

Cure kinetics of amine-cured diglycidyl ether of bisphenol A epoxy blended with poly(ether imide)

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Accepted 23 August 1999

Abstract

An epoxy based on the diglycidyl ether of bisphenol A (DGEBA) has been modified with poly(ether imide) (PEI) and cured with 1,3-bisaminomethylcyclohexane (1,3-BAC). The curing kinetics of the neat resin and of a PEI/epoxy blend were analysed and compared by differential scanning calorimetry. The results showed that the PEI has effect on curing reaction, reaching less conversion in this process than for the neat system. The experimental data for both systems showed an autocatalytic behaviour and the phenomenological model of Kamal was proposed to obtain the activation energies for the rate constants. The values of the activation energies for the PEI/epoxy blend system are higher than the values for the neat system. Diffusion control is incorporated to describe the cure in the latter stages predicting the cure kinetics over the whole range of conversion. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Blend; Cure kinetics; DSC; Epoxy resin; Poly(ether imide)

1. Introduction

Epoxy resins have been used extensively as matrices in fiber-reinforced composites, which are finding increasing use in the industry, since they fulfil the requirements of high modulus and high temperature performance. However, such good properties in an epoxy resin require a high level of crosslinking, which usually results in a brittle behaviour. Toughening epoxy matrices using liquid reactive rubbers has been widely reported in the literature [1]. The best

results for rubber toughening have been obtained with difunctional epoxies [2] which have a relatively low crosslink density. In this work, the kinetics of an epoxy system containing a diglycidyl ether of bisphenol A (DGEBA) and 1,3-bisaminomethylcyclohexane (1,3-BAC) as curing agent and its blend with poly(ether imide) (PEI) at 10 phr (where phr represents the number of parts of PEI per hundred parts of DGEBA epoxy resin) was studied.

Curing kinetic models are generally developed by analysing experimental results obtained by differential thermal analysis techniques. Differential scanning calorimetry (DSC), both in the isothermal and dynamic mode, has been used extensively, assuming a proportionality between the heat evolved during the cure and the extent of reaction.

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In general, the curing reactions of the systems based on diglycidyl ether show kinetics characterised by an initial acceleration due to autocatalysis, while the later stages may exhibit retardation due to the onset of gelation. As cure proceeds and the resin crosslinks, the glass transition temperature, T_g , of the curing resin increases. For cure temperatures above T_g , the rate of reaction between the epoxy and hardener reactive groups is chemically kinetically controlled. When T_g approaches the curing temperature, the resin passes from a rubbery state to a glassy state and the curing reactions become diffusion controlled, and will eventually become very slow and finally stop [3].

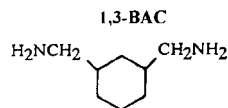
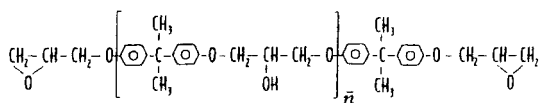
The curing reactions of epoxy-amine modified systems have been widely investigated, and several rate expressions have been proposed in the literature [4,5]. The objective of this paper is to investigate the epoxy system modified not only in the first stages of cure reaction but also in the later stages where the vitrification effect is dominant and the reaction is controlled by diffusion.

2. Experimental

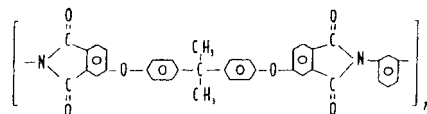
2.1. Materials

The studied system is based on a commercial diglycidyl ether of bisphenol A (DGEBA), Shell Epikote 828, with weight per epoxy equivalent of 192.2 g eq^{-1} which was determined by hydrochlorination [6]. The neat epoxy resin and its blend with the poly(ether imide) (PEI) (GE Ultem 1000) were cured with a cycloaliphatic diamine hardener, 1,3-bis(aminomethyl)cyclohexane (1,3-BAC), from Mitsubishi Gas Chem., with molecular weight of 142.18 and manufacturer purity value of >99% according to the supplier. All components were commercial products, and were used as received without purification. The chemical structures of DGEBA, 1,3-BAC and PEI are as follows:

DGEBA



PEI



An epoxy/PEI blend resin mixture with 10 phr of PEI, was prepared. First, PEI was held in an oven at 70°C in order to dehydrate, then it was dissolved in dichloromethane and the resulting polymer solution was then mixed with 100 g of the epoxy resin at room temperature. The solvent in the mixture was vaporised in a thermic bath at 80°C . Subsequently, 18.5 g of 1,3-BAC were slowly added, with continuous stirring, to the epoxy/PEI mixture at room temperature.

2.2. Techniques

A differential scanning calorimeter (Perkin-Elmer DSC 7, equipped with an intracooler and supported by a Perkin-Elmer computer for data acquisition/analysis) was used for the dynamic and isothermal cure experiments and data analysis. The temperature scale and the energy output of the calorimeter were calibrated using the melting point of high purity indium. A predetermined average temperature control setting was chosen and the indicated melting point was determined at different heating rates. The indicated melting point at zero heating rate (isothermal calibration) was determined by extrapolation. The calibration was performed frequently. Dry nitrogen was used as purge gas. Samples of about 5 mg were enclosed in aluminium DSC capsules.

Isothermal and dynamic heating experiments were conducted under a nitrogen flow of 40 ml min^{-1} . For dynamic heating experiments, five different heating rates were investigated: 2.5, 5, 7.5, 10 and $15^\circ\text{C min}^{-1}$ from 20°C to 200°C .

Isothermal experiments were conducted at five temperatures (80°C , 90°C , 95°C , 100°C , and 105°C) in order to obtain both the cure rate and the

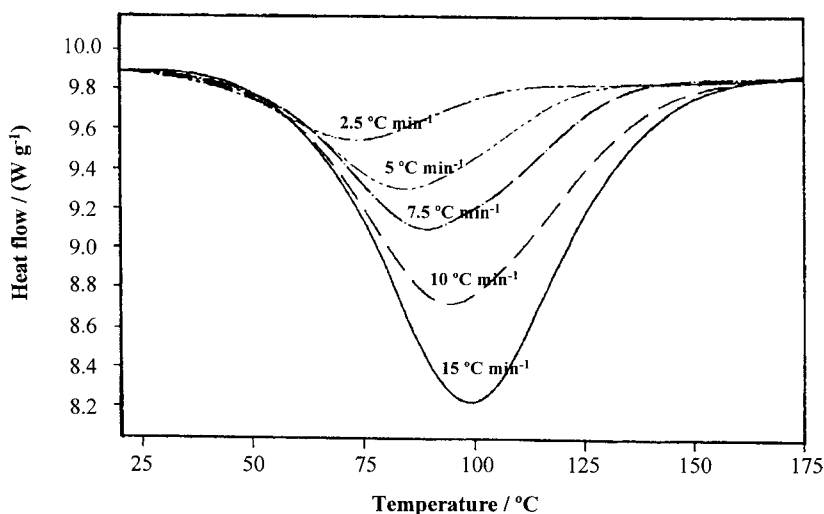


Fig. 1. Heat flow measured by DSC during cure at different heating rates: 2.5, 5, 7.5, 10, and 15 °C min⁻¹ for DGEBA/1,3-BAC/PEI.

extent of cure as a function of time. The reaction was considered complete when the signal returned to the baseline, which generally took about 6 min. The origin ($t = 0$) was obtained by rerunning the experiment on the reacted sample, under the same conditions, to obtain the true baseline.

3. Results and discussion

To calculate the total heat of reaction generated to reach full conversion, ΔH_0 , the DSC dynamic scans at different heating rates were performed (Fig. 1) and the total area under the thermogram was determined. Replicate experiments were performed at each heating rates. The overall heat evolved in the reaction has been determined as the average value of reaction heats calculated in each thermogram. The corresponding value found for the DGEBA/1,3-BAC/PEI system was $\Delta H_0 = 313 \text{ J g}^{-1}$. This value was smaller than the obtained value of the neat system [7]. Isothermal DSC curves are shown in Fig. 2. Because the masses of the samples are small and the reaction rates obtained are relatively low, the effect of the sample temperature variation in the course of the reaction was not considered.

For kinetic studies by means of DSC, the following expression is applied:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} \quad (1)$$

The phenomenological model used in this paper, which is widely used in the literature for epoxy systems [8,9], has been developed by Kamal [10]. The rate of conversion, $d\alpha/dt$, and the extent of reaction, α , are related to one another as follows:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n, \quad (2)$$

where m and n are the kinetic exponents of the reaction and their sum represents the overall reaction order and k_1 and k_2 are the reaction rate constants with two different activation energies and preexponential factors, besides k_1 can be calculated if the initial reaction rate at $\alpha = 0$ can be estimated. Both constants depend on temperature according to the Arrhenius law.

Eq. (2) embodies the experimental observations (Fig. 2) that the maximum rate of cure corresponding to the peak exotherm in the isothermal occur at slightly above >0 and that the rate of cure at $t = 0$ is finite.

To compute Eq. (2) parameters from experimental data, several methods have been proposed previously [11,12], in many of them it was assumed that the total reaction order was 2, $m + n = 2$, restraining the range

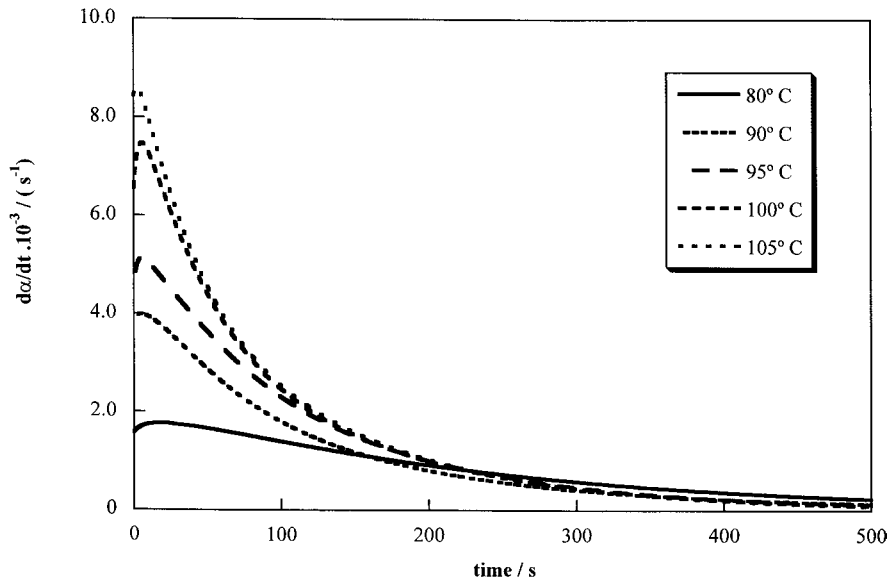


Fig. 2. Isothermal DSC curves for DGEBA/1,3-BAC/PEI concentration of 10 phr at different temperatures.

of application of the proposed model. In the present study, the parameters m , n , k_1 , k_2 , were estimated without any constraints on them, using a least squares method. Fig. 3 shows DSC data plotted as $d\alpha/dt$ vs. α at different temperatures. The plots show a maximum

reaction rate at time greater than zero, thereby negating simple n th-order kinetics, however the maximum rate is observed at conversions too low to be a pure autocatalytic reaction, because an autocatalysed thermoset usually has its maximum heat evolution higher.

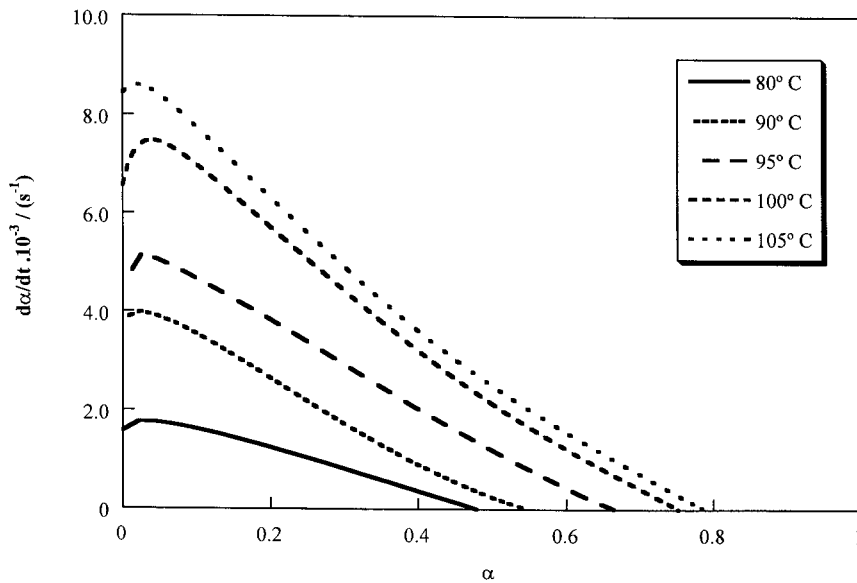


Fig. 3. Reaction rate, $d\alpha/dt$, vs. conversion, α , curves at different curing temperatures.

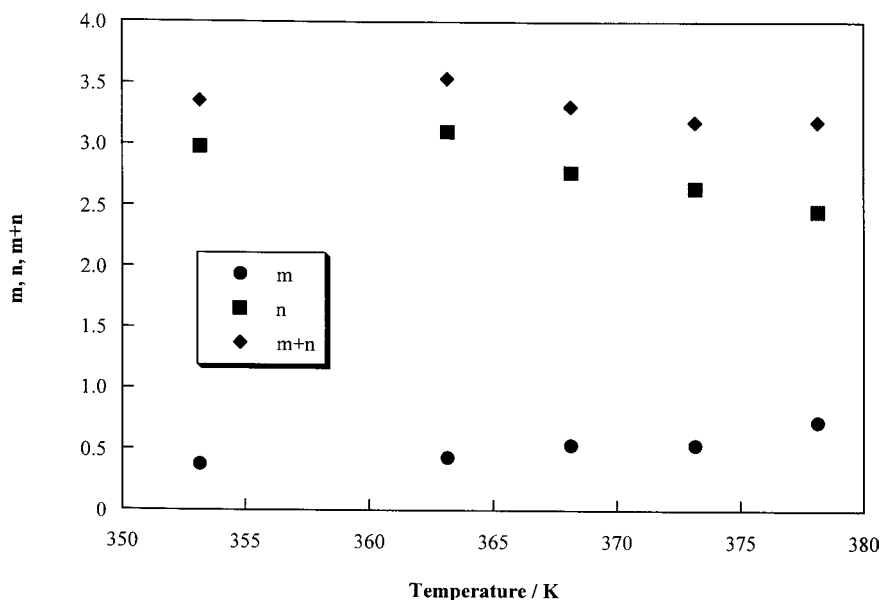


Fig. 4. Estimated values of m and n and their sum, for the system DGEBA/1,3-BAC/PEI at different curing temperatures.

The values of the reaction orders, m and n , obtained for each curing temperature for the system DGEBA/1,3-BAC/PEI are shown in Fig. 4. This figure shows that the sum of the exponent factors ($m + n$) is constant in the range 3–3.5, slightly higher than the sum of the reaction orders for the system without PEI, which was in the range 2.5–3.

Rate constants k_1 and k_2 are shown in Table 1. With these data and Arrhenius equation, values of 73 and 80 kJ mol⁻¹ for the associated activation energies were obtained. These values are higher than those

Table 1
Estimated values of k_1 and k_2 at different temperatures for both systems^a

Temperature (°C)	k_1 (s ⁻¹)		k_2 (s ⁻¹)	
	System 1	System 2	System 1	System 2
80	0.0019	0.0016	0.0047	0.0015
90	0.0029	0.0038	0.0080	0.0027
95	–	0.0046	–	0.0061
100	0.0043	0.0066	0.013	0.0092
105	–	0.0085	–	0.0082
110	0.0063	–	0.022	–

^a System 1: DGEBA/1,3-BAC; system 2: DGEBA/1,3-BAC/PEI.

obtained for this system without PEI [13]. These results and the values of the reaction orders seem to indicate that the poly(ether imide) hinders the reaction of the resin with the hardener.

Figs. 5 and 6 present comparisons between experimental data and predictions of the autocatalytic model (Eq. (2)), with values of model parameters determined above for the epoxy system with and without PEI. In both cases, good fits are observed up to 0.60 and 0.35 of conversion, respectively, for the cured at 80°C. The model, however, predicts higher conversions for the latter stages of the cure reaction, the behaviour for this system with PEI is similar to the system without it, but the conversions are smaller.

To consider diffusion effect we have used a semi-empirical relationship, used by other researchers [14,15]. When the degree of cure reaches a critical value, α_c , diffusion becomes controlling and the rate constant k_d is given by

$$k_d = k_c \exp[-C(\alpha - \alpha_c)], \quad (3)$$

where k_c is the rate constant for chemical kinetics and C is a parameter. Eq. (3) corresponds to a rather abrupt onset of diffusion control at $\alpha = \alpha_c$, though the onset is somewhat more gradual and there is a region where both chemical and diffusion factors are controlling.

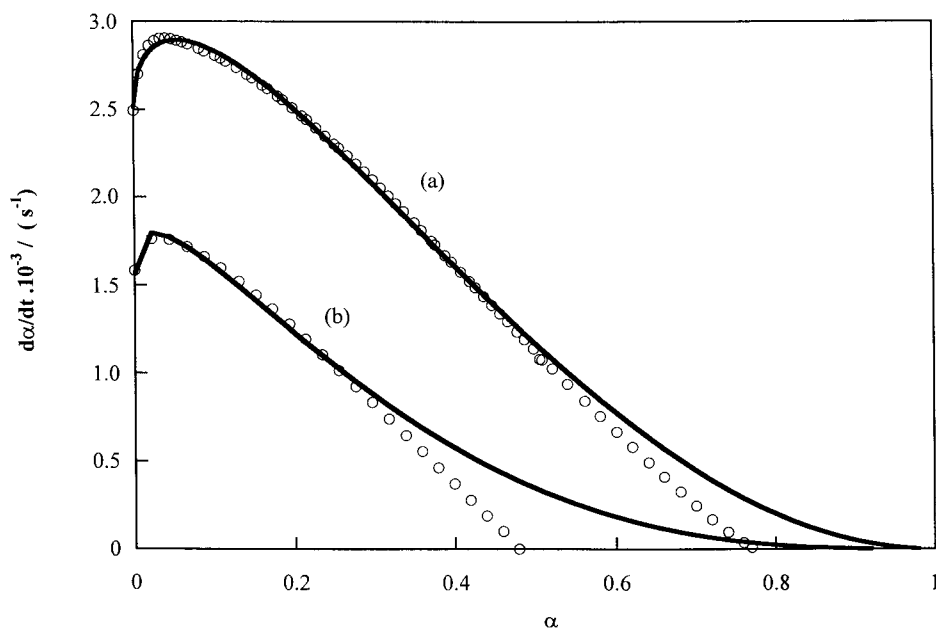


Fig. 5. Reaction rate, $d\alpha/dt$, as a function of conversion, α , at cure temperature 80°C . The solid lines represent the autocatalytic model. (a) DGEBA/1,3-BAC, (b) DGEBA/1,3-BAC/PEI.

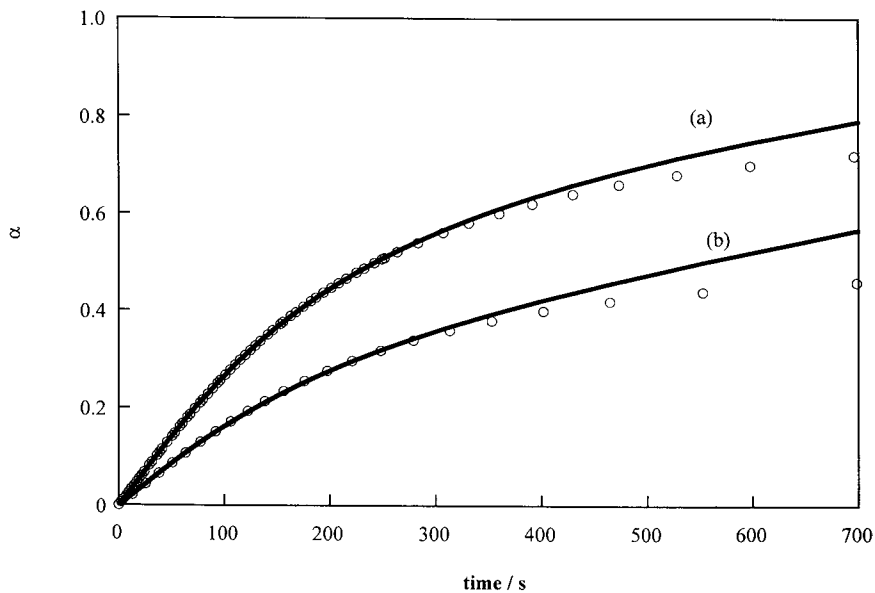


Fig. 6. Degree of cure as a function of cure time at 80°C . The kinetic model predictions are shown by the curves and the symbols are the measured values. (a) DGEBA/1,3-BAC, (b) DGEBA/1,3-BAC/PEI.

According to the expression for the overall effective rate constant, k_e , expressed in terms of k_d and k_c is

$$\frac{1}{k_e} = \frac{1}{k_d} + \frac{1}{k_c}, \quad (4)$$

it can be combined with Eq. (3), and to obtain the diffusion factor $f(\alpha)$

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]}. \quad (5)$$

When α is much smaller than the critical value, $\alpha \ll \alpha_c$, then $f(\alpha)$ approximates unity, the reaction is kinetically controlled and the effect of diffusion is negligible. As α approaches α_c , $f(\alpha)$ begins to decrease and approaches zero as the reaction effectively stops. The effective reaction rate at any conversion is equal to the chemical reaction rate multiplied by $f(\alpha)$.

As in the previous studies [16] for DGEBA/1,3-BAC, $f(\alpha)$ was obtained as the ratio of experimental reaction rate to the reaction rate predicted by the autocatalytic model in Eq. (2). Fig. 7 shows the behaviour of $f(\alpha)$ with increasing conversion at different curing temperatures for DGEBA/1,3-BAC/PEI. The decrease in $f(\alpha)$ and hence, in the effective

Table 2

Values of critical conversion α_c , and of C parameter at different curing temperatures for the PEI/epoxy blend system

Temperature (°C)	α_c	C
80	0.42	24.20
90	0.46	19.86
95	0.60	29.77
100	0.71	54.64
105	0.75	63.48

reaction rate due to onset of diffusion at higher conversions is seen.

Values of α_c and C obtained by applying non-linear regression to $f(\alpha)$ vs. α data to Eq. (5) are listed in Table 2. While a moderate increase in α_c was observed in the neat system with increasing temperature, this increment for α_c was stronger for the system with PEI, but for the coefficient C no discernible trend is found in agreement with the studies of Cole et al. [17] on epoxy-amine systems.

It may be noted that the critical conversion is not an adjustable parameter because it reflects the onset of diffusional limitation that occurs only in the latter stages of reaction. It is also not an observable quantity

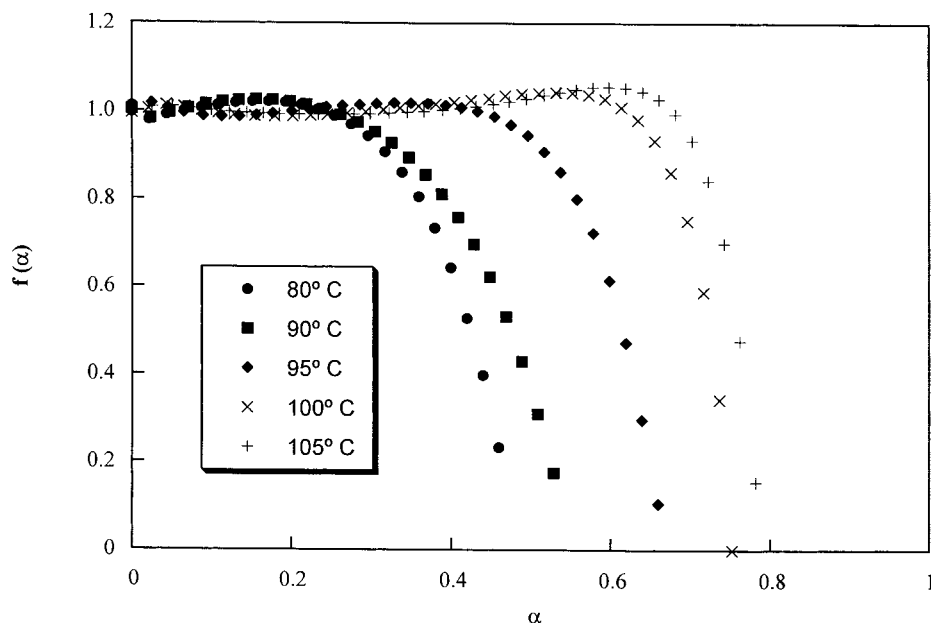


Fig. 7. Plot of diffusion factor, $f(\alpha)$, vs. conversion, α , at different curing temperatures.

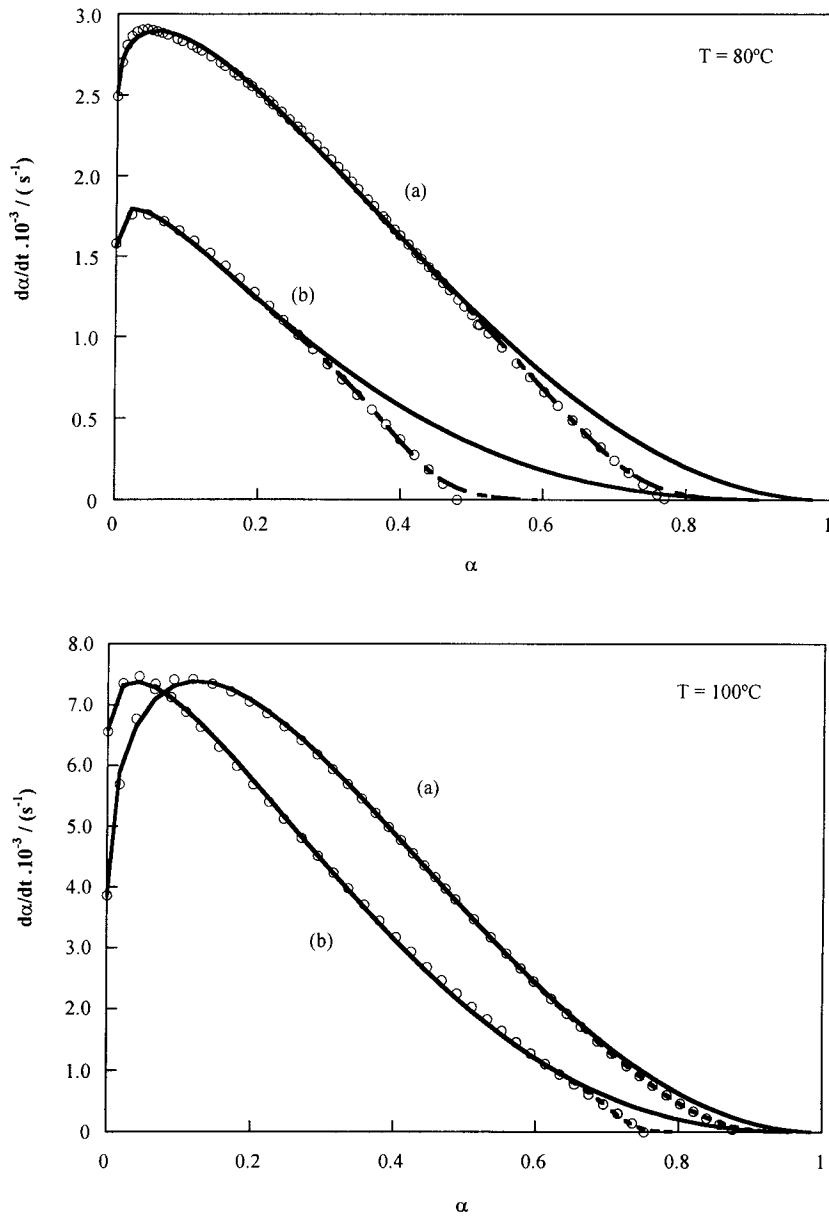


Fig. 8. Comparison of experimental data with model predictions: reaction rate, $d\alpha/dt$, vs. conversion, α , at temperatures 80°C and 100°C . (●●●) Experimental; (—) Autocatalytic model; (---) Autocatalytic model with diffusion. (a) DGEBA/1,3-BAC, (b) DGEBA/1,3-BAC/PEI.

since the transition to the diffusion regime is gradual. As cure proceeds, the mobility of the reacting species is reduced and this leads to diffusional effects. Hence, α_c would reflect the state of cure of the system rather than the temperature of cure.

Figs. 8 and 9 show the results for the curing temperature of 80°C and 100°C , where the experimental values of $d\alpha/dt$ are compared with those calculated by the autocatalytic model, coupled with the diffusion factor, according to Eq. (5).

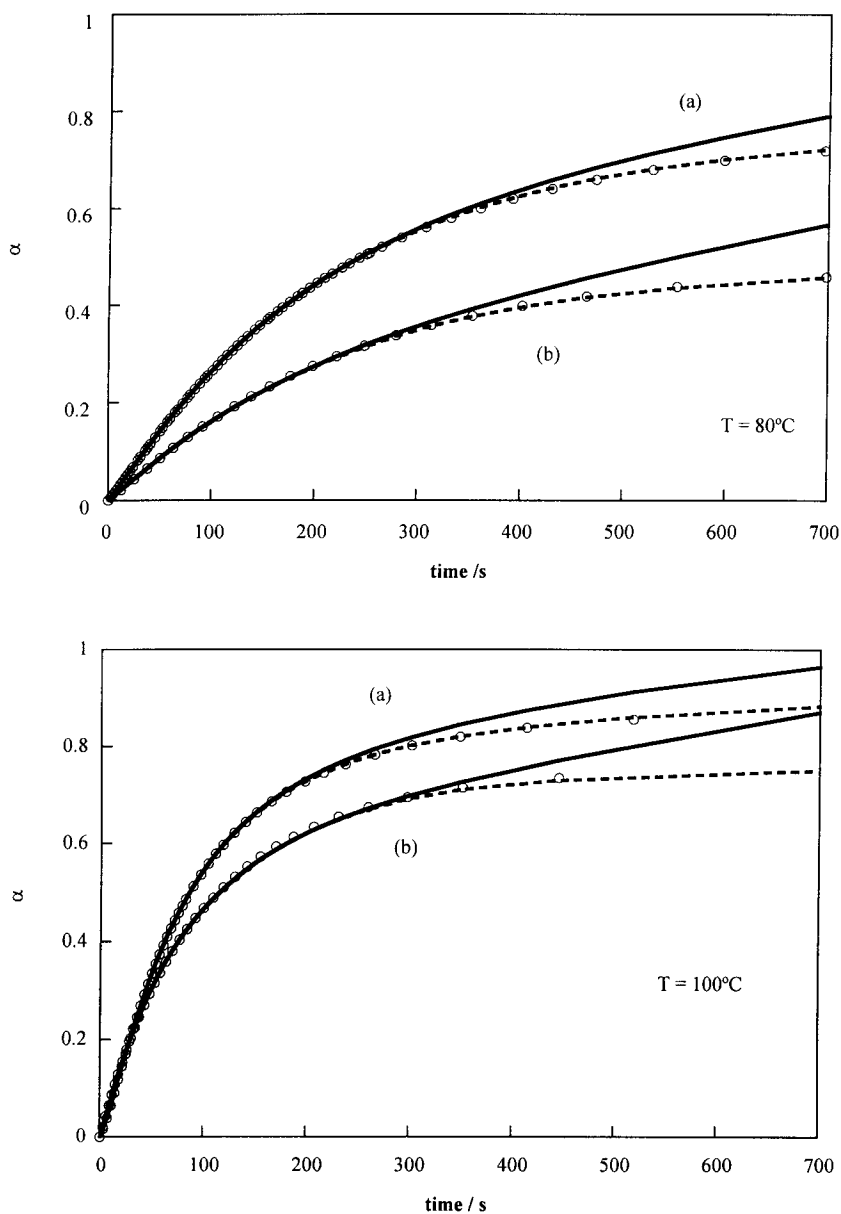


Fig. 9. Comparison of experimental data with model predictions: conversion, α , vs. time at temperatures 80°C and 100°C. (○○○) Experimental; (---) Autocatalytic model; (—) Autocatalytic model with diffusion. (a) DGEBA/1,3-BAC, (b) DGEBA/1,3-BAC/PEI.

4. Conclusions

An autocatalytic mechanism was observed for an amine-cured epoxy/poly(ether imide) blend. Kinetic parameters for the epoxy blend were obtained and the proposed kinetic model describes well the cure

kinetics of the epoxy and its blend, up to the vitrification point.

In order to describe the cure in the latter stages of reaction (post-vitrification region) a diffusion factor has been introduced. With the introduction of this factor it is possible to fit the experimental data well

to the model and calculate with good precision the degree of conversion over the whole range of cure temperature.

The reaction mechanism of epoxy blend remained the same as that of the neat epoxy. In all range of temperatures, the neat system reached conversions higher than the blend system. The obtained values for the activation energies were higher in the system with PEI, this could be due to PEI hinders the reaction of the resin with the hardener.

Acknowledgements

Financial support for this work has been provided by Xunta de Galicia, through grant XUGA-17201B97.

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