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Rheokinetic variations during curing of a tetrafunctional epoxy resin modified with two thermoplastics

B. Fernández, M.A. Corcuera, C. Marieta, I. Mondragon *

Dpto. Ing. Química y M. Ambiente, Escuela Universitaria de Ingeniería Tecnica Industrial, Universidad del País Vasco/Euskal Herriko Unibertistatea, Avda. Felipe IV, 1B, 20011 San Sebastián/Donostia, Spain

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Abstract

The curing kinetics of an epoxy matrix based on tetraglycidyl diamino diphenyl methane polymerized with diamino diphenyl methane and those for its mixtures with poly(methyl methacrylate) and poly(ethersulfone) (PES) at compositions ranging from 0 to 15 wt.% were studied using differential scanning calorimetry in isothermal and dynamical conditions. Rheological properties were also measured to follow curing evolution. Apparent activation energies were calculated from the so obtained gelation times. Thermoplastic addition to the thermosetting resin delayed the polymerization, and above all in the PES case but it does not modify the cure kinetics of the thermosetting matrix. A modified autocatalytic kinetic model which contains the diffusional term was used. Satisfactory results were obtained as conversion curves fitted quite well the experimental data. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy resin; Poly(methyl methacrylate); Poly(ethersulfone); Cure kinetics; Rheology

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1. Introduction

Epoxy resins are extensively used as coatings, electrical or electronic materials, adhesives, and in structural applications because of their high performances, such as good mechanical, thermal, and electrical properties [1]. However, further growth of these highly crosslinked materials is limited because of their inherent brittleness. Generally, it is widely recognized that rubber toughening or hard filler modification cannot lead to massive yielding with highly crosslinked matrices [2]. As an alternative to rubbers, toughening of highly crosslinked resins has been explored by physical blending with high performance engineering thermoplastics (TP), such as poly(ethersulfone) (PES) [3,4], polysulfone (PSU) [5–7], poly(ether ether ketone) (PEEK) [8] and poly(ether imide) (PEI) [9,10]. The improvement in fracture toughness by making polymer alloys of thermosets with thermoplastics can be achieved without losses in high modulus and high temperature performance of the epoxy matrix [2].

The mechanical properties of the cured composites are determined by the extent of cure, which depends on processing conditions [11]. Therefore, a clear understanding of the curing mechanism and the ability to develop suitable kinetic models to simulate the curing reaction are essential to predict and to control the end properties of the crosslinked materials [12].

In the present work, a preliminary study performed on thermoplastic modified tetrafunctional epoxy matrices, that ultimately are being used for studies on mechanical and fractures toughness properties of carbon fiber composites, has been performed. The specific objective of this research was to estimate the kinetic parameters of an epoxy matrix (tetraglycidyl diamino diphenyl methane/diamino diphenyl methane (TGDDM/DDM) modified with poly(methyl methacrylate) (PMMA) or PES. The relationship between kinetics and rheology of curing is also presented.

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[*] Corresponding author. Fax: +34-943-471097.
E-mail address: iapmoegi@sc.ehu.es (I. Mondragon).

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2. Experimental

2.1. Materials

The epoxy resin used in this work was a TGDDM, Rutapox VE 2895/LV, kindly supplied by Bakelite Ibérica, with an epoxy equivalent weight of 120 g/eq as measured by titration. The hardener was DDM, Fluka quality. The PMMA was Altuglas Gr 9E-Elf Atochem. The PES was Basf Ultrason E 2010. The amine/epoxy stoichiometric ratio was held constant at $r = 1.0$, whilst varying the thermoplastic content from 0 to 15 wt.%.

Sample preparation was the same for both thermoplastic modified mixtures: PMMA or PES, in powder form, were dissolved in methylene dichloride at around 10 wt.%, furtherly adding the TGDDM at room temperature. The solution was then heated in an oil bath at 100°C to drive off as much solvent as possible, and residual solvent was removed under vacuum at 100°C for 12 h. The DDM hardener was then added with vigorous stirring at the same temperature for 5 min. The mixture was immediately frozen to room temperature, and then stored in a refrigerator.

2.2. Differential scanning calorimetry

Calorimetric measurements were carried out using a Perkin–Elmer differential scanning calorimeter (Model DSC-7). Calibration was carried out with high purity indium.

Samples were removed from the refrigerator and allowed to warm to room temperature before testing. Small quantities of the samples (2–6 mg) were placed in hermetically sealed aluminum pans.

Isothermal experiments were conducted in the 80–140°C temperature range in order to obtain the cure rate and the extent of cure as a function of time. After completion of isothermal cure, samples were cooled rapidly in the DSC to 35°C and then reheated to 250°C at 10°C min^{-1} in order to determine the residual heats of reaction. The sum of the isothermal and the residual heats of reaction would represent the total heat of cure, ΔH_{T}, but in this work, it has been obtained from dynamic DSC experiments. The reaction was considered to be complete when DSC thermograms levelled off to the baseline.

The extent of reaction, x, at any instant during isothermal curing is given by the following equation:

$$x = \Delta H_{\mathrm{i}}(T)/\Delta H_{\mathrm{T}} \tag{1}$$

where $\Delta H_{\mathrm{i}}(T)$ is the reaction enthalpy released at a certain time t during each isothermal experiment.

The reaction rate, $\mathrm{d}x/\mathrm{d}t$, has been calculated through equation:

$$\mathrm{d}x/\mathrm{d}t = (\mathrm{d}H/\mathrm{d}t)_t/\Delta H_{\mathrm{T}} \tag{2}$$

where $(\mathrm{d}H/\mathrm{d}t)_t$ is the heat flow as a function of the curing time obtained from the isothermal DSC experiment.

2.3. Rheological measurements

The rheological properties during curing were measured at 10 Hz using a Metravib viscoanalyzer with an annular pumping device. Around 4 g of the sample were introduced in a steel cylinder of 10 mm diameter. Oscillatory flow measurements were made with a device of 1 mm diameter. Although tests at several frequencies are necessary for accurate gelation time determination being this physical phenomenon associated with time to which the loss factor, $\tan\delta$, is independent of frequency using multiwave time tests [13], in this work the maximum peak in $\tan\delta$, based on the point where there is a maximum difference between the elastic and viscous behavior of the system has been arbitrarily chosen for determination of gelation time [14,15].

An overall activation energy for polymerization can be obtained from gelation times, assuming that cure reactions may be described by differential equations containing one unique apparent activation energy [16, 17], as follows:

$$\mathrm{d}x/\mathrm{d}t = A\exp(-E_{\mathrm{a}}/RT)f(x) \tag{3}$$

where A is a constant factor, E_{a} is the apparent activation energy for the overall reaction, R is the gas constant, T is the absolute isothermal cure temperature, and $f(x)$ is a function of the reaction mechanism and the extent of reaction and is assumed to be independent of the cure temperature.

Integration of this equation from $x = 0$ to $x = x_{\mathrm{gel}}$ by taking natural logarithms leads to:

$$\ln\int_0^{x_{\mathrm{gel}}}\frac{\mathrm{d}x}{f(x)} = \ln A + \ln(t_{\mathrm{gel}}) - \left(\frac{E_{\mathrm{a}}}{RT}\right) \tag{4}$$

Based on the Flory theory [18], the extent of reaction at gelation point is constant, so the above equation can be expressed as:

$$\ln(t_{\mathrm{gel}}) = \mathrm{constant} + E_{\mathrm{a}}/RT \tag{5}$$

Thus, from the slope of the plot for the linear relationship between $\ln(t_{\mathrm{gel}})$ and the inverse of temperature the apparent activation energy can be calculated.

3. Results and discussion

3.1. Kinetic analysis

Dynamic DSC experiments were performed in the temperature range from 35°C to 250°C at 10°C min^{-1} for the TGDDM/DDM matrix and for the modified mixtures at 5, 10 and 15 wt.% TP contents. Figs. 1 and 2 show the dynamic thermograms for the PMMA and PES-modified epoxy mixtures, respectively. The integrated area of the exothermic curve was used to calculate ΔH_T. These values along with the peak temperature, T_p, are listed in Table 1 for every PMMA- and PES-modified epoxy mixtures.

The exothermic peak temperature was higher with increasing the concentration of the modifier. This displacement was higher for PES than for PMMA modification, so indicating that both PMMA but above all PES delayed the curing reaction rate of the neat epoxy matrix. Nevertheless, both thermoplastics apparently did not modify the mechanism of the epoxy polymerization as ΔH_T decreased proportionally to the PMMA and PES amount in the mixture. This tendency was also observed by others authors when adding a thermoplastic to the neat epoxy resin [19,20]. Thus, the delay in polymerization should mainly correspond to physical reasons such as dilution effect and/or viscosity increase because of thermoplastic addition [20–22] or by the decrease of the density of reaction groups [23]. However, in the case of PES modification some stoichiometrical imbalance could have occurred through curing or some epoxy could remain in the PES-rich phase after phase separation as the total enthalpy was slightly lower than that corresponding to the amount of neat epoxy in the modified mixtures.

The neat epoxy was also studied during isothermal curing at 80°C, 90°C, 100°C, 110°C and 140°C in order to determine the evolution of curing. Typical plots of x versus time are shown in Fig. 3. The shape of these plots is similar to that observed for other epoxy matrices being similar to that expected for an autocatalytic process [24,25]. As expected, the reaction rate and the final conversion increases with increasing cure temperature.

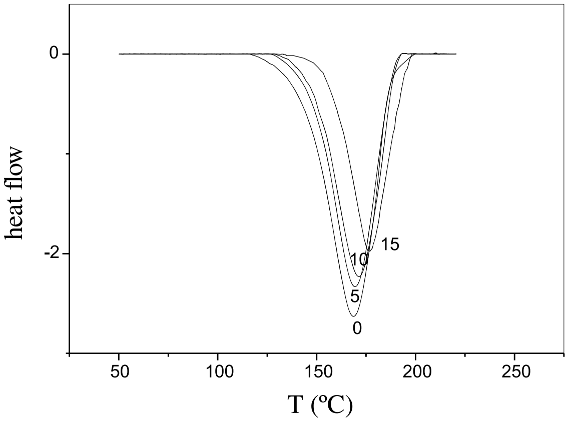

Fig. 1. Dynamic thermograms for neat and epoxy matrices with several contents of PMMA.

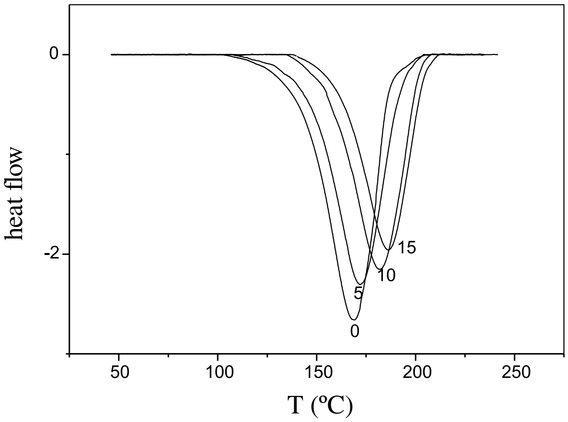

Fig. 2. Dynamic thermograms for neat and epoxy matrices with several contents of PES.

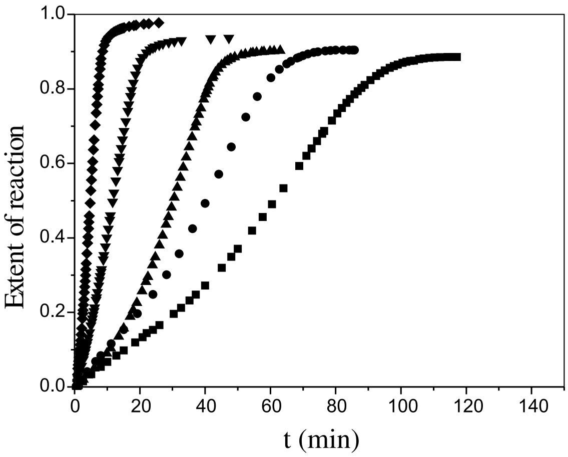

Fig. 3. Conversion versus time profiles for the neat epoxy matrix for different curing temperatures: (■) 80°C, (●) 90°C, (▲) 100°C, (▼) 110°C, (◆) 140°C.

Table 1
ΔH_T and T_p for neat and PMMA- and PES-modified matrices

TP	PMMA				PES			
	0	5	10	15	0	5	10	15
ΔH_T (J g^{-1})	484	463	450	437	484	426	413	399
T_p (°C)	168	169	171	177	168	172	182	186

This increase indicates that reactions reach vitrification – physical transformation from a liquid or rubbery state to a glass state as a result of the increase in crosslinking density at progressively higher conversion when higher reaction temperatures are used [19] as this phenomenon occurs when the glass transition temperature, T_g, becomes equal to the curing temperature.

Figs. 4 and 5 show, respectively, the effect of PMMA or PES addition to the neat matrix in the curing evolution at 100°C. These plots show the slight delay in the reaction evolution when adding PMMA and a higher decrease on reaction rate upon PES addition as earlier discussed from the dynamic results. Similar final conversions after isothermal curing were found by Jenniger et al. [23] for the diglycidyl ether of bisphenol A (DGEBA)/DDM/PES system.

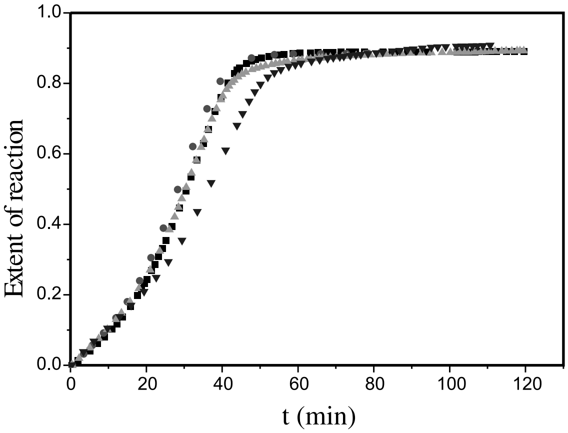

Fig. 4. Conversion versus time profiles at 100°C for the epoxy matrix (■) and PMMA-modified matrices: (●) 5 wt.%, (▲) 10 wt.%, and (▼) 15 wt.%.

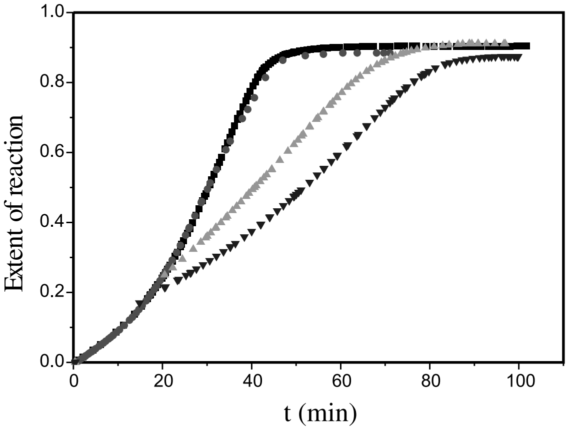

Fig. 5. Conversion versus time profiles at 100°C for the epoxy matrix (■) and PES-modified matrices: (●) 5 wt.%, (▲) 10 wt.%, and (▼) 15 wt.%.

3.2. Rheological analysis

Gelation is a phenomenon that takes place during thermosetting polymer curing. As cure reaction proceeds, the molecular weight increases and several chains link together into networks of infinite molecular weight [26–29]. This sudden and irreversible transformation from a viscous liquid to an elastic gel is defined as the gelation point; and the time at which it occurs, at a given isothermal cure temperature, is the gelation time [27]. This gelation time can be experimentally determined following different procedures [14].

Flory [18] considered that gelation is the point in which a molecular chain reaches a theoretical infinite molecular weight. Based on this theory, this phenomenon occurs for a determined extent of reaction, which can be expressed as follows:

$$x_{\text{gel}} = \left[\frac{1}{(f_e - 1)(f_a - 1)r}\right]^{1/2} \tag{6}$$

where x_{gel} is the extent of reaction at gelation point, f_e and f_a are the epoxy and amine functionalities, respectively, and r is the amine/epoxy stoichiometric ratio.

In a first approximation, for the stoichiometric TGDDM/DDM matrix x_{gel} is around 0.36 by supposing that the rate constants for primary and secondary amine addition, are equal. Thus, the gelation time, obtained through the extent of reaction versus time curves from the kinetic study, can be theoretically approximated by means of thermal measurements. Table 2 shows gelation times obtained through rheological study and isothermal DSC experiments for the neat matrix and for 10 wt.% thermoplastic containing mixtures at 100°C, 110°C and 140°C. A slight increase in gelation times occurs on adding PMMA and PES to the resin. These results confirm the kinetic study where little changes of the reaction rate for the epoxy–amine system were obtained in the modified mixtures.

Gelation times obtained from DSC are shorter than those obtained from rheological measurements, confirming that small differences in sample volume, thermal history or atmosphere used in different techniques can lead to a certain uncertainty in the comparison of results [30]. Eloundou et al. [31] found, as well, a phase difference between the gelation time obtained by kinetic analysis and that for rheological one. These authors pointed out two possible reasons to explain the delay in gelation times: (a) the time to reach the thermal equilibrium is higher when higher the mass of the sample used is, yielding a delay in the onset of the kinetics; in this study the mass of the sample used in the rheological study was higher than that used in the kinetic one; (b) the catalytic effect of the water vapor present in the atmosphere in which the sample was prepared. This effect is higher when smaller the mass of the samples is as the

Table 2
Gelation times at different cure temperatures obtained by rheological and thermal measurements

Matrix	T (°C)	Gelation time (min) ($\tan\delta_{\max}$) (rheology)	Gelation time (min) ($x_{\mathrm{gel}} = 0.36$) (DSC)
Neat epoxy	100	34	25
	110	15	10
	140	3	3
10 wt.% PMMA	100	35	26
	110	20	16
	140	4	5
10 wt.% PES	100	38	30
	110	21	20
	140	4	6

relationship (contact area with the air/mass of the sample) is higher in the case of small samples. In this work, conditions similar to those given by Eloundou et al. [31] have been employed. Besides, nor the approximation used for x_{gel} calculation through Flory's theory is exact since the primary amine addition rate constant is usually higher than that for the secondary amine addition neither the neat resin is completely pure, so doing that the approximation used can only be used as for qualitative comparison of the cure kinetics of the mixtures analyzed.

Values of $\ln(t_{\mathrm{gel}})$ obtained by rheological tests are plotted against $1/T$ in Fig. 6. The activation energy values (71, 73, and 69 for the neat, the PMMA- and PES-modified matrices, respectively) are almost equal for all mixtures, so the addition of PMMA and PES does not modify the reaction mechanism of TGDDM/DDM matrix. This means that the same reactions take place, although the reaction rate changes upon thermoplastic addition.

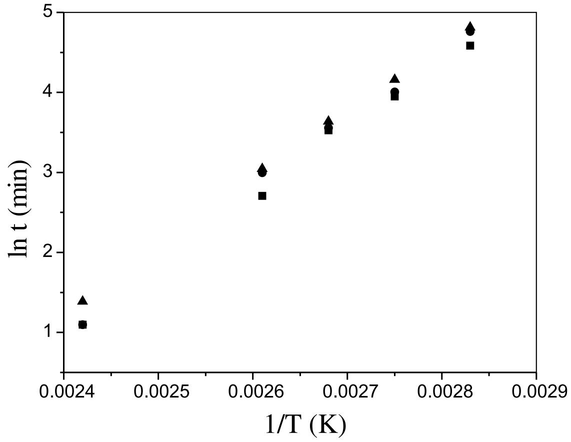

Fig. 6. Variation of t_{gel} with cure temperature for (■) neat matrix, (●) modified with 10 wt.% PMMA, and (▲) modified with 10 wt.% PES.

3.3. Kinetic model

The study of the curing kinetics of the tetrafunctional epoxy matrix has been based on the kinetic model proposed by Horie et al. [32] and simplified by Sourour and Kamal [33]. This model assumes that the epoxy–amine reaction is the unique reaction that takes place during curing. This reaction can be catalyzed by the hydroxyl groups formed during the reaction or by those existing in the neat resin or by acidic impurities present in the system. It also assumes that all the primary and secondary amine hydrogens have the same degree of reactivity towards epoxy groups.

The kinetic model commonly used for epoxy resins and other thermosetting resins is [34,35]:

$$\mathrm{d}x/\mathrm{d}t = (k_1 + k_2 x^m)(1 - x)^n \tag{7}$$

where k_1 is the rate constant for the reaction catalyzed by groups initially present in the resin, k_2 is the rate constant for the reaction catalyzed by hydroxyl groups formed in the reaction, and $m + n$ is the overall reaction order.

Several simplifications have been suggested in the literature survey, among which a widely employed one makes use of the observation that, in general, the curing reaction of epoxy resins is a second-order process, that is, $m + n = 2$ [12]. In this form, the above equation does not take into consideration the fact that, as the conversion increases and the T_g of the material approaches the reaction temperature, the process becomes diffusion controlled. The reaction rate would decrease and go to zero before reaching full conversion. So, as the final conversion is usually strongly dependent on the reaction temperature, Musto et al. [12] have suggested that this effect could be accounted for by substituting the term $(1 - x)$ on the right side with the term $(x_{\max} - x)$, where $x_{\max}$ represents the final conversion reached at the investigated temperature. So, with this assumption, Eq. (7) reduces to:

$$\mathrm{d}x/\mathrm{d}t = (k_1 + k_2 x^m)(x_{\max} - x)^n \qquad (8)$$

The extent of reaction has been determined using isothermal DSC experiments at three diferent temperatures: 100°C, 110°C, and 140°C through Eq. (1) and the rate of reaction, $\mathrm{d}x/\mathrm{d}t$, through Eq. (2).

TGDDM/DDM matrix with a stoichiometric composition has been employed to test the accuracy of Eq. (8) with $m = 1$ and $n = 1$.

Plotting of $(\mathrm{d}x/\mathrm{d}t)/(x_{\max} - x)$ versus x, a straight line should be obtained with intercept k_1 and slope k_2. These constants follow an Arrhenius relationship with the cure temperature,

$$k_i = A_i \exp(-E_i/RT) \quad i = 1,2 \qquad (9)$$

Plotting $\ln k_i$ versus $1/T$, gives straight lines of slope $-E_i/R$ and intercept $\ln A_i$. These plots are given for k_1 and k_2 in Figs. 7 and 8, respectively, for the neat matrix. Table 3 shows the values of the parameters so obtained.

The values of E_1 and E_2 obtained in this study for the neat amine-cured TGDDM epoxy, 73 and 70 kJ mol^{-1}, respectively, are closed to each other, suggesting that an unique activation energy could represent the overall curing reaction, as reported by some authors, [16,17,36]. This global activation energy is in agreement with the value obtained for this matrix in the rheological study. Moreover, E_1 and E_2 agree well with those reported in the literature survey [19,37]. The autocatalytic kinetic model and the rate constants obtained, were used to calculate conversion versus time profiles for the TGDDM/DDM matrix at three isothermal cure temperatures.

Fig. 9 shows the results for the neat tetrafunctional matrix at each cure temperature, where plots of experimental values of conversion versus time are compared with those calculated by the autocatalytic kinetic model represented by Eq. (8), with $m = 1$ and $n = 1$. The conversion curves fit quite well the experimental data in all conversion range, above all up to conversions higher than for gelation and also for that corresponding to vitrification of the epoxy network at each cure tempera-

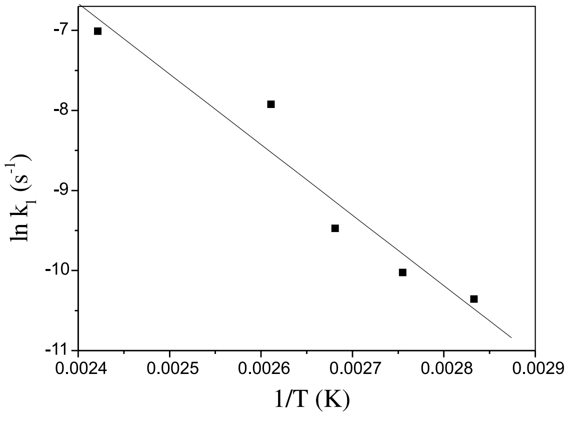

Fig. 7. Arrhenius plot of k_1 rate constant for TGDDM/DDM matrix.

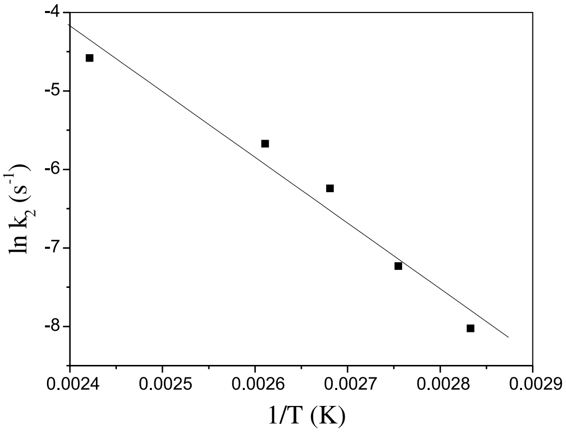

Fig. 8. Arrhenius plot of k_2 rate constant for TGDDM/DDM matrix.

Table 3
Kinetic parameters from isothermal DSC experiments for TGDDM/DDM matrix

T (°C)	k_1 (min^{-1})	k_2 (min^{-1})
80	1.91×10^{-3}	1.97×10^{-2}
90	2.66×10^{-3}	4.34×10^{-2}
100	4.62×10^{-3}	1.17×10^{-1}
110	2.18×10^{-2}	2.06×10^{-1}
140	5.42×10^{-2}	6.18×10^{-1}
A_i (min^{-1})	11.64×10^{7}	4.94×10^{8}
E_i (kJ mol^{-1})	73.2	69.6

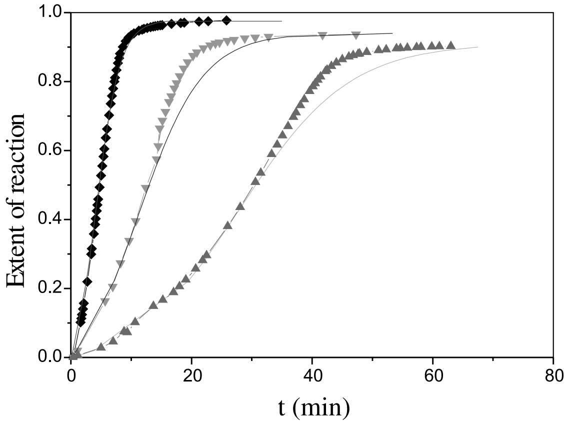

Fig. 9. Comparison of experimental data with Eq. (8) predictions at three different temperatures for TGDDM/DDM matrix: (▲) 100°C, (▼) 110°C, (◆) 140°C, (—) model.

ture. So the kinetic model presented in Eq. (8) appears to be a suitable model as compared to Eq. (7) since the latter only describes accurately the cure behavior in the early stages of the curing progress [12].

4. Conclusions

The kinetic effects caused by the presence of a thermoplastic, PMMA or PES, during the cure of an epoxy–amine system have been studied.

Both kinetic and rheological studies illustrate that PMMA but above all PES delayed the curing reaction rate of the neat epoxy matrix. This delay is generally attributed to the dilution effects because of thermoplastic addition. As the total enthalpy was slightly lower in the case of PES modification than that corresponding to the amount of neat matrix, some stoichiometric imbalance in the epoxy phase could have occurred during curing.

The apparent activation energy values were almost the sames for all mixtures, indicating that the addition of PMMA and PES did not modify the reaction mechanism of the neat matrix. This means that, although the reaction rate changed upon thermoplastic addition the same reactions took place.

An autocatalytic kinetic model, taking into account the vitrification phenomenon through curing, was employed to calculate the kinetic parameters for the curing reaction of the amine-cured tetrafunctional epoxy resin. The activation energies so obtained were found to be in close agreement with the values obtained by fitting the kinetic model to the experimental rheological data.

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