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Thermal analysis of standard and toughened high-performance epoxy matrices [1]

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Abstract

The reaction kinetics of commercial high-performance matrices has been characterized by differential scanning calorimetry (DSC). Standard and new toughened epoxy matrix prepregs based on tetraglycidyl diamino diphenyl methane–diamino diphenyl sulfone (TGDDM–DDS) formulations have been studied. The toughened epoxy matrix prepreg, modified by addition of a second thermoplastic phase, is characterized by a lower reactivity, probably affected by the presence of the second non-reactive thermoplastic phase. The effect of diffusion control phenomena on the reaction kinetics, associated with evolution of the glass transition temperature as a function of the degree of polymerization and crosslinking, has been considered in the formulation of a modified *n*th-order kinetic model. This describes incomplete reactions in isothermal tests and the heating rate dependence of dynamic test results, and can thus be used to describe the behaviour of the reactive matrix during processing under complex thermal conditions.

INTRODUCTION

High-performance structural composite laminates for aviation applications are generally produced by the Autoclave/Vacuum Degassing Laminating Process. In this process, preimpregnated plies (prepregs) of the desired shape are laid in a prescribed orientation to form a laminate. The laminate is placed on a smooth metal tool. The entire system is then placed in an autoclave, where the polymerization reactions of the thermoset matrix are activated and the composite is consolidated. Most laminates are currently fabricated by using carbon or aromatic fibres, with an epoxy matrix based on tetraglycidyl diamino diphenyl methane (TGDDM)–diamino diphenyl sulfone (DDS) formulations. In recent years, new chemical systems have been incorporated into the family of high-performance matri-

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ces for structural composites. The standard TGDDM–DDS epoxy systems that dominated the field for many years have been modified with rubber inclusions or a thermoplastic second phase, primarily to improve their impact behaviour.

Prepreg consolidation is accompanied by polymerization (curing) and rheological changes of the matrix that strongly influence the final properties and the quality of the laminate. Curing is also coupled with heat generation as a result of exothermic thermosetting reactions. The relative rates of heat generation and transfer thus determine the values of the composite temperature, and, hence, of the progress of the reaction and the viscosity through the thickness of the laminate. Uncontrolled polymerization may cause undesired and excessive thermal and rheological variations inducing microscopic and macroscopic defects in the composite part. Processing of polymeric composites based on thermoset matrices thus requires optimization of the curing parameters, as well as adequate formulation and characterization of the reacting system.

In previous papers, a general model for the description of the thermo-chemo-rheological behaviour of classical epoxy and polyester matrices during the processing of thermoset-based composites has been proposed [1,2]. Kinetic and rheological sub-models correlating the thermal and the chemo-rheological behaviour of different matrices to the molecular and chemical characteristics of the reactive systems were integrated into a heat transfer model. The master model describes the behaviour of the main variables (temperature, degree of reaction viscosity) during processing of the composite, and can be used for simulation and optimization of the process under different conditions. The effect of the variable physical properties of epoxy matrices on the reaction kinetics in the form of diffusion control related to the evolution of the glass transition temperature as a function of the degree of polymerization and crosslinking, has been also reported [3].

This paper describes the application of this approach to comparison of the kinetic behaviour of standard and toughened epoxy matrices through the formulation of a kinetic model from the results of thermal analysis. Isothermal and dynamic DSC tests were used to calculate its parameters and to determine its validity. Experiments with complex thermal conditions of the type used in autoclave processes were also employed for this purpose.

THERMAL ANALYSIS OF EPOXY MATRICES

Physical aspects

Polymerization of a thermoset polymer generally involves transformation of a fluid resin into a rubber (gelation), and then into a solid glass (vitrification) through chemical reactions between active groups that form a progressively denser network. Gelation corresponds to the incipient formation of an infinite network of crosslinked polymer molecules, and vitrification corresponds to transformation of the gel into a glass owing to the increase in molecular weight. Processing of thermoset matrices is strongly dependent on the physical properties characterizing curing stages. Polymer viscosity increasingly affects the mobility of the reactive groups, thus modifying the reaction kinetics. This effect is strongly marked near vitrification, where the reaction generally ceases. It may indeed be quenched by vitrification, and subsequent exposure to temperatures higher than cure temperatures could result in further reaction. These concepts have been stated clearly in the literature. Their influence on kinetic characterization, however, has not been extensively investigated.

Under isothermal conditions, thermal analysis can be used to follow gelation and vitrification as a function of time. The physical behaviour of thermoset systems in isothermal processes has been analysed extensively by Gillham and co-workers [4,5] with a time–temperature–transformation (TTT) diagram predicting the times to gelation and to vitrification versus temperature. When a heating rate is imposed, however, the physical properties are affected by both structural modifications and temperature changes. Adabbo and Williams [6] have used Gillham's concepts to analyse the behaviour of thermosetting systems in a conversion–temperature phase diagram and discuss curing process under different isothermal and non-isothermal conditions.

Isothermal and dynamic experiments conducted by differential scanning calorimetry (DSC) have also been widely used [1–7] for the indirect determination of the progress of curing in thermosetting systems. A kinetic model can be constructed by processing the data thus obtained. A recent approach accounts for diffusion control effects in formulation of the kinetic model by considering the effect of the evolution of the glass transition temperature as a function of the degree of reaction.

Reaction kinetics

Considerable research has been devoted to the curing of epoxy resins and matrices. Comprehensive reviews of kinetic characterization of epoxy systems by DSC have been presented by Prime [7] and Barton [8]. The principal developments in this field will now be discussed.

DSC has been employed for determination of the progress of curing by assuming that the heat evolved during a polymerization reaction is proportional to the extent of reaction. In addition, it has often been used to formulate and check theoretical and empirical kinetic models, and to calculate their parameters.

For the interpretation of DSC data, the degree of reaction α has been defined as [9]

$$\alpha = H(t)/H_{\mathrm{T}} \tag{1}$$

where $H(t)$ is the heat developed between the starting point and a given time t and H_{T} is the total heat developed, calculated by integrating the total area under the DSC curve. The reaction rate is thus given by the expression

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{1}{H_{\mathrm{T}}} \frac{\mathrm{d}H}{\mathrm{d}t} \tag{2}$$

where $\mathrm{d}H/\mathrm{d}T$ is the rate of generation of heat as measured directly from the DSC thermogram. This information can be processed to construct a kinetic model for α as a function of time and temperature.

Processing of epoxy matrix composites involves very complex reactions. Nevertheless, several equations have been proposed to describe their general behaviour as an overall kinetic process with a generic α, usually in the form

$$\mathrm{d}\alpha/\mathrm{d}t = kf(\alpha) \tag{3}$$

where k is the temperature-dependent rate constant and $f(\alpha)$ is a function to be determined by best-fitting of the experimental results. Horie et al. [10] used isothermal DSC to investigate the curing kinetics of epoxies with amines and concluded that the curing reaction of diglycidyl ether of bisphenol A (DGEBA) with aliphatic tetrafunctional diamines proceeds through a third-order mechanism followed by a diffusion-controlled mechanism. Prime [9] employed an empirical single nth-order equation to fit the isothermal DSC data for DGEBA resin cured with amines

$$\mathrm{d}\alpha/\mathrm{d}t = k(1-\alpha)^{n} \tag{4}$$

while a different equation was proposed for dynamic DSC tests characterized by dependence of the experimental signal on the heating rate. Barton [11] proposed superposition of isothermal results to interrelate isothermal and dynamic DSC results for epoxy-based systems, irrespective of the kinetic model used, but no direct correlation between experimental and model results was found. Souror and Kamal [12] assumed that both primary amine hydrogen atoms have equal reactivity, so that the total rate of consumption of epoxies could be expressed by modifying the Horie et al. model [10], i.e.

$$\mathrm{d}\alpha/\mathrm{d}t = (k_1 + k_2\alpha)(1-\alpha)(B-\alpha) \tag{5}$$

Isothermal DSC experiments have been used to test eqn. (5) and calculate its parameters. The model fitted the isothermal experimental data, except in the later stages where the reaction mechanism is diffusion controlled.

Ryan and Dutta [13] proposed a method for estimating the parameter values of the following kinetic expression applied to the reaction kinetics of epoxy systems

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1-\alpha)^n \tag{6}$$

but provided no experimental confirmation. Chern and Poehlein [14] have presented a kinetic model that comprises several simultaneous different reactions and also considers diffusion control effects by relating changes in the free volume to changes in the reaction rate constants after vitrification. This model has been applied to the results of Horie et al. [10].

The TGDDM–DDS system has been the subject of specific research [15–19]. Stark et al. [15] used Prime's model (eqn. (4)) to analyse the reaction kinetics of high-performance commercial TGDDM–DDS matrices. They found that its kinetic parameter values determined by dynamic DSC depend on the heating rate of the scan, although their direct determination was prevented by the complexity of the reaction mechanism. Mijovic et al. [16] used eqn. (6) to describe the autocatalytic behaviour of the polymerization reaction of commercial TGDDM–DDS formulations. Isothermal DSC data were employed to calculate the model parameters and check the kinetic model. The influence of the reactive kinetics of TGDDM–DDS matrices (eqn. (4)) on the chemo-rheological behaviour of commercial prepregs in the autoclave process has been described by Kenny et al. [1].

Despite considerable research on kinetic characterization of epoxy systems, the correlation between isothermal and dynamic DSC is not clear, and little has been done to test models under the complex thermal conditions characteristic of the processing of epoxy-based composites. We have recently proposed [3] a new model for the kinetic behaviour of TGDDM–DDS systems that takes into account the later diffusion-controlled effects. Its application to comparison of the kinetics of standard and toughened high-performance epoxy matrices, and its validation through isothermal, dynamic and more complex experiments, are described in this paper.

EXPERIMENTAL

Unidirectional Fiberite HY-E/HMF1034K prepreg with standard TGDDM–DDS epoxy matrix, and unidirectional Fiberite HY-E1377-2T prepreg with toughened TGDDM–DDS matrix were examined in a Mettler TA 3000 differential scanning calorimeter (DSC) operating between −50 and 450°C in nitrogen atmosphere, and equipped with a liquid nitrogen cooling system. The tests were performed on prepreg samples weighing 40–50 mg to ensure a resin content of 12–15 mg.

RESULTS AND DISCUSSION

Complete DSC characterization was undertaken to develop a kinetic model of the polymerization reaction and to calculate its parameters. Figure 1 shows the dynamic thermogram for both samples at 5°C min^{-1}. The marked difference in their reactivity range shows that the toughened epoxy system is less reactive. The thermogram peak is shifted to higher temperatures, while the heat of reaction is slightly lower. The delay in the reaction peak of the toughened system can probably be attributed to dilution by a second, non-reactive phase in the resin formulation.

Curing of TGDDM–DDS systems is a complex process involving three principal reactions at normal temperatures [17–19]. Addition of the primary amine to the epoxy ring is one order of magnitude faster than the other two reactions and dominates the process, whereas the etherification reaction between the hydroxyl and epoxy groups dominates the later stages. Addition of the secondary amine does not seem to be important in normal polymerization conditions. The main reaction peak is principally associated with addition of the primary amine, while the last part corresponds to etherification. DSC characterization of these reactions has given different heat of reaction and activation energy values [19]. A single model, therefore, cannot accurately describe the complete kinetics. However, for practical purposes, an engineering approach can be adopted, i.e. formulation of a single empirical model and its experimental validation.

The total heat developed during dynamic tests was estimated by integration of the thermogram peaks (Table 1). The dispersion of the data is of the order of the experimental error and no correlation can be established between the heat of reaction and the heating rate. Their average value was used as a reference value for the total heat of reaction for modelling purposes, as discussed later.

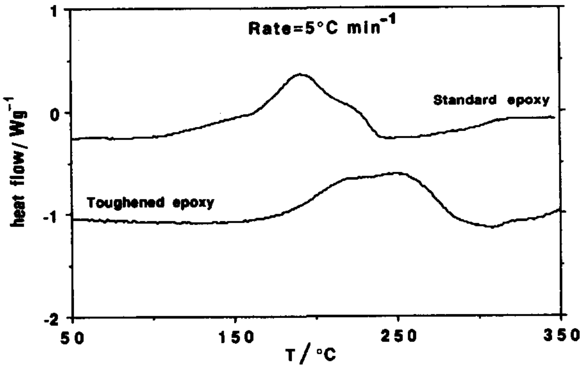

Fig. 1. Dynamic thermograms obtained on the prepreg samples at a heating rate of 5°C min^{-1}.

TABLE 1

Total heat of reaction associated with the peak of dynamic thermograms at different heating rates and referred to the mass of the prepreg sample [a]

Standard epoxy		Toughened epoxy	
Hr (°C $\min^{-1}$)	H_T (J g^{-1})	Hr (°C $\min^{-1}$)	H_T (J g^{-1})
3	140.3	2	156.4
5	136.9	5	147.7
10	136.6	10	122.8
15	133.8	10	138.9

[a] Hr = Heating rate; H_T = heat of reaction.

Commercial DSC apparatus use specific software to develop kinetic models and calculate their parameters by processing dynamic or isothermal test data. The most common model is the single *n*th-order reaction (eqn. (4)) with a temperature-dependent rate constant *k*. Its parameters are normally calculated by regression analysis. However, it has been shown that the model parameters obtained from dynamic and isothermal data are rarely comparable [3,7]. In addition, dynamic data are not enough to describe the complete behaviour of the polymerization reaction. Autocatalytic and diffusion control effects, for example, are only detected in isothermal experiments. Isothermal tests were therefore performed at different temperatures to obtain more complete DSC characterization.

The shape of the thermograms at 180°C (Fig. 2) shows a maximum reaction rate near the starting point. This corresponds to the autocatalytic effect reported for epoxy-based matrices and is very evident in the toughened system. However, the test temperature is stabilized in the first 1–2 min and the data in the first zone of the thermogram are not very reliable. If the effect of the autocatalytic behaviour is ignored and it is assumed that the maximum reaction occurs at the beginning of the test, the signal can be

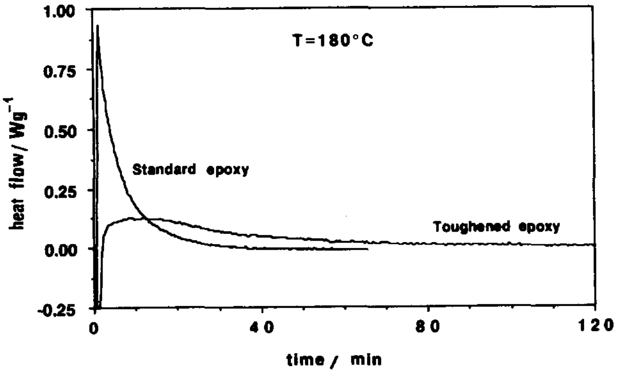

Fig. 2. Isothermal thermograms obtained at 180°C.

TABLE 2

Heat of reaction (referred to the mass of the prepreg sample) and maximum degree of reaction developed in isothermal tests

T (°C)	Standard epoxy				Toughened epoxy			
	H_{ic} [a]	α_m [b]	H_R [c]	H_T^* [d]	H_{ic} [a]	α_m [b]	H_R [c]	H_T^* [d]
150	93.0	0.68	30.5	123.5				
150	98.5	0.72	29.5	128.0				
158	105.3	0.77	24.6	129.9				
158	110.8	0.81	22.5	133.3				
165	113.5	0.83	20.6	134.1				
165	113.5	0.83	21.3	134.8				
175	120.4	0.88	10.1	130.5				
175	122.0	0.89	8.9	130.9				
180	121.4	0.89	6.0	127.4	119.2	0.84	16.0	135.2
180	127.2	0.93	5.5	132.7	114.1	0.81	21.6	135.7
185					124.9	0.88	14.0	138.9
185					121.9	0.86	15.3	137.2
190	135.4	0.99	2.9	138.3	130.4	0.92	8.7	139.1
190	136.8	1.00	2.4	139.2	123.9	0.88	14.8	138.7
195					132.9	0.94	8.0	140.9
195					133.8	0.95	7.0	140.8
200	138.1	1.00	0.0	138.1	136.6	0.97	5.1	141.7
200					133.9	0.95	7.4	141.3

[a] H_{ic}, isothermal heat of reaction (J g^{-1}).

[b] α_m, maximum extent of reaction.

[c] H_R, residual reactivity (J g^{-1}).

[d] $H_T^* = H_{ic} + H_R$ (J g^{-1}).

corrected manually by adopting the procedure previously reported [3] so as to develop a model that cannot describe the reaction mechanism, but can be successfully used for modelling.

Several isothermal tests were performed at different temperatures. The total heat of reaction values calculated by integration of the corrected thermograms, H_{ic} (columns 2 and 6 in Table 2), are significantly lower than those obtained in dynamic tests, because during low-temperature isothermal tests polymerization is not completed and the final α value is an increasing function of the test temperature. The residual reactivity of these materials can be determined by dynamic testing of an isothermally cured sample and integration of the thermogram peaks. Addition of the residual reactivity heat (H_R, columns 4 and 8 in Table 2) to that developed in isothermal tests (H_{ic}) gives the total heat of reaction (H_T^*) (columns 5 and 9 in Table 2). H_T^* values are of the same order as those obtained in the dynamic tests.

As mentioned earlier, incomplete reaction during isothermal processes is attributed to diffusion control owing to the loss of mobility of the reacting molecules within the developed network. Structural changes produced by polymerization are associated with an increase in the glass transition temperature T_g of the reactive polymer [21]. When T_g approaches the isothermal cure temperature, mobility is strongly reduced. When the system reaches vitrification, the reaction becomes diffusion controlled and eventually ceases, or perhaps decreases to a minimum value [4,5]. For practical purposes, however, considering the time scale associated with the normal processing of thermoset-based materials, it can be assumed to stop although this assumption means that eqn. (4) cannot be used to interpret isothermal results, because it predicts that the reaction rate becomes zero when $\alpha = 1$, i.e. when the system is fully cured. The model can be modified mathematically in two ways in order to overcome this limitation. The first way is to modify k when diffusion control becomes dominant. Here the overall reaction rate is a function of the temperature, concentration of reactants, reaction mechanism and the local viscosity (which in turn is a function of the molecular weight and temperature) [4,5]. Then, eqn. (3) can be rewritten as

$$\mathrm{d}\alpha/\mathrm{d}t = k_0 f(T) f(\alpha) f(\mu_\mathrm{L}) \tag{7}$$

where k_0 is the pre-exponential factor of the rate constant, $f(T)$ is a function of temperature, generally given by an Arrhenius-type equation, $f(\alpha)$ is unchanged and $f(\mu_\mathrm{L})$ is a function of the local viscosity. Diffusion control, manifested through dependence of the reaction rate on the local viscosity, is sometimes considered by including a conversion-dependent term in the rate constant [14,20]. For example, Chern and Poehlein [14] related changes in free volume to changes in the reaction rate constants with conversion by adopting a semi-empirical equation previously used for free radical polymerization. The expression for the reaction rate constant is now

$$k_\alpha / k_\mathrm{c} = \exp[-V^*(1/V_\mathrm{f} - 1/V_\mathrm{fc})] \tag{8}$$

where k_α is the rate constant at a given conversion, k_c is the chemical-reaction-controlled rate constant, V_f is the fractional free volume of the reacting system at a given conversion, V_fc is the critical fractional free volume when the three-dimensional cross-linking network is just formed, and V^* is an adjustable parameter regarded as an index of the degree of diffusion control of the reaction. When V_f, depending on conversion and temperature, becomes equal to V_fc, k_α takes the value of k_c and a change in the reaction velocity is observed.

Alternatively, eqn. (4) can be modified empirically to provoke zero prediction of the reaction rate at the vitrification point. The average value of the total heat H_T developed in dynamic tests is used as a reference to determine the final degree of reaction during the isothermal tests ($\alpha_\mathrm{m} = H_\mathrm{ic}/H_\mathrm{T}$); α_m values for all the tests on both materials are also shown in

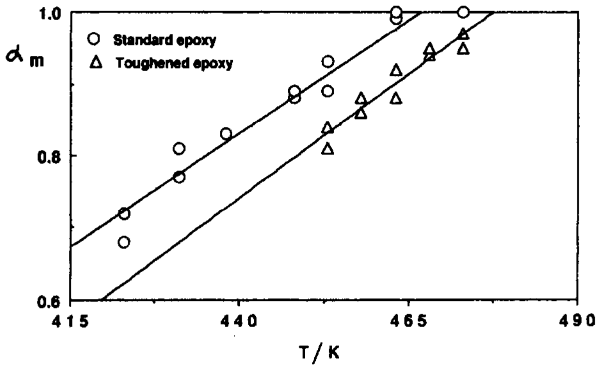

Fig. 3. Maximum degree of cure obtained in isothermal experiments vs. isothermal test temperature.

Table 2. For modelling purposes, it is convenient to determine the behaviour of α_m as a function of the isothermal test temperature. The linear dependence of α_m on T illustrated in Fig. 3 recalls the dependence between T_g and α for a reactive polymer [21]. As discussed above, the T_g value reached by the polymeric matrix can be assumed to be of the same order as the isothermal test temperature. We have found a simple linear dependence to express the empirical dependence of α_m on T

$$\alpha_m = pT + q \tag{9}$$

The similarity of the p and q values for both matrices (Table 3) is reflected in the parallel straight lines shown in Fig. 3. The line for the toughened matrix is shifted to lower final conversions in keeping with its lower reactivity in the dynamic tests. Equation (4) can be now be re-written to allow for the behaviour represented by eqn. (9)

$$d\alpha/dt = k(\alpha_m - \alpha)^n \tag{10}$$

This clearly predicts the expected behaviour: the reaction rate during an isothermal process will be zero when the degree of reaction equals α_m. The value of k was determined by using preliminary values computed graphically as the initial values of a computer regression program to find the best values of n, K_0 and E; k values computed from this regression analysis are

TABLE 3

Model parameter values from thermal characterization of the two systems

	H_T ($J\,g^{-1}$)	E_a ($kJ\,mol^{-1}$)	$\ln k_0$ (s^{-1})	n	q	p (K^{-1})
Standard epoxy	136.9	62.4	10.4	1.07	−1.96	0.00635
Toughened epoxy	141.4	69.5	10.8	0.94	−2.18	0.00665

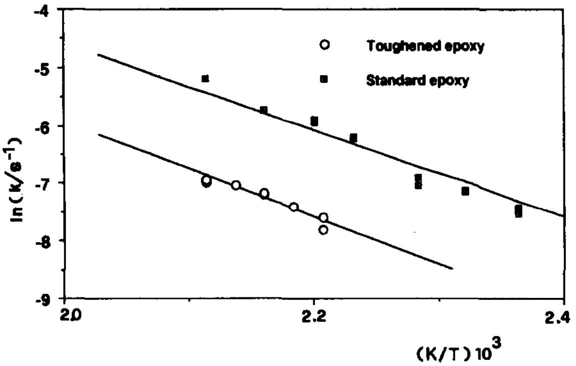

Fig. 4. Arrhenius plot of the kinetic constants computed from isothermal test as a function of $1/T$.

represented as a function of $1/T$ in a semi-log plot in Fig. 4. The data are well fitted by straight lines, indicating an activated behaviour predicted by an Arrhenius-type equation

$$k = k_0 \exp(-E/RT) \tag{11}$$

The values of the kinetic parameters of the general model given by eqns. (9)–(11) are listed in Table 3. Despite the difference in the kinetic behaviour of the two prepregs, the comparable activation energy values indicate that the reactive process is characterized by the same temperature dependence, suggesting that the main chemical reaction is similar in both systems.

The ability of eqns. (9)–(11) to represent the kinetic behaviour has been tested by comparison of model and experimental results. Reaction rate data plotted as a function of time obtained from the isothermal DSC experiments and from eqn. (10) predictions, are shown in Fig. 5. Theoretical curves (full lines) were computed using the average parameter values

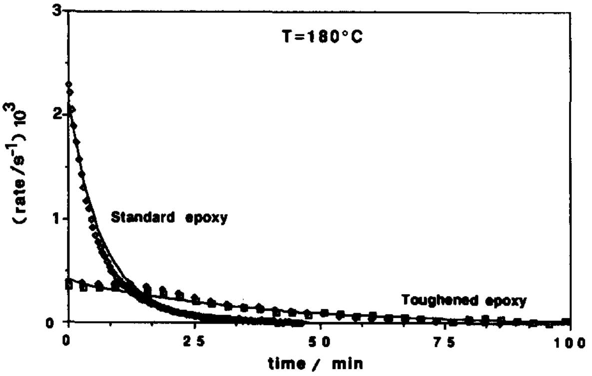

Fig. 5. Reaction rate vs. time for two isothermal tests at 180°C: comparison between experimental DSC data (points) and model predictions (full lines).

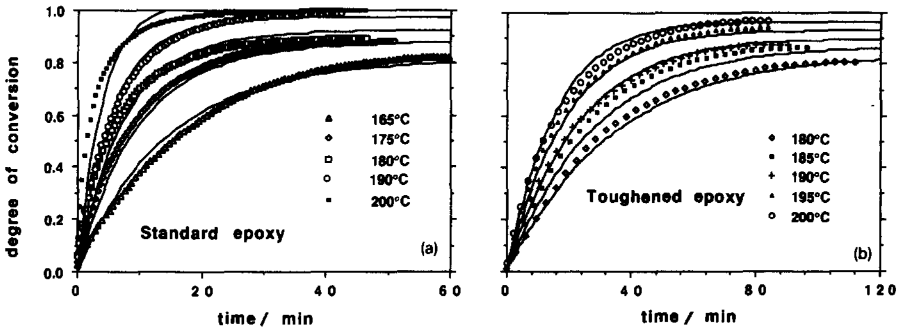

Fig. 6. Degree of reaction rate vs. time for different isothermal tests: comparison between experimental DSC data (points) and model predictions (full line) for the standard epoxy matrix prepreg (a) and for the toughened epoxy matrix prepreg (b).

listed in Table 3. The good fit corroborates the soundness of the procedure used to formulate the model. The results of the kinetic model can also be expressed in terms of α as a function of time (eqn. (1)) by partial integration of the experimental DSC signal. Alternatively, eqn. (10) can be mathematically integrated to give

$$\alpha = \alpha_{\mathrm{m}} - \left[\alpha_{\mathrm{m}}^{(1-n)} + (n-1)kt\right]^{1/(1-n)} \qquad (12)$$

The closeness of the experimental and theoretical values for α as a function of time at several test temperatures (Fig. 6) provides additional confirmation of the model.

The shape and parameters of the eqns. (9)–(11) model were obtained from isothermal tests. The complete model, however, should also describe dependence of the reaction rate on temperature during a dynamic test. Therefore, the complete model was tested by comparison with experimental dynamic thermograms. Close fits can be seen in Figs. 7a and 7b, where the reaction rate is shown as a function of time for different heating rates. Dotted lines correspond to experimental DSC results, full lines to model predictions from the values in Table 3.

Practical employment of the model was investigated through a mixed isothermal-dynamic DSC experiment on the prepregs. In the lamination process, prepregs are placed in the autoclave at room temperature and heated at a controlled rate (dynamic process) to the final process temperature which is maintained constant (isothermal process) for about 2 h. The system is then cooled to room temperature and the composite laminates are taken out of the autoclave. Polymerization reactions in the epoxy matrix were analysed by experimental simulation using DSC under the same thermal conditions. The results expressed as the reaction rate as a function of time are shown in Figs. 7c and 7d (dotted line). The left part of the figures corresponds to the dynamic process performed at a specified heating rate, the right to the isothermal process. These processes were also

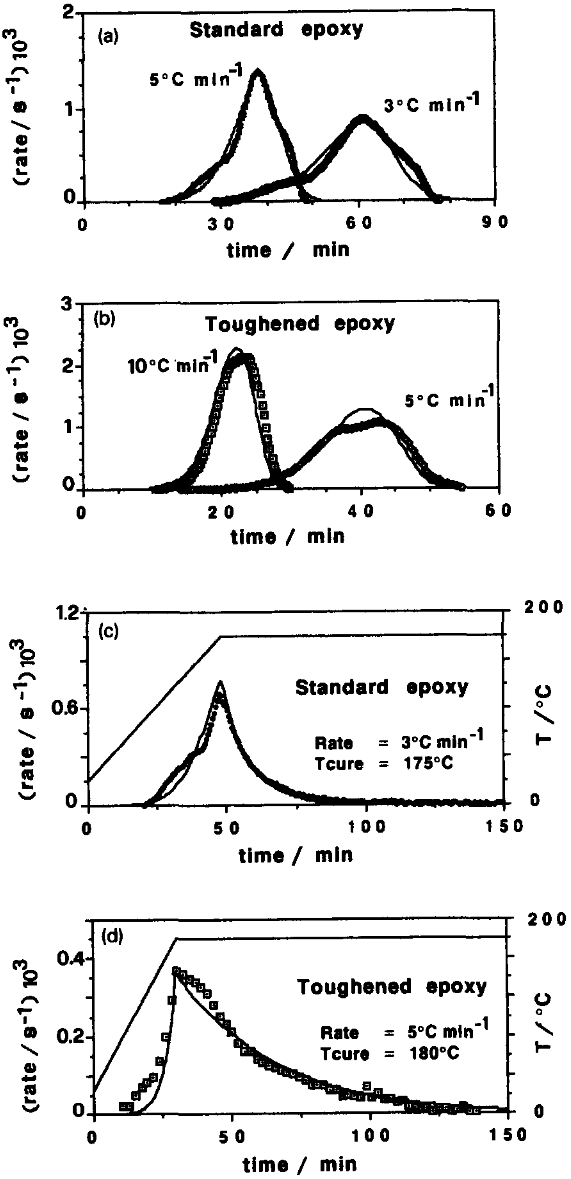

Fig. 7. Reaction rate vs. time for different dynamic tests: comparison between experimental DSC data (points) and model predictions (full lines) at different heating rates for the standard epoxy matrix prepreg (a) and for the toughened epoxy matrix prepreg (b), and for a cure cycle simulation (c and d).

mathematically simulated by applying the developed model (Figs. 7c and 7d (full line)).

The excellent agreement obtained between the experimental and model results indicates that the model can reproduce and predict the behaviour of epoxy matrices during simple isothermal and dynamic tests, and also under more complex conditions, such as those characteristic of autoclave lamination. However, the application of the model to industrial processes should also consider the complex thermal processes associated with the polymerization reaction as a consequence of the geometry of the laminate, and of the heat transfer from the air and tool to the prepregs. In this case, a simple scaling of DSC results is not sufficient and the kinetic model must be included in a general model considering the characteristics of the lamination process [1].

CONCLUSIONS

The kinetic behaviour of a standard and a toughened commercial high-performance TGDDM–DDS epoxy matrix has been characterized by DSC analysis of their prepregs. A simple *n*th-order equation was modified to include diffusion control effects and tested for formulation of a kinetic model able to reproduce the experimental results of isothermal, dynamic and more complex tests. The lower reactivity observed in the toughened epoxy matrix is attributed to the dilution effect produced by the presence of a second, non-reactive phase. However, the calorimetric and kinetic behaviour of both systems is essentially similar, and no significant modifications of their processing conditions are expected.

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