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Blends of an epoxy/cycloaliphatic amine resin with poly(ether imide)

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Abstract

By employing differential scanning calorimetry we have studied, under isothermal and dynamic conditions, the kinetics of the cure reaction for an epoxy based in the diglycidyl ether of bisphenol A (DGEBA) modified with different contents of poly(ether imide) (PEI) and cured with 1,3-bisaminomethylcyclohexane (1.3-BAC), over the temperature range of 80–105°C. Kinetic analysis were performed using three kinetic models: Kissinger, Flynn–Wall–Ozawa and the phenomenological model of Kamal as result of its autocatalytic behaviour. Diffusion control is incorporated to describe the cure in the latter stages predicting the cure kinetics over the whole range of conversion. The values of the activation energies for all the PEI/epoxy blends are higher than the values for the neat system. The autocatalytic mechanism was observed in the neat system as in its blends. The reaction rates are higher with PEI, however the reached conversions decrease with the PEI content. A different behaviour was found between the neat system and the systems with 5 and 7.5 phr of PEI, and the systems with higher content in PEI, being more pronounced in the system with 15 phr of PEI. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy–poly(ether imide) blends; Cure kinetics; Differential scanning calorimetry

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1. Introduction

Epoxy resins have been used extensively as matrices in fibre-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 brittle behaviour. The modification of epoxy networks with high performance ductile thermoplastics has been studied [1] as an alternative to reactive rubbers for improving their toughness without sacrificing other useful properties such as glass transition temperature (T_g) and stiffness.

Most of the studies on thermoplastic/thermoset blends are mainly focused on mechanical properties and final morphologies [2]. Only a few of them try to investigate the effect of the modifier on the kinetics [3,4].

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

Usually, the curing reactions of the systems based in diglycidyl show kinetics characterized by an initial acceleration due to autocatalysis, while the later stages may exhibit retardation owing to the onset of gelation. As cure proceeds and the resin crosslinks, the glass transition temperature of the curing resin increases. For cure temperatures below T_g, the rate of reaction between the epoxy and hardener reactive groups is kinetic and is chemically 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 [5].

In this study, the cure kinetics of an epoxy system containing the diglycidyl ether of bisphenol A (DGEBA) and 1,3-bisaminomethylcyclohexane (1,3-BAC) as the curing agent and its blends with poly(ether imide) (PEI) at 5, 7.5, 10 and 15 phr (where phr represents the number of parts of PEI per hundred parts of DGEBA epoxy resin) were studied.

2. Experimental

2.1. Materials

The system studied is based on a commercial DGEBA, Araldite GY 260 CIBA, with weight per epoxy equivalent of 205.1 g eq^{-1}, which was determined by hydrochlorination [6]. The neat epoxy resin and its blends with the poly(ether

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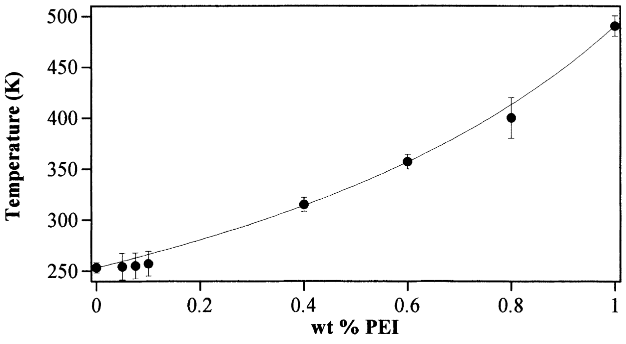

Fig. 1. Relationship between T_g (from DSC) and composition in DGEBA/PEI blends: (●●●) experimental points; (—) Eq. (1).

imide) (PEI) (GE Ultem 1000), whose value of average molar mass in number is $\bar{M}_n = 12\,000$ and specific gravity of 1.27 according to data specified by thermoplastics' manufacturers, were cured with a cycloaliphatic diamine hardener, 1,3-bisaminomethylcyclohexane (1,3-BAC), from Aldrich Chemical, with molecular weight of 142.25 and manufacturer purity value of >99% according to the supplier. All components were commercial products, and were used as received without purification.

2.2. Technique

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 thermal response and the temperature were calibrated with the heat of fusion and the melting point of pure indium. A dry nitrogen flow of 40 ml min^{-1} was used as purge gas. Samples of about 5 mg were enclosed in aluminium DSC capsules.

2.3. Initial miscibility

Initial miscibilities of the epoxy resin/poly(ether imide) mixtures were studied. PEI was held at 70°C in an oven 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 vaporized in a thermic bath at 80°C. These samples were quenched at −30°C and then, were tested by DSC at a heating rate of 5°C min^{-1}, to 300°C. In order to check reproducibility the procedure was repeated a further two or three times.

2.4. Cured blends

Epoxy resin/PEI mixtures with 5, 7.5, 10 and 15 phr of PEI, were prepared. PEI was dehydrated, dissolved in dichloromethane and mixed with the epoxy resin with the same process as described above. Subsequently, 17.0 g of 1,3-BAC were slowly added, with continuous stirring, to the epoxy resin/PEI mixture at room temperature.

For dynamic heating experiments, five different heating rates were investigated: 2.5, 5, 7.5, 10 and 15°C min^{-1} from 20 to 200°C. Isothermal experiments were conducted at five temperatures: 80, 90, 95, 100, and 105°C in order to obtain both the cure rate and the extent of cure as a function of time. The reaction was considered complete when the signal levelled off the baseline, which generally took about 20 min. A second scan was performed to calculate the total heat under the exotherm curve. The isothermal conversion at time t, was defined as $a(t) = \Delta H_t/\Delta H_0$, where ΔH_t is the heat under the exotherm curve at time t, calculated by integration of the DSC isothermal signal and ΔH_0 is the total heat of reaction generated to reach full conversion, and it is calculated by the total area under the thermograms for each blend of PEI.

3. Results and discussion

3.1. Binary DGEBA/PEI blends: miscibility

Whereas heterogeneous blends show separate glass transitions of the components, binary blends of PEI with the DGEBA resin exhibited a single glass transition; hence, it is a homogeneous system, as shown in Fig. 1, indicating complete miscibility over the entire composition range.

The T_g data from DSC measurements are compared in the quoted figure with the predictions of an equation relating the T_g of a miscible binary polymer to the weight fractions ω_1 and ω_2 of its components. A good fit is obtained from the Fox equation [7]

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g_1}} + \frac{\omega_2}{T_{g_2}} \tag{1}$$

where T_{g_1} and T_{g_2} are, respectively, the T_gs of components 1 and 2, respectively.

3.2. Ternary epoxy/hardener/PEI blends: kinetic analysis procedures

The neat epoxy resin and its blends with 5, 7.5, 10, and 15 phr of PEI were tested at five different heating rates and were cured at five different isothermal temperatures. Kinetic analysis were performed using three kinetic models: Kissinger and Flynn–Wall–Ozawa [8,9] methods, that were used by their wide applicability in comparison with other non-isothermal methods, because, it is not necessary to have a prior knowledge of the reaction mechanism to quantify kinetic parameters; and the phenomenological model developed by Kamal [10], which has been successfully utilized to describe the cure of DGEBA/1,3-BAC in our previous papers [11,12]. It was interesting to use the same kinetic model in order to compare the kinetic parameters of the neat epoxy system with those of the system with PEI.

If one assumes that the extent of reaction, α, is proportional to the heat generated during reaction, the reaction rate

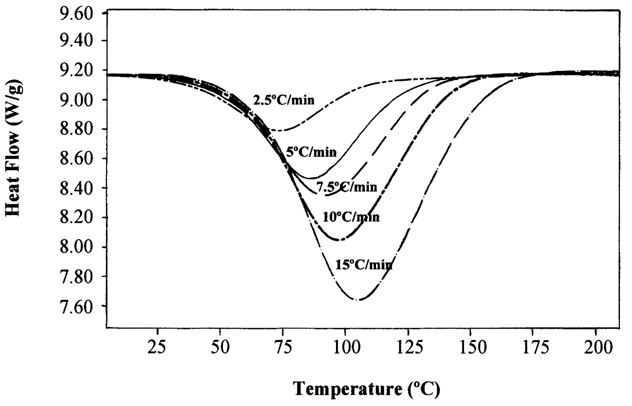

Fig. 2. Heat flow measured by DSC during cure at different heating rates: 2.5, 5, 7.5, 10 and 15°C min^{-1} for the 7.5 phr PEI/epoxy blend.

can be expressed by means of the general law

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{2}$$

where t is the time, $k(T)$ is the rate constant, and $f(\alpha)$ is a function of the dependence of conversion. An integrated form of the above equation often appears as

$$g(\alpha) = \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = k(T)t \tag{3}$$

where $g(\alpha)$ is the integrated form of the conversion dependence function.

The dependence of the rate constant, $k(T)$, on the temperature may be described by the Arrhenius expression

$$k(T) = A\exp\left(-\frac{E}{\mathrm{R}T}\right) \tag{4}$$

where A is the frequency factor, E is the activation energy, and R is the universal gas constant.

3.3. Dynamic kinetic methods: Kissinger and Flynn–Wall–Ozawa methods

For dynamic heating analysis, two kinetic methods were utilized: the Kissinger method and the Flynn–Wall–Ozawa method. According to the method of Kissinger, the activation energy is obtained from the maximum reaction rate where $\mathrm{d}(\mathrm{d}\alpha/\mathrm{d}t)/\mathrm{d}t$ is zero under a constant-heating rate condition. The resulting relation can be expressed as

$$\frac{\mathrm{d}[\ln(q/T_{\mathrm{m}}^2)]}{\mathrm{d}(1/T_{\mathrm{m}})} = -\frac{E}{\mathrm{R}} \tag{5}$$

where T_{m} is the maximum rate temperature and q is a constant heating rate. Therefore, a plot of $\ln(q/T_{\mathrm{m}}^2)$ versus $1/T_{\mathrm{m}}$ gives the activation energy without a specific assumption of the conversion-dependent function.

Table 1
Heats of reaction of epoxy blends with various PEI contents at different heating rates

q (°C min^{-1})	ΔH_0 (J g^{-1})			
	5 phr	7.5 phr	10 phr	15 phr
2.5	454.0	368.1	321.2	181.5
5	465.0	374.4	310.4	168.4
7.5	465.7	364.0	309.9	187.3
10	409.9	363.9	296.8	194.4
15	402.2	341.2	325.3	162.6
Average value	439.4	362.3	312.7	178.8

Based on the Doyle's approximation [13] for the integral $p(x)$ an alternative method was developed by Flynn–Wall–Ozawa for the calculation of activation energy. They expressed the equation $g(\alpha)$ as

$$\log(q) = \log\left[\frac{AE}{g(\alpha)\mathrm{R}}\right] - 2.315 - \frac{0.457E}{\mathrm{R}T} \tag{6}$$

Starting with this equation, a more accurate value of activation energy can be obtained by iteration or least-squares techniques in order to improve the linear approximation on the temperature integration term.

These two methods were applied to the dynamic heating experimental data obtained at the heating rates between 2.5 and 15°C min^{-1} that were utilized in this work. To calculate the total heat of reaction generated to reach full conversion, ΔH_0, the DSC dynamic scans at different heating rates were performed and the total area under the thermogram was determined for all blends. Fig. 2 shows the heat flow measured by DSC during cure at the different heating rates and for 7.5 phr PEI/epoxy blend. Replicate experiments were performed at each phr of PEI.

The overall heat evolved in the reaction has been determined as the average value of reaction heats calculated in each thermogram and as can be seen for each blend, these values do not vary with the heating rate, and the standard deviations are smaller than 8% in all the cases. The individual values of ΔH_0 and the average values are shown in Table 1 which shows that the total heats of reaction were influenced by the presence of PEI, with the average values of ΔH_0 decreasing with the PEI content in the epoxy blends. The average value [11] for neat resin was previously determined as 495.5 J g^{-1}. The decrease of ΔH_0 with the increase in PEI should not be taken as a result, rather, this was an indication that the reaction mechanism was likely to be changed by the presence of PEI in the blend.

Without any assumptions on conversion-dependent functions, the Flynn–Wall–Ozawa method can provide activation energies for different conversion levels, but in this study it was only applied to the maximum rate where the peak appears; where it is assumed that when the exothermic peak is reached the degree of conversion is independent of the heating rate [14].

Applying the Flynn–Wall–Ozawa and Kissinger methods to the maximum reaction rates (peaks of DSC thermogram) the activation energies were determined by the slopes of the lines in Fig. 3(a)–(e). The obtained activation energies were shown for the different blends and it can

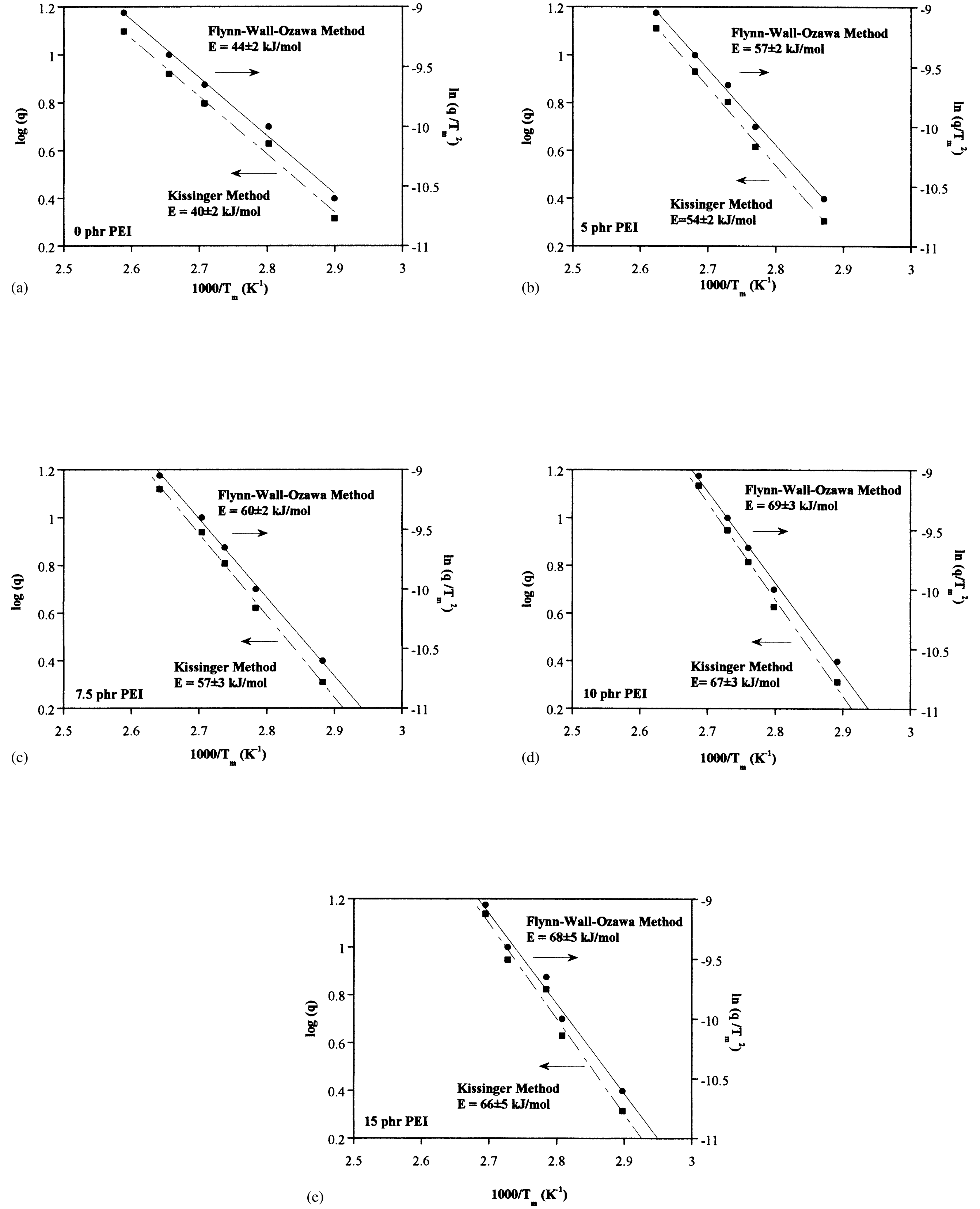

Fig. 3. Activation energies obtained by Flynn–Wall–Ozawa and Kissinger methods: (a) neat system; (b) 5 phr PEI; (c) 7.5 phr PEI; (d) 10 phr PEI; and (e) 15 phr PEI.

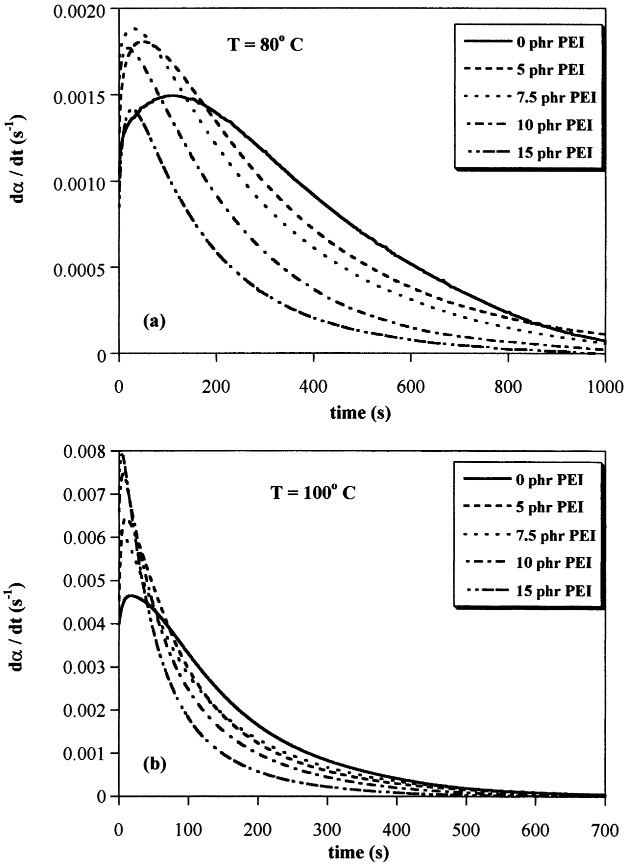

Fig. 4. Plot of the reaction rate versus time for neat epoxy and blends at temperatures of 80 and 100°C.

be seen that the values obtained by the Flynn–Wall–Ozawa method are slightly higher than the values obtained by the Kissinger method for the all blends, but these values are very similar. The results yield that the activation energy increase with the content in PEI, which means that PEI hinders the reaction between the epoxy and the amine.

3.4. Isothermal kinetic analysis: autocatalytic model

The autocatalytic model is a phenomenological approach. In this model a general equation is assumed for the curing process of many amine-cured epoxy systems is as follows [15–17]:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \tag{7}$$

where α is the conversion, k_1 and k_2 are the rate constants with two different activation energies and pre-exponential factors; m and n are the kinetic exponents of the reactions, and $m + n$ the overall reaction order. The constant k_1 of Eq. (7) can be calculated if the initial reaction rate at $\alpha = 0$ can be estimated. Both kinetic constants, k_1 and k_2 depend on temperature according to Arrhenius law.

For the determination of the cure kinetics by means of an autocatalytic model, first the isothermal cure in DSC is realized at several temperatures, then the experimental rate equation $(\alpha, d\alpha/dt)$ is determined for the complete course of the reaction, and finally the experimental results are adjusted with the kinetic equation. Thus, the reaction orders and the rate constants are obtained for each temperature. Finally, using the Arrhenius equation for the dependence of the rate constants on the temperature, the activation energies and the frequency factors are determined. To compute the parameters in Eq. (7) from experimental data, several methods have been proposed previously [18]. In the present study, the parameters m, n, k_1 and k_2 were estimated without any constraints on them, using a least squares method.

Isothermal DSC curves at 80 and 105°C of the neat epoxy resin and its blends of PEI are shown in Fig. 4 plotted as $d\alpha/dt$ versus time. These rate curves are of autocatalytic nature, with the maximum rate of conversion after the start of the reaction; which is similar at behaviour of other epoxy systems [19]. The results shown in these figures also demonstrate that the presence of PEI in the epoxy resin does not vary the autocatalytic nature. However, the behaviour of the reaction rate of the epoxy is modified by the presence of PEI content in the epoxy blends.

Whereas if the temperature of the isothermal is low, the rate of conversion is affected by the presence of poly(ether imide) enhanced with reference to the neat resin and decreasing when PEI contents increase. Moreover, if the temperature of the isothermal is close to T_g ($T = 100$°C) (Fig. 4(b)) the reaction rate of the epoxy is clearly increased by the presence of PEI since the maximum rate increases with the PEI content in the epoxy blends.

Since there are two kinetic constants, k_1 and k_2, two activation energies E_1 and E_2 could be obtained for the neat epoxy and its blends. The rate constants, which were obtained through considerable iteration and graphic procedures, are listed in Table 2.

The overall reaction order, $m + n$, is in the range 2.5–3 with $n \approx 2$ and m varying from 0.5 to 1 for the neat resin, and the blends with 5 and 7.5 phr of PEI. The values are slightly higher for the blend of 10 phr of PEI. The blends of 15 phr of PEI show anomalous values of n very high at low temperatures, decreasing at higher temperatures, as in these blends, the autocatalytic model can fit well only for the initial stage of reaction, probably owing to the high viscosity. This fact suggests that this model is not applicable in these cases.

The values of E_1 and E_2 obtained for the neat amine-cured DGEBA epoxy were 44 and 57 kJ mol^{-1}, respectively [12]. In comparison to DGEBA epoxy, the amine-cured DGEBA/PEI blends exhibited higher activation energies for E_1, due to the fact that the poly(ether imide) hinders the reaction of the resin with the hardener in the first stages. The activation energy for k_2 of the epoxy blends remained at lower values compared with that of the neat epoxy.

The comparison between the neat epoxy and its blends were developed. Fig. 5 shows the reaction rate against

Table 2
Autocatalytic model constants for PEI-modified DGEBA epoxy blends

T (°C)	m	n	$m+n$	$k_1 \times 10^3$ (s^{-1})	$k_2 \times 10^3$ (s^{-1})	$\ln A_1$	$\ln A_2$	E_1 (kJ mol^{-1})	E_2 (kJ mol^{-1})
Neat epoxy									
80	0.52	2.1	2.6	2.5	3.4	8.69	14.12	43.84	57.20
90	0.57	2.1	2.7	3.6	7.2				
100	0.49	2.1	2.6	3.8	16.0				
Epoxy/PEI (5 phr)									
80	0.47	2.01	2.48	1.3	2.8	17.22	9.88	69.80	45.89
90	0.88	1.97	2.85	3.2	5.9				
95	0.52	2.00	2.52	4.2	5.5				
100	0.41	2.00	2.41	4.6	8.4				
105	0.53	1.91	2.44	6.6	7.7				
Epoxy/PEI (7.5 phr)									
80	0.61	2.55	3.17	1.69	2.89	18.94	6.07	74.60	35.59
90	0.40	2.50	2.89	2.67	2.40				
95	0.54	2.42	2.95	4.30	3.35				
100	0.76	1.99	2.75	6.12	5.54				
105	0.81	1.93	2.74	8.81	5.57				
Epoxy/PEI (10 phr)									
80	0.38	2.98	3.36	1.6	1.5	18.89	7.30	74.22	40.40
90	0.43	3.10	3.54	3.8	2.7				
95	0.30	2.27	2.56	4.6	2.5				
100	0.23	2.03	2.26	6.6	2.9				
105	0.50	2.19	2.70	8.4	4.2				
Epoxy/PEI (15 phr)									
80	0.33	5.87	6.20	0.7	2.9	34.05	13.01	121.07	55.37
90	0.32	4.71	5.03	2.1	3.3				
95	0.53	4.24	4.77	4.6	11.8				
100	0.44	3.29	3.73	7.4	6.8				
105	0.51	2.7	3.21	10.5	8.9				

conversion curves for the epoxy resin and its blends with PEI (5, 7.5, 10 and 15 phr) at the temperature of 95°C. This figure shows that the behaviour of the epoxy and the blends is different, meanwhile the maximum reaction rate takes place at the same conversion, the conversions reached decrease with the content in PEI. The reaction rate versus conversion at other cure temperatures (90, 100 and 105°C) for the epoxy blends also demonstrated similar trends. If the curing temperature is low (80°C) the maximum reaction rate is obtained at higher conversions.

After vitrification any further progress in the cure reaction is virtually stopped, and so, therefore, the extent of cure is limited. This indicates that the cure kinetics in the later stage was indeed subjected to diffusion control as a result of vitrification. Differences between model predictions and experimental data were found to be greater when the curing temperature decreases.

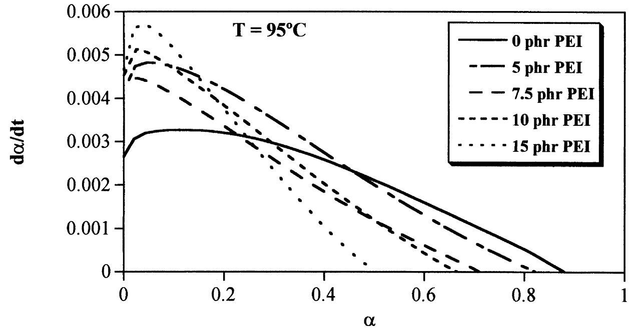

Fig. 5. Plots of the reaction rate, $d\alpha/dt$, versus conversion, α, for neat epoxy and its blends of PEI, at 95°C.

A semiempirical relationship, based on free-volume considerations, to explain the diffusion control in cure reactions was used by other researchers [20,21]. When the degree of cure reaches a critical value, α_c, diffusion becomes controlling and the rate constant k_d is given by

$$k_d = k_c \exp[-C(\alpha - \alpha_c)] \tag{8}$$

where k_c is the rate constant for chemical kinetics and C is a parameter. Eq. (8) corresponds to a rather abrupt onset of diffusion control at $\alpha = \alpha_c$, though the onset is gradual and there is a region where both chemical and diffusion factors are controlling. An overall effective rate constant, k_e, can be expressed in terms of k_d and k_c by the relation

$$\frac{1}{k_e} = \frac{1}{k_d} + \frac{1}{k_c} \tag{9}$$

This equation is combined with Eq. (8) to obtain the diffusion factor $f(\alpha)$ therefore

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \tag{10}$$

When α is much smaller than the critical value, $\alpha \ll \alpha_c$, then $f(\alpha($ is approximately unity, the reaction is kinetically

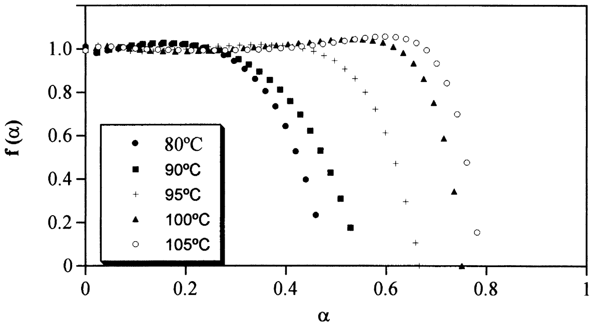

Fig. 6. Plot of diffusion factor, $f(\alpha)$, versus conversion, α, at different curing temperatures for the 10 phr PEI/epoxy blend.

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 [22] 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. (7). Fig. 6 shows the behaviour of $f(\alpha)$ with increasing conversion at different curing temperatures for DGEBA/1,3-BAC/PEI 10 phr. The decrease in $f(\alpha)$ and, hence, in the effective reaction rate due to onset of diffusion at higher conversions is seen. The diffusion factor, $f(\alpha)$ versus conversion at other three epoxy blends with PEI (5, 7.5 and 15 phr) also demonstrated similar trends.

Table 3
Values of critical conversion α_c, and of C parameter at different curing temperatures for each PEI/epoxy blend system

T (°C)	α_c	C
Neat epoxy		
80	0.71	18.10
90	0.79	25.33
100	0.86	20.02
Epoxy/PEI (5 phr)		
80	0.71	21.28
90	0.80	44.67
95	0.77	32.88
100	0.82	48.65
105	0.87	58.40
Epoxy/PEI (7.5 phr)		
80	0.62	49.03
90	0.61	30.81
95	0.66	31.00
100	0.81	41.28
105	0.84	43.14
Epoxy/PEI (10 phr)		
80	0.42	24.19
90	0.47	19.55
95	0.60	24.45
100	0.70	20.12
105	0.75	39.26
Epoxy/PEI (15 phr)		
80	0.27	43.77
90	0.32	22.17
95	0.45	34.30
100	0.54	26.53
105	0.62	21.95

Values of α_c and C obtained by applying nonlinear regression to $f(\alpha)$ versus α data to Eq. (10) are listed in Table 3. While a moderate increase in α_c was observed in the neat system and the blends of 5 and 7.5 phr of PEI when temperature increases, this increment for α_c is stronger for the other systems when the contents in PEI is larger. No discernible trend is found for the coefficient C, in agreement with the studies of Cole et al. [23] 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 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.

Fig. 7 shows the experimental values of $d\alpha/dt$ versus α and the corrected data in relation to the model with diffusion for the curing temperature of 100°C and Fig. 8 displays the curves of α versus t comparing the data calculated by the autocatalytic model, coupled with the diffusion factor, according to Eq. (10). Good agreement was found over the whole curing temperature range and for each concentration of poly(ether imide) and for all temperatures mentioned.

4. Conclusions

We have studied the system based on the diglycidyl ether of bisphenol A (DGEBA) modified with poly(ether imide) (PEI) (5, 7.5, 10 and 15 phr) and 1,3-bisaminomethylcyclohexane (1,3-BAC) as a curing agent. Kinetic analysis was performed using three kinetic models: Kissinger, Flynn–Wall–Ozawa and the phenomenological model developed by Kamal. Diffusion control is incorporated to describe the cure in the latter stages predicting the cure kinetics over the whole range of conversion.

In this work, the total heats of reaction were influenced by the presence of PEI showing a decrease of ΔH_0 with the increase in PEI, nevertheless, this fact should not be taken as a result, only as an indication that the reaction mechanism was likely to be changed by the presence of PEI in the blend. The results of the two dynamic methods yield that the systems with PEI need more energy that the neat system. An autocatalytic mechanism was observed for amine-cured epoxy–poly(ether imide) blends over a range of composition, although the addition of PEI has a marked effect on cure kinetics in DGEBA/1,3-BAC resin system. In general, the initial reaction rates of blends are higher that the neat resin, however for low temperature this behaviour is less clear. The maximum conversions reached decrease with the phr

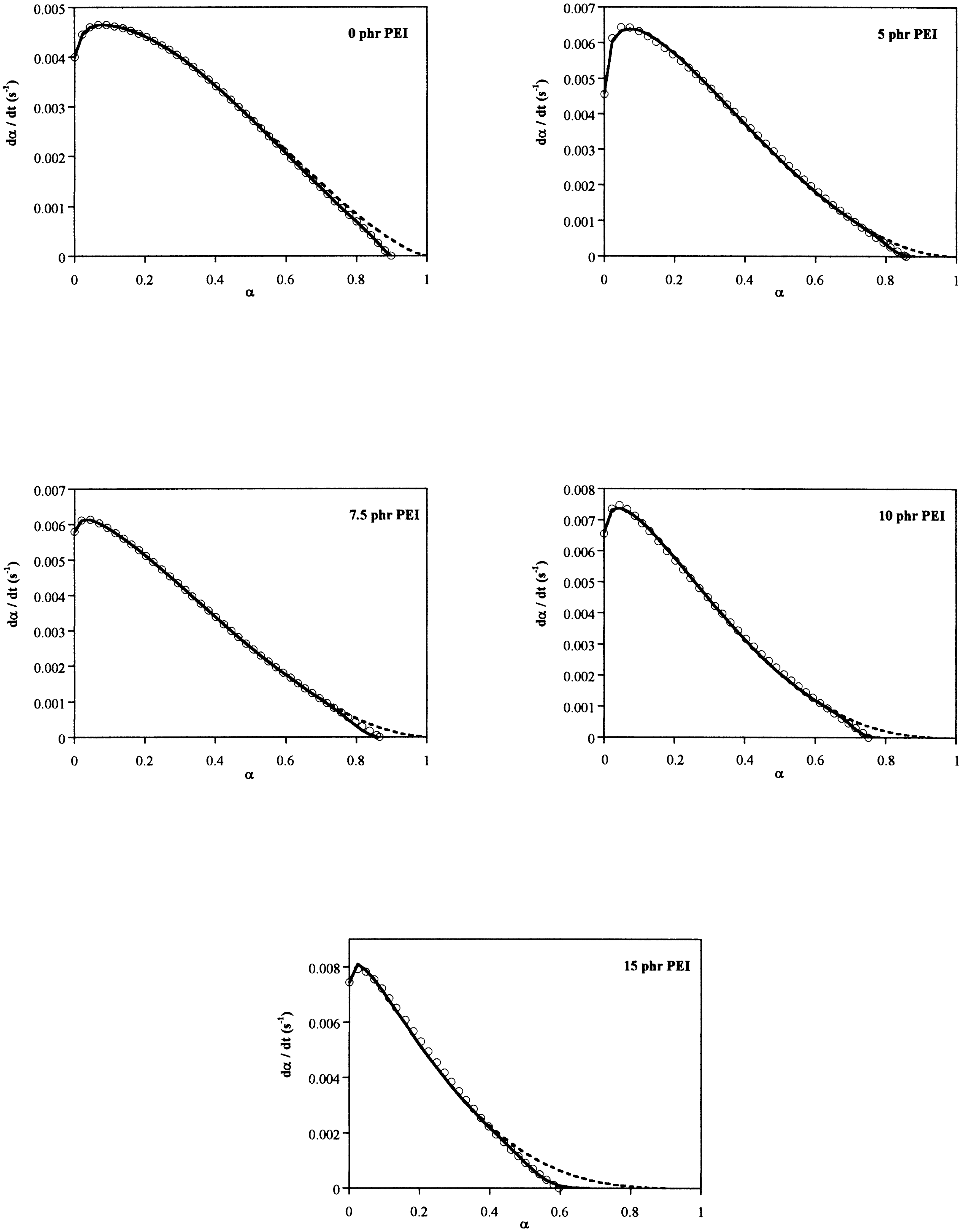

Fig. 7. Comparison of experimental data with model predictions: reaction rate, dα/dt, versus conversion, α, at 100°C for all the blends: (○ ○ ○) experimental; (- - - -) autocatalytic model; (—) autocatalytic model with diffusion.

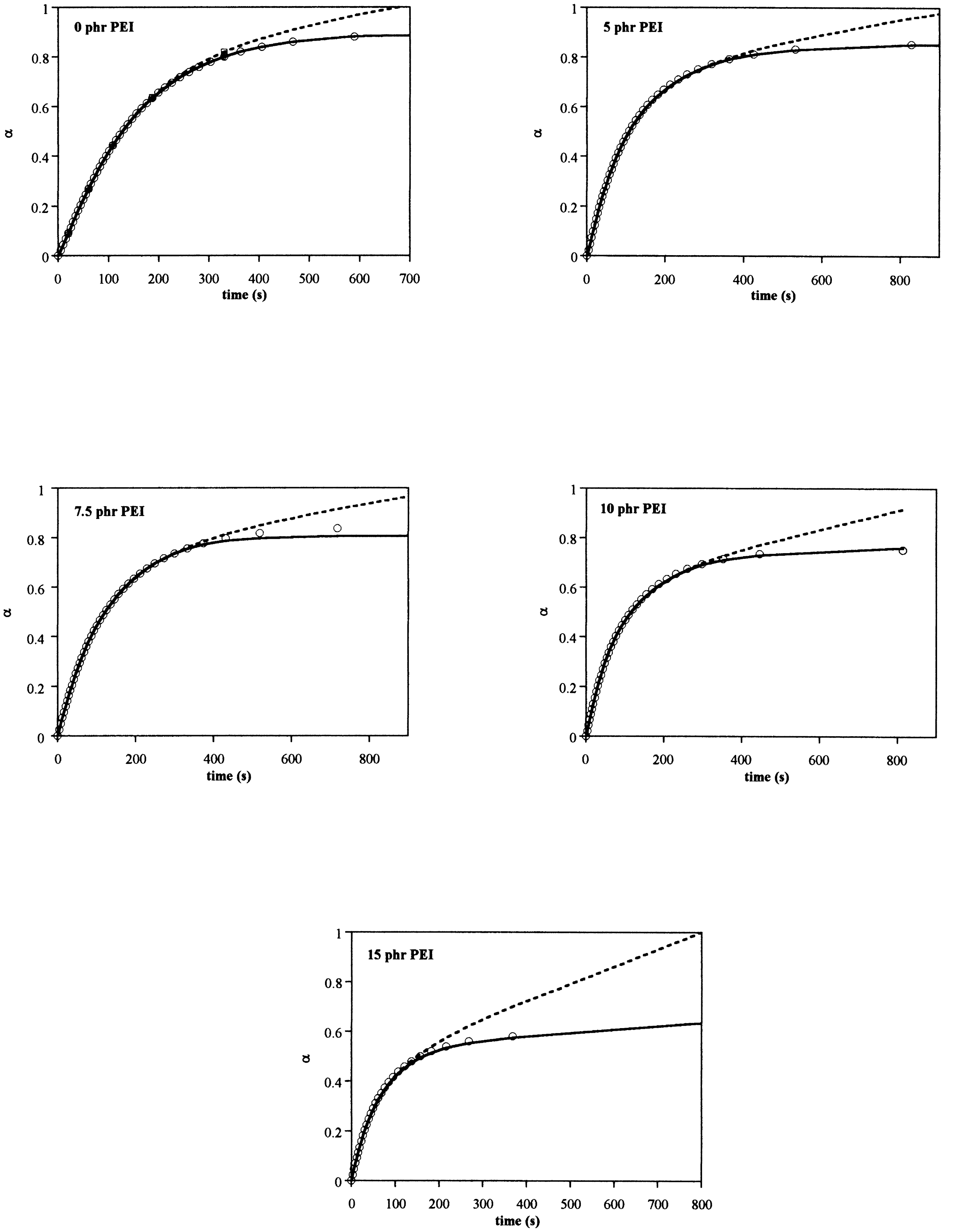

Fig. 8. Comparison of experimental data with model predictions: conversion, α, versus time at 100°C for all the blends: (○ ○ ○) experimental; (- - - -) autocatalytic model; (—) autocatalytic model with diffusion.

of PEI, so, it seems that PEI hinders the reaction between epoxy and hardener.

The kinetic parameters for the epoxy blends were obtained and the proposed kinetic model was found to describe the cure behaviour of the epoxy and its blends up to the vitrification point. Although the reaction mechanism of the epoxy blends remained the same as that of the neat epoxy, the reaction rates of the blends were found to be higher than the latter. The blends of 15 phr of PEI show an anomalous behaviour if the cure temperature is low. This fact suggests that this model is not applicable in these cases.

In order to describe the cure in the later 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. It was observed that the behaviour of the blends of 5 and 7.5 phr of PEI is the same as that for the neat system, whereas the blends of 10 and 15 phr show a different kinetic behaviour.

The advantage of the autocatalytic adjustment is that it can provide kinetic parameters, such as the rate constants at different temperatures, the reaction orders, the activation energy and the frequency factors. A disadvantage is that such a complex process as curing is associated with a single reactive process with a single activation energy, so the interpretation of the kinetic parameters is difficult. These advantages and disadvantages were the same for the system with and without PEI, hence this method is applicable in both cases.

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