Curing Kinetics of Epoxy-Urethane Copolymers

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ABSTRACT: The cure of the epoxy resin diglycidyl ether of bisphenol A (Araldyt GY9527) with a mixture of cycloaliphatic amines (Distraltec) was studied, and the focus was on the effect of the copolymerization with a commercial polyurethane (PU) elastomer (Desmocap 12). A simplified phenomenological model was proposed to represent the copolymerization reaction. It considered the effect of the temperature and the concentration of the elastomer on the reaction rate, and it was simple enough to be included in models of processing conditions. A nonlinear regression analysis of the experimental conversion data obtained from differential scanning calorimetry was utilized to find the best fitting parameters to Kamal's equation for the chemically controlled part of the reaction (short times) under isothermal and constant heating-rate conditions. The Rabinowitch approach together with the Addam–Gibbs theory was utilized to introduce the effect of diffusion control at the end of the reaction on the overall constant for the reaction rate. The Di Benedetto equation was used to predict the conversion at which vitrification takes place for each run. Experimental results for conversions higher than this critical conversion were utilized to obtain information about the diffusion kinetic constant using a nonlinear regression analysis as previously. The overall model obtained was used to calculate a calorimetric conversion and reaction rate as functions of time, which was in excellent agreement with the experimental results. The addition of PU elastomers affected the values of the activation energies of the chemically and diffusion controlled parts of the reaction, as well as the final conversion reached by the epoxy–amine system. The proposed model allowed prediction of all the observed features using parameters that were independent of the temperature of the curing reaction. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1771–1779, 2001

Key words: epoxy–amine; modified epoxy resins; polyurethane modifiers; curing kinetics; diffusion control

INTRODUCTION

Among thermoset materials, epoxy–amine networks have received considerable attention from the basic and applied research fields. From a basic point of view, they offer an interesting research field for chemists[1,2] or materials researchers studying the relations between the structure–morphology and the final properties.[3,4] The commercial interest in these thermosets is due to their various applications as adhesives, coatings, or structural materials (matrices for high performance composites). However, because of their intrinsic low impact resistance, they have been frequently combined with elastomeric second phases to improve that response. In this work, an epoxy resin is copolymerized with a cycloaliphatic amine and a

minor addition of a polyurethane (PU) elastomer.

Different approaches for the study of network formation from purely mechanistic ones to the phenomenological type appear in the literature. Some of the latter models include the effect of the vitrification of the system at relatively low curing temperatures. This was done using a fictitious advance of the reaction, $\zeta = x/x_{max}$, where x_{max} is the maximum conversion reached at a given curing temperature. These models can be used under only isothermal conditions, because the value of x_{max} is a constant that depends on the curing temperature.[5] The other type of approach requires the inclusion of the diffusion control at high conversions in the overall kinetic rate constant. This was done previously using Williams–Landel–Ferry types of equations or equations that include the overcoming of an energy barrier for diffusion.[6,7] However, there are not many published results indicating that the same kinetic parameters obtained from isothermal runs can also be used satisfactorily in the prediction of nonisothermal curing conditions. This is an important point to consider for the modeling of reactive processes, where temperature profiles are usually developed in the piece.

In the present work, a simplified phenomenological model is proposed to represent the copolymerization reaction. It includes the effect of diffusion control and can represent isothermal and nonisothermal curing reaction conditions equally well. The model together with the numerical method used to find the corresponding kinetic parameters allow the calculation of the overall reaction rates in the neat system and also in the elastomer modified epoxy–amine networks. The trends showed by the calculated parameters can be related to physical features of the reactive mixtures being considered.

Theoretical Background

The curing of epoxy resins with amines is frequently modeled using Kamal and Sourour's kinetic expression for the reaction rate.[8,9]

$$\frac{dx}{dt} = (k_1 + k_2 x^m)(1 - x)^n \tag{1}$$

This type of equation is very useful in describing systems where there is a maximum in the isothermal reaction rate at a time larger than zero. This is a characteristic of autocatalytic processes, such as that of the cure of an epoxy resin with an amine. In this case the reaction is being catalyzed by the presence of OH groups, which are generally present in very small amounts at the beginning of the reaction and are further generated during the reaction of curing.

If the noncatalyzed path of the reaction is negligible with respect to the autocatalyzed path, then the above expression can be simplified to

$$\frac{dx}{dt} = k_c x^m (1 - x)^n \tag{2}$$

where the constant $k_1 = 0$. This model requires the use of a "seed" to be numerically solved (an initial conversion), whose size may be of importance, depending of the rate of the reaction. (It may shift the curve of conversion vs. time on the time scale.) In this case the initial conversion (seed at time = 0) was taken as 10^{-9}. Lower values of the initial conversion did not produce changes in the fitting parameters obtained from the nonlinear regression analysis nor in the predictions obtained by integration of the expression of the rate of reaction in the complete model.

Another usual simplification of the kinetic expression as applied to epoxy–amine curing is the assumption that the sum of the exponents in eq. (2) must be 2, as in[10,11]

$$\frac{dx}{dt} = k_c x^m (1 - x)^{2-m} \tag{3}$$

These models are flexible enough to give good fitting curves for the autocatalytic regime of the reaction. Isothermal runs are usually utilized to obtain the kinetic constants at fixed temperatures, and then an Arrhenius type of equation is used to represent the functionality of k_c with temperature. A nonlinear regression analysis, based on the Marquardt method, was used on the experimental data, which allowed us to include nonisothermal runs (i.e., dynamic runs at 10°C/min). With this approach the set of kinetic parameters found can reproduce isothermal and nonisothermal curing conditions very efficiently if the reaction does not become diffusion controlled at high conversions.

As discussed previously in the literature, epoxy–amine systems cured under isothermal conditions may not reach complete conversion because the reactive mixture may reach vitrification

at a lower conversion if the curing temperature is lower than the glass-transition temperature of the completely cured system ($T_{g\infty}$). In that case, the reaction becomes diffusion controlled. Different approaches were proposed to deal with this effect. The Rabinowitch model has the simplicity of considering that the overall time for the reaction is the sum of the time for the diffusion of the reactants and the time for the chemical reaction.[6]

$$\frac{1}{k_o(T, x)} = \frac{1}{k_c(T)} + \frac{1}{k_d(T, x)} \qquad (4)$$

where k_c and k_d are the rate constants of the chemically and diffusion controlled reaction steps, respectively; and k_o is the overall rate constant of the reaction.

This equation shows that the overall rate constant is governed at the beginning of the reaction by the kinetic rate constant (before vitrification) and at the end of the reaction by the diffusion rate constant (after vitrification) when the diffusion of the chemical reactants becomes the limiting step. The constant k_o is then used in eqs. (2) or (3) to replace the value of k_c, and the expression obtained by this procedure is valid for the entire conversion range:

$$\frac{dx}{dt} = k_o x^m (1 - x)^{2-m} \qquad (5)$$

The Addam–Gibbs theory was selected to represent the temperature dependence of the diffusion rate constant. In this approach the molecular mobility is assumed to be the consequence of a cooperative rearrangement of structural units due to thermal fluctuations, which allows the overcoming of the energy barrier that separates the initial and final conformation. Their treatment leads to the following expression:

$$\ln k_d = \ln k_{d0} - \frac{s}{T_c \ln\left(\dfrac{T_c}{T_g - 50}\right)} \qquad (6)$$

with

$$s = \frac{E_d \ln 2}{\Delta C_P}$$
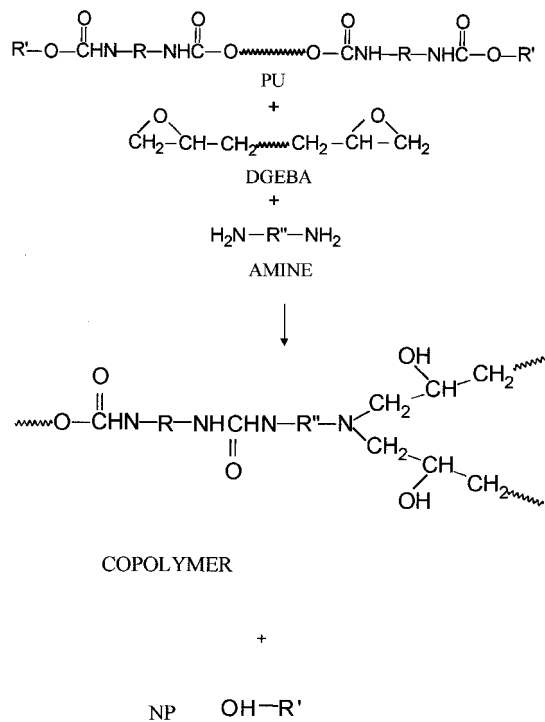
Figure 1 A schematic of the copolymerization reaction.

where E_d is the activation energy of the diffusion mechanism and ΔC_P is the change in specific molar heat of the sample at T_g.

EXPERIMENTAL

Materials

The epoxy resin used was a diglycidyl ether of bisphenol A (DGEBA, 189.8 g epoxy equiv wt, Araldyt GY9527) from Ciba Geigy Co. The crosslinker was a mixture of cycloaliphatic amines (59.5 g amine equiv wt, Distraltec). The modifier was a commercial elastomer based on a linear PU with terminal isocyanate groups blocked by an alkylphenol [2470 g isocyanate (NCO) equiv wt, Desmocap 12, Bayer].

The schematic of the copolymerization reaction is shown in Figure 1 and it was discussed in a previous publication.[3] The amine group reacts with the epoxy groups by ring opening or with isocyanate groups by deblocking of the terminal isocyanate of the PU elastomer and formation of a urea group. The displaced alkylphenol remains in the reactive mixture and acts as a catalyzer of the epoxy–amine reaction. The reaction between

Table I   Stoichiometry of Samples, Total Heats of Reaction (ΔH_T), and Glass-Transition Temperatures of Completely Cured Samples ($T_{g\infty}$)

	EA	EA + 10% PU	EA + 20% PU
Mass of epoxy (g)[a]	1.9642	1.8597	2.0641
Mass of amine (g)[a]	0.6196	0.5817	0.6687
Mass of PU (g)[a]	—	0.1996	0.5136
r[b]	0.994	1.004	1.005
NCO/E × 100 (%)	—	0.37	0.85
ΔH_T (J/g)[c]	371.2 ± 20	353.9 ± 15.0	307.8 ± 8.4
ΔH_T (kJ/mol)[c]	92.7 ± 4.9	95.6 ± 4.2	91.1 ± 2.4
$T_{g\infty}$ (K)	403.0	396.0	390.6

EA, epoxy–amine; r, stoichiometric ratio.
[a] The reported values correspond to one of the different samples prepared for each system.
[b] r = (equiv epoxy + equiv NCO)/equiv amine.
[c] The values shown are the average of at least three specimens. The heat (kJ/mol) indicates the moles of defective reactive groups (e.g., amine or epoxy + isocyanate).

amine groups and isocyanates is extremely fast, and under the reaction conditions the replacement of the alkylphenol by the amine is favored. Etherification reactions can occur at high temperatures; thus, they were not considered in the scheme of the reaction.

Methods

Differential scanning calorimetry (DSC) was used to investigate the rate of the reaction. This technique is based on the implicit assumption that a proportionality exists between the heat evolved during cure, (ΔH_i), and the x.

$$x = \frac{\Delta H_i}{\Delta H_T} \tag{7}$$

where ΔH_T is the total heat evolved during a dynamic run to reach complete conversion.

The initial mixtures were completely miscible but very viscous. The epoxy and PU elastomer were mixed manually at 80°C for 30 min. Then they were degassed under a vacuum for 2 h. Finally, the amine was added and mixed slowly to avoid mechanical heating of the reactive mixture. All samples were prepared in stoichiometric conditions (number of epoxy groups + number of isocyanate groups = number of amine groups) and run at constant temperatures (isothermal runs at 70, 85, and 100°C) at a constant heating rate of 10°C/min (dynamic runs). Samples smaller than 10–15 mg were used for the DSC measurements with a Shimadzu DSC-50.

RESULTS AND DISCUSSION

Experimental Conversion

The addition of the PU elastomer led to the copolymerization of the epoxy with the amine and the elastomer. However, the elastomer was added in small amounts (10 and 20% by weight with respect to the epoxy resin), which represents a negligible concentration of reactive groups, because the PU is a long linear chain with reactive terminal groups. This feature is reported in Table I for one of the specimens prepared for each system.

The amount of isocyanate groups was only a small percentage of the number of epoxy groups; thus, the reaction was essentially that of the epoxy–amine. This should not lead to the conclusion that the addition of the elastomers had no effect on the cure reaction. As discussed in detail below, the reaction was accelerated and the vitrification delayed.

The dynamic runs of the reactive mixtures allowed us to measure the heat of reaction corresponding to complete conversion, which is also included in Table I. If the values of ΔH_T are expressed by the weight of the sample, the dilution effect of the PU addition becomes evident. A decrease of about 17% of the total heat of reaction occurred with the 20% PU system with respect to the neat epoxy–amine reactive mixture. On the contrary, if the heat was expressed by the moles of defective reactive groups (amine or epoxy + isocyanate), ΔH_T was approximately constant, considering the experimental error.

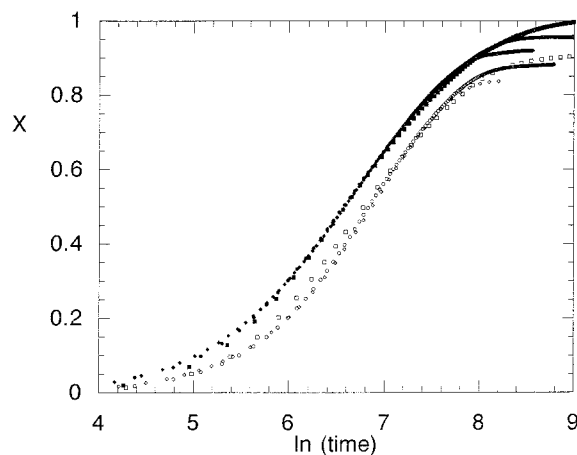Figure 2 shows the experimental data of the conversion versus time, calculated as mentioned
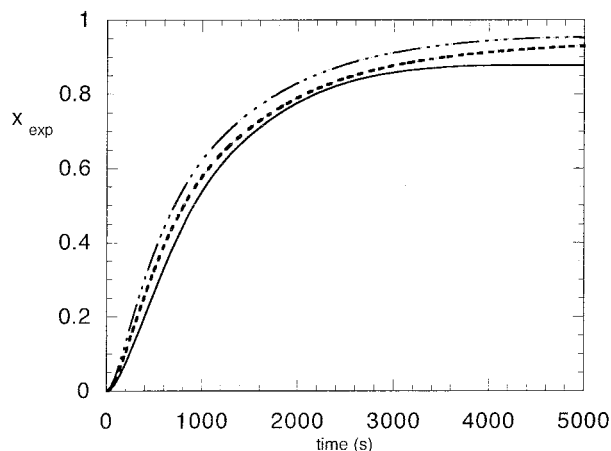
Figure 2 The experimental conversion versus time at 85°C for the (—) neat epoxy–amine system and the epoxy–amine with (- - -) 10% elastomer and (— - - - —) 20% elastomer.

Figure 3 A master curve of the experimental conversion versus ln(time) at a reference temperature of 85°C. ($\diamond$, $\bigcirc$, $\square$) The epoxy–amine system, and ($\blacklozenge$, $\bullet$, $\blacksquare$) the epoxy–amine + 20% PU; ($\blacklozenge$, $\diamond$) 70, ($\bullet$, $\bigcirc$) 85, and ($\blacksquare$, $\square$) 100°C.

above, for an isothermal run ($T_{cure} = 85°C$) of the neat epoxy–amine system and the modified mixtures (10 and 20% elastomer). It is clear from the figure that the reaction was faster with the addition of the PU and the ultimate conversion increased with the elastomer concentration.

Reaction at Short Times: Chemical Control

Equations (2) and (3) show that the rate of the reaction is the product of a kinetic constant and a function of the conversion. Following the reasoning of Wisanrakkit and Gillham,[6] in those conditions, the curves of conversion versus the ln(time) obtained from isothermal runs should have the same functional form and should only show a displacement in the ln(time) axis. This was only true for the chemically controlled step of the reaction. At those short times the curves should be superposable by simply shifting each curve along the ln(time) axis relative to the curve at the reference temperature by a shift factor $a_{(T)}$. Figure 3 shows the resulting master curve for the epoxy–amine system and that for the system modified with the addition of 20% elastomer at a reference temperature of 85°C. The superposition is quite good in both cases, which demonstrates that for each system the reaction mechanism was the same, irrespective of the curing temperature. The individual curves separate from the master curve at the point where vitrification sets up.

A nonlinear regression analysis based on the Marquardt algorithm was used to find the best fitting parameters to eqs. (2) and (3).[12] The re-

sults are summarized in Table II. The values of the parameters obtained for both equations indicated that the assumption of $m + n = 2$ were reasonable results for the systems studied here; thus, simplified eq. (3) was utilized for the rest of the study.

The values of the activation energy found for the epoxy–amine system were in close agreement with those found in the literature for similar systems,[13] and the addition of the PU elastomer reduced that value. This effect was in agreement with the proposed scheme of the reaction in which the amine reacts with the isocyanate group of the

Table II Values of Fitting Parameters for Chemically Controlled Part of Reaction

	ln A	E_c (kJ/mol)	m	n
Eq. (2)				
EA	11.30	53.07	0.277	1.417
EA + 10% PU	10.20	48.94	0.300	1.567
EA + 20% PU	8.18	42.31	0.321	1.744
Eq. (3)				
EA	11.18	52.06	0.340	1.660
EA + 10% PU	10.23	48.88	0.310	1.690
EA + 20% PU	8.16	42.32	0.315	1.685
Master curve				
EA		45.22		
EA + 10% PU		44.89		
EA + 20% PU		43.39		
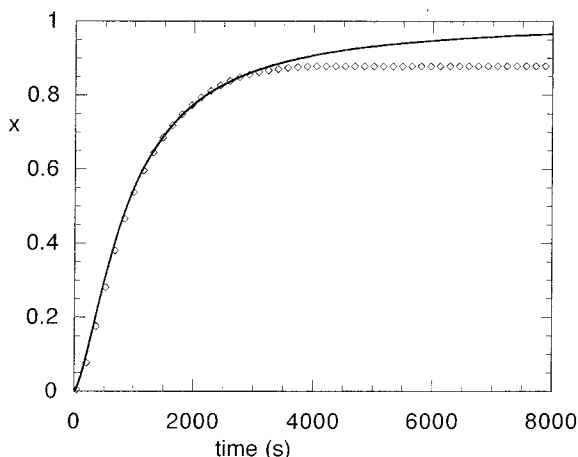
Figure 4 A comparison of experimental and predicted values of conversion versus time. Calculated values were obtained using only the chemical kinetic constant.

PU, freeing in the reactive mixture the blocking agent alkylphenol, which catalyzes the reaction epoxy amine.

The master curve obtained by superposition of the data of x versus the ln(time) can give additional information.[6] The shift factors obtained can be written as

$$a_{(T)} = \ln(\text{time}) - \ln(\text{time}_{\text{ref}}) = \ln k_{(T)} - \ln k_{(T\text{ref})}$$
$$= -E_c/RT + E_c/RT_{\text{ref}} \quad (8)$$

where T_{ref} is the temperature selected as the reference. The activation energy of the kinetically controlled part of the reaction can be derived from the calculated values of $a_{(T)}$. The results are also included in Table II. This method does not give a complete set of kinetic parameters; however, its results are included to show that two completely different numerical approaches lead to similar values for the activation energies. It also confirms the observed trend of decreasing activation energies for systems with increasing amounts of elastomer.

On the other hand, the nonlinear regression method gave a complete set of kinetic parameters from the simultaneous consideration of isothermal and dynamic DSC runs. The energy values calculated from any of the two methods were in agreement with results published previously for similar systems.[13] Figure 4 shows the excellent fit of the model to the experimental conversion versus the time data. As expected, the kinetic model represents the experimental results up to the point where vitrification sets in.

Reaction at Long Times: Diffusion Control

From the previous discussion it is clear that a purely kinetic model cannot represent the isothermal curing when the material reaches the T_g (branching off the master curve shortly after vitrification). Thus, it is important to know the glass transition evolution of the system as a function of the conversion. In this work we utilized the Di Benedetto equation,[14]

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda x}{1 - (1 - \lambda)x} \quad (9)$$

where T_{g0} is the T_g of the system at the initial time and λ is $T_{g0}/T_{g\infty}$ according to the work of Pascault and Williams.[15] This is a rough approximation that was also used in the past in the absence of experimental values for the system.[16,17]

The T_{g0} value was found to be 241 K as measured on the neat epoxy resin using DSC, which is in excellent agreement with published data.[15] Experimental values of the $T_{g\infty}$ are reported in Table I. They were measured from DSC second runs after a dynamic cure.

Using this last equation and replacing the value of T_g by T_{cure}, it was possible to calculate the conversion at which vitrification was reached. The values are reported in Table III. Figure 3 shows that the rate of reaction was greatly reduced after reaching this conversion, x_{glass}. From the values reported for x_{glass} it is evident that vitrification occurred at lower conversions for lower temperatures of curing, a feature already expected. It is also seen that an increment in the PU concentration resulted in an increment of the conversion at which vitrification took place (delay of the diffusion control of the reaction).

Table III   Calculated Conversions at Which Vitrification Takes Place Under Isothermal Curing Conditions

T_{cure} (°C)	70	85	100
EA	0.740	0.813	0.880
EA + 10% PU	0.760	0.835	0.904
EA + 20% PU	0.777	0.854	0.924

Table IV   Values of Fitting Parameters for Diffusion Controlled Part of Reaction

	$\ln kd_0$	s
EA	11.44	731.04
EA + 10% PU	13.04	577.21
EA + 20% PU	10.37	401.44

Because the mobility of the segments carrying reactive groups was highly reduced in the last part of the reaction, the calculation of x_{glass} allowed us to select the range of conversions that gave more information about the diffusion rate constant k_d. The nonlinear analysis method used in the first part of the work was again used to find the best fitting diffusional parameters of the complete model . The experimental data of conversion and time, at conversions higher than x_{glass}, were used in this case, keeping constant the already calculated parameters of the chemically controlled part of the reaction. The diffusional parameters are reported in Table IV. The value of the parameter s in the table, which is directly proportional to the activation energy for the diffusion process, shows a decreasing trend with the increment of the PU elastomer concentration in the reactive mixture. This is explained by the increased mobility of the segments in the reactive mixture with the addition of the elastomer, which reduces the T_g of the network.

Overall Reaction Rate

At this point, all the parameters that appear in the overall expression for the reaction rate are known and can be utilized to predict the rates of reaction and conversion as functions of the time for the complete range of conversions under different curing conditions (i.e., isothermal or dynamic runs). Figures 5 and 6 show the comparison of the experimental and calculated values of x and dx/dt versus time for the different systems studied. The figures show an excellent agreement between the experimental and calculated data of conversions, as well as reaction rates. The predictions are equally good for the isothermal and dynamic curing conditions. The incomplete final conversion of the systems cured at low temperatures is well reproduced, as are the position (time) and magnitude of the reaction rates in all cases. The model also shows excellent performance in reproducing the behavior of the PU modified systems.

The complete model can cover the two ends of the reaction controlled by kinetics or by diffusion of the reactants. It reproduces different curing conditions and in this respect it can be very useful to predict the results of curing in a mold, as well as other commercial processing conditions. (It could reproduce conversion profiles in a piece associated with temperature profiles developed during curing.) The use of the Rabinowitch equation allows the finding of a complete expression that can reproduce the effects of the vitrification on the overall reaction rate quite well and the obtaining of a sample with a final conversion lower than 1.

The addition of the PU elastomer reduces the activation energy of both the chemically controlled step of the reaction and that of the diffusion controlled step. For the first part of the reaction, the decrease of the energy barrier, E, is explained by the increase in the concentration of OH groups from the alkylphenol released during the copolymerization with amine. For the diffusion controlled part of the reaction, the activation energy for diffusion is reduced because of the increased mobility of the segments containing reactive groups. The presence of the elastomer reduces the T_g of the material and thus delays the onset for vitrification in the reacting sample.

In agreement with the above reasoning, the final conversion reached by the epoxy–amine system under isothermal conditions increases with the elastomer concentration.
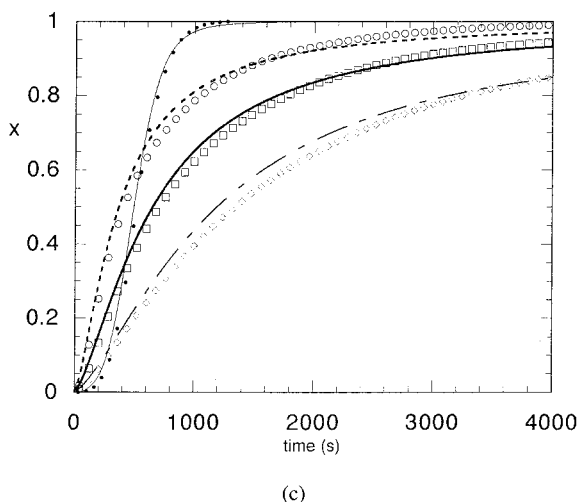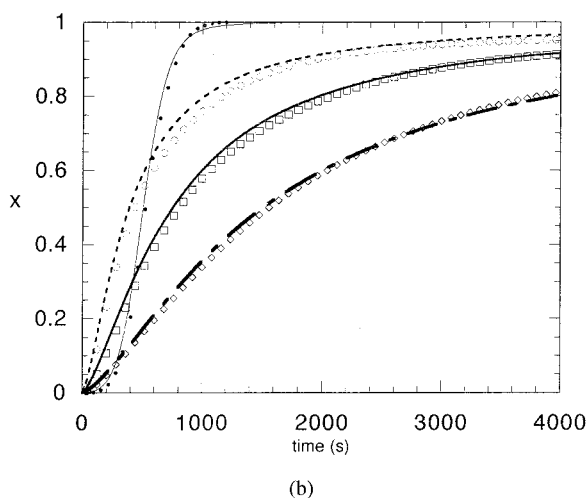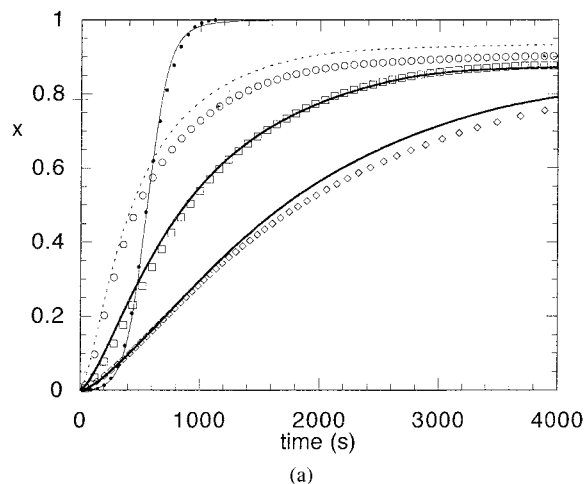
CONCLUSIONS

The overall reaction rates of an epoxy–amine system and PU coreacted systems were modeled using the modified Kamal's model, which includes diffusion control through the use of Rabinowitch's equation and the Addams–Gibbs theory.
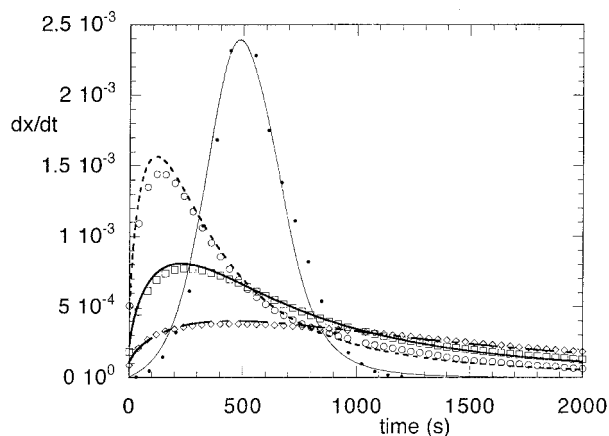
The chemically controlled part of the reaction was well represented by a simplified model, which considered only the autocatalytic path of the reaction (one kinetic constant). The numerical solution of the system with exponents m and n as independent parameters showed that the simplification $n + m = 2$ was valid.

The nonlinear regression analysis was an excellent tool, which allowed the simultaneous use of isothermal and dynamic DSC results.

The Gillham approach allowed us to confirm that the mechanism of reaction did not change with temperature, as could also be concluded from the numerical fit of isothermal and dynamic runs

Figure 6 A comparison of experimental and predicted values of reaction rates (dx/dt) versus time for the epoxy–amine + 10% PU system; ($\diamond$) 70, ($\square$) 85, and ($\bigcirc$) 100°C; ($\bullet$) the dynamic run (10°C/min).

Figure 5 A comparison of experimental and predicted values of conversion versus time for (a) epoxy–amine, (b) epoxy–amine + 10% PU, and (c) epoxy–amine + 20% PU. (—) Predictions of the model were obtained using the overall kinetic constant; ($\diamond$) 70, ($\square$) 85, and ($\bigcirc$) 100°C; ($\bullet$) the dynamic run (10°C/min).

to a single kinetic expression. The master curve obtained confirmed the values of the activation energy of the chemically controlled part of the reaction for the neat and modified systems.

The application of nonlinear regression analysis to the experimental data at conversions higher than that of vitrification (isothermal runs) gave very good results for the kinetic constants of the diffusion controlled part of the reaction. A single set of parameters was used for each system, independent of the temperature, with very good results.

The predictions obtained from the complete model showed excellent agreement with the experimental results in a wide variety of curing conditions (isothermal or dynamic runs with or without vitrification taking place during cure). All the calculated parameters were valid for a given system and independent of the working temperature. Thus, they could be very useful in modeling actual processing conditions.

The addition of the reactive elastomer produced the decrease of the T_g of the system; thus, the conversion at which vitrification was reached increased and the system achieved higher final conversions during curing at low temperatures.

The elastomer acted as a catalyzer of the autocatalytic path of the chemically controlled part of the reaction; as a result, the E of the process diminished. It also increasing the segmental mobility of the reactive species, thus reducing the energy barrier for diffusion.

The complete model reproduced all the experimental features with excellent results.

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