction are listed in Table 2. It shows that the value for the non-catalysed reaction is always higher than that for

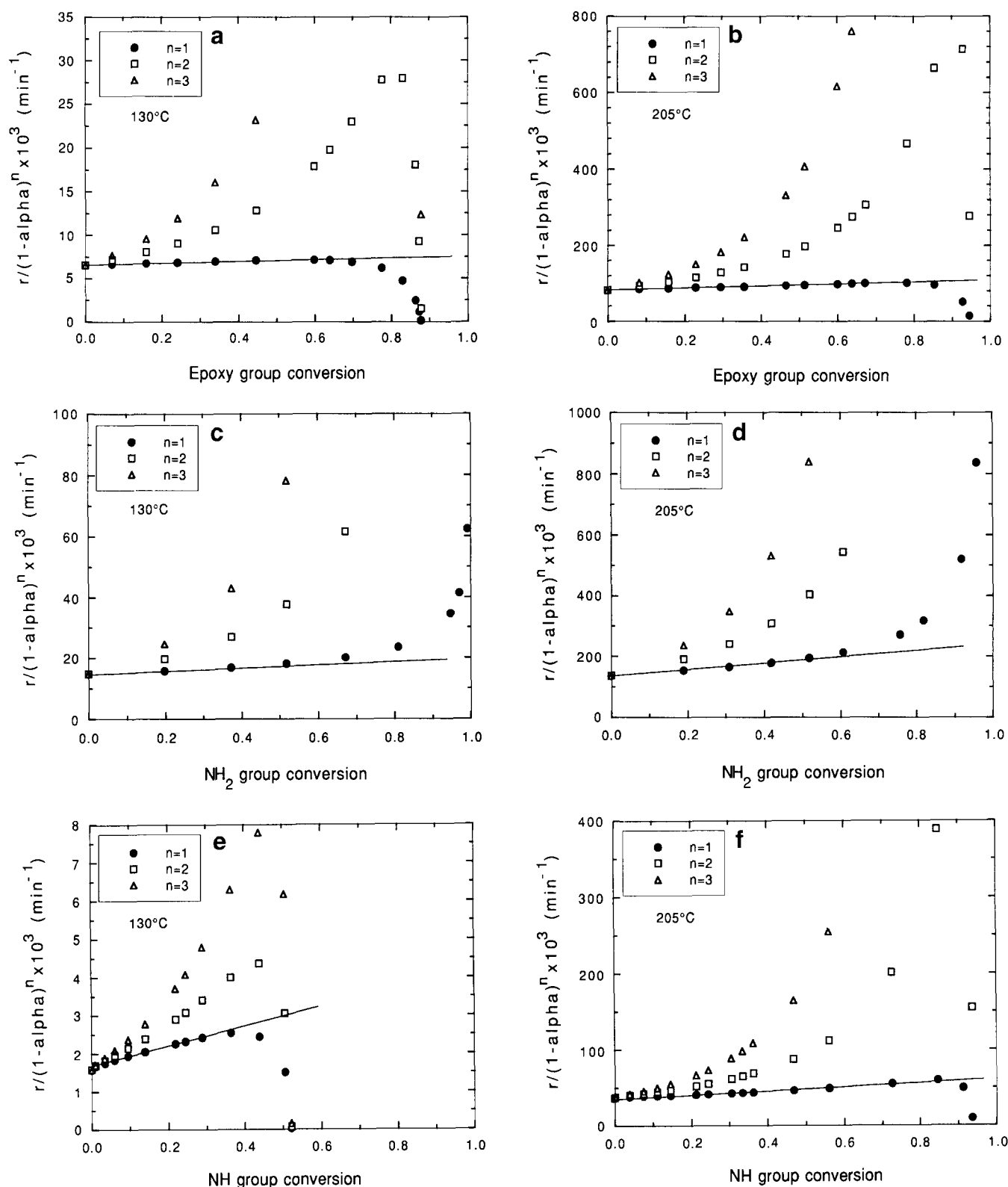


Figure 5 Plot of the reduced rate ($r/(1-\alpha)^n$) versus conversion for overall ((a) and (b)) and elementary ((c)–(f)) reactions. The straight line expresses the fit with the autocatalytic kinetic model when $n=1$

the autocatalysed reaction, except for the secondary amine–epoxy reaction at low temperature (130°C), where the opposite trend is observed. The anomalous phenomenon observed in the secondary amine–epoxy reaction at low temperature indicates that the secondary amine reacts with epoxy more easily through an autocatalysed reaction than through a non-catalysed reaction when the system viscosity is high. It is also

noteworthy that the reactivity ratio of secondary to primary amine for the non-catalysed reaction (k_1 for the secondary amine–epoxy reaction versus k_1 for the primary amine–epoxy reaction) is 0.11 at 130°C and 0.27 at 205°C, which agree well with the values obtained from the n th-order kinetic model (0.12 at 130°C and 0.26 at 205°C). Meanwhile, the reactivity ratio for the autocatalysed reaction (k_2 for the secondary amine–epoxy reaction

Table 2 The autocatalytic kinetic parameters for elementary reactions of a stoichiometric DGEBA/DDS epoxy system^a

Parameters	$k_1 \times 10^3$ (min ⁻¹)	$k_2 \times 10^3$ (min ⁻¹)	Fit range in α	E (kJ mol ⁻¹)	ln A
Epoxy					
130°C	6.5	1.3	0 to 0.60		
205°C	81.7	27.8	0 to 0.75	54 (65)	11.1 (12.7)
NH ₂					
130°C	14.7	4.8	0 to 0.40		
205°C	137.5	114.8	0 to 0.50	48 (68)	10.0 (14.9)
NH					
130°C	1.7	2.6	0 to 0.30		
205°C	37.2	22.1	0 to 0.85	66 (46)	13.4 (7.74)

^aThe data in parentheses are for the autocatalysed reaction, derived from the plots of $\ln k_2$ versus $1/T$

versus k_2 for the primary amine–epoxy reaction) is 0.54 at 130°C and 0.19 at 205°C, which show that the reactivities of the primary and secondary amines are equivalent at low temperature whereas at high temperature the reactivity of the primary amine is about 2.6 times higher than that of the secondary amine. This result supports the exceptionally higher rate constant for the autocatalysed secondary amine–epoxy reaction (2.6) than that for the non-catalysed reaction (1.7), at low-temperature cure. On the other hand, in the phenomenological kinetic analysis, the reactivity ratio is often estimated from the rate constants for bulk reactions (overall reaction, epoxy reaction in this study)¹. The ratio for bulk reactions (k_2/k_1 , where k_1 and k_2 are for the epoxy reaction) in our system is 0.2 at 130°C and 0.33 at 205°C. The value of 0.2 at 130°C comes between the values of 0.11 for the non-catalysed reaction and 0.54 for the autocatalysed reaction, but closer to the value for the non-catalysed reaction. However, the value of 0.33 at 205°C is higher than both values; 0.27 for the non-catalysed reaction and 0.19 for the autocatalysed reaction. These observations can be important evidence showing that the approach, used to estimate the value of the reactivity ratio from the rate constants for bulk reactions, may result in overestimation, especially for a high-temperature cure system.

The data of the activation energy (E_a) and the pre-exponential factor (A) for the autocatalytic model were derived from Figure 6 and are given in Table 2. The values of the activation energy for the non-catalysed reaction, 54, 48 and 66 kJ mol⁻¹ for epoxy, primary amine and secondary amine reactions respectively, are in good agreement with the values of 54, 49 and 66 kJ mol⁻¹ obtained from the n th-order kinetic analysis. In addition, the activation energy for the autocatalysed reaction is higher than that for the non-catalysed reaction in the primary amine–epoxy reaction, whereas the opposite trend is seen in the secondary amine–epoxy reaction. The activation energies for the non-catalysed and autocatalysed bulk reactions, 54 and 65 kJ mol⁻¹ respectively, differ significantly from the values of 85.3 and 42.8 kJ mol⁻¹ reported by Barton³ for a similar DGEBA/DDS system.

Finally, the experimental data for r versus α for epoxy, primary and secondary amine reactions are compared in Figure 7 with the data obtained using the kinetic models in equations (1) and (3) with the values of the mechanistic kinetic parameters obtained. It can be seen that the

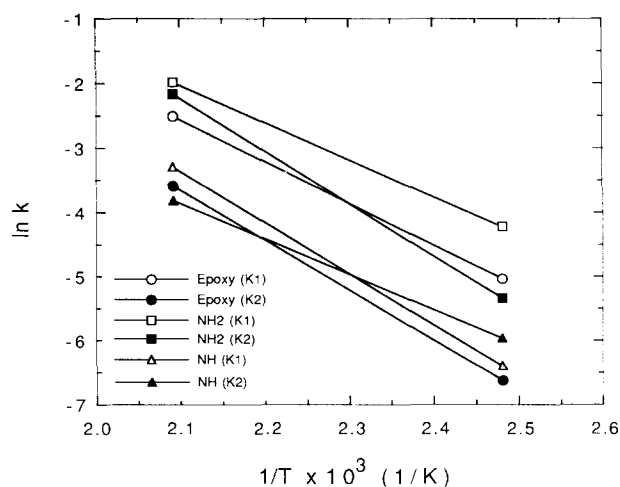


Figure 6 Plot of $\ln k_1$ and $\ln k_2$ against $1/T$ for overall and elementary reactions. The kinetic parameters, E and $\ln A$, for non-catalysed and autocatalysed reactions were obtained from the slope and the intercept of the plots respectively

primary amine–epoxy reaction is described well by the proposed n th-order kinetic model (see Figures 7c and 7d) whereas the secondary amine–epoxy reaction is described better by the autocatalytic model (see Figures 7e and 7f). The comparison of the reaction pathways of these elementary reactions to that for epoxy reaction, shown in Figures 7a and 7b, suggests that the autocatalytic reaction phenomenon, which has frequently been observed at the later stage of the cure, is mainly due to the autocatalytic reaction characteristic of the secondary amine–epoxy reaction.

CONCLUSIONS

The cure kinetics for the elementary reactions (primary amine–epoxy and secondary amine–epoxy reactions) in addition to that for the overall reaction that occur in a stoichiometric DGEBA/DDS system were investigated in terms of individual molecular mechanisms. The conversion versus time data for each reaction were analysed by both an n th-order and an autocatalytic kinetic model. The primary amine–epoxy reaction was described well by the n th-order kinetic model over the whole range of conversion, whereas the secondary amine–epoxy reaction was described by both kinetic

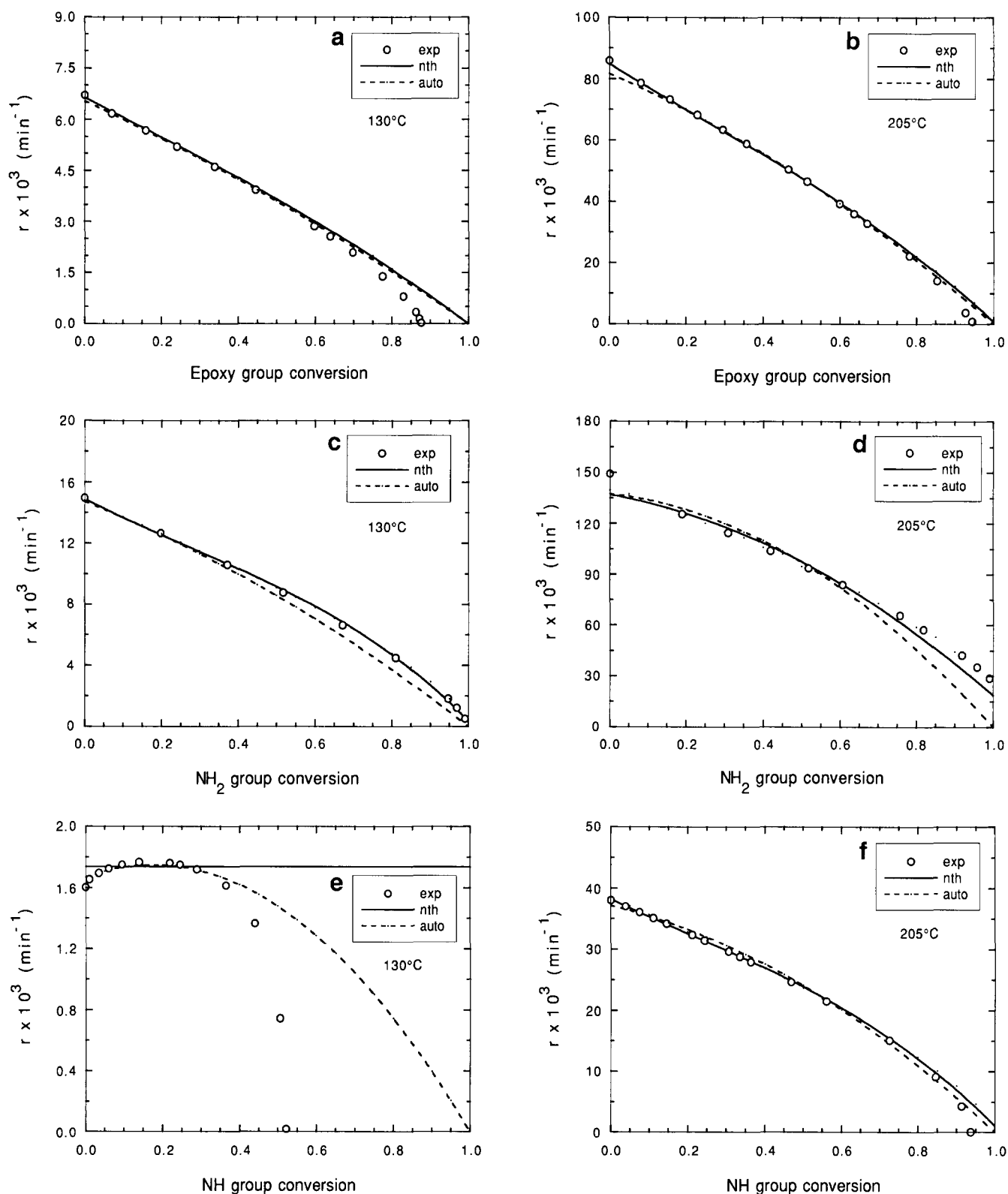


Figure 7 The comparison plot of the experimental r versus α data for overall ((a) and (b)) and elementary ((c)–(f)) reactions with those predicted from the proposed n th-order kinetic (equation (1)) and first-order autocatalytic kinetic models (equation (3))

models only in limited ranges. The reactivity ratio of the secondary to primary amine for the non-catalysed reaction increased with increasing cure temperature, whereas the opposite trend was observed for the autocatalysed reaction. Finally, this mechanistic analysis, based on the details of elementary reactions, revealed new aspects of the reaction pathways that could not have been detailed by the phenomenological kinetic analysis.

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