

Modeling the Chemorheological Behavior of Epoxy/Liquid Aromatic Diamine for Resin Transfer Molding Applications

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ABSTRACT: The analysis of the chemorheological behavior of an epoxy prepolymer based on a diglycidylether of bisphenol-A (DGEBA) with a liquid aromatic diamine (DETDA 80) as a hardener was performed by combining the data obtained from Differential Scanning Calorimetry (DSC) with rheological measurements. The kinetics of the crosslinking reaction was analyzed at conventional injection temperatures varying from 100 to 150°C as experienced during a Resin Transfer Molding (RTM) process. A phenomenological kinetic model able to describe the cure behavior of the DGEBA/DETDA 80 system during processing is proposed. Rheological properties of this low reactive epoxy system were also measured to follow the

cure evolution at the same temperatures as the mold-filling process. An empirical model correlating the resin viscosity with temperature and the extent of reaction was obtained to carry out later a simulation of the RTM process and to prepare advanced composites. Predictions of the viscosity changes were found to be in good agreement with the experimental data at low extents of cure, i.e., in the period of time required for the mold-filling stage in RTM process. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4228–4237, 2006

Key words: differential scanning calorimetry (DSC); curing; kinetics; rheology; modeling

INTRODUCTION

Advanced fiber-reinforced composite materials are applied in a wide range of structural applications in the automotive and aerospace industry.^{1,2} Such composites are desirable because they possess many properties such as high tensile strength and modulus, offer design flexibility, and can be mass produced. One of the processes for manufacturing these high-performance polymer composites is resin transfer molding (RTM), which is one of the current industrial processes among liquid composites molding (LCM). The greatest benefit of RTM relative to other manufacturing techniques is the separation of the molding process from design of the fiber architecture, which combines the potentially high rate of production with high quality of the finished parts.^{3,4}

Large polymer composite parts with complex shapes can be efficiently fabricated by RTM process by impregnation of the preforms based on glass or carbon fibers as compared to the traditional prepreg layup-autoclave cure process.^{5–7}

The RTM process is a closed mold processing technique, which involves loading the fiber perform into a mold cavity in the desired orientation, according to the shape of the finished part. After the mold is securely closed, a low viscosity reactive resin is injected under moderate pressure, i.e., few bars, and at an elevated temperature, and then the resin is cured in situ to form directly the composite part.^{8–10} At the end of cure reaction, the net-shape component is removed from the mold.

During the processing, the mold is usually heated to facilitate mold filling and fiber impregnation by the resin. As a consequence, the chemical reaction in the reactive mixture used as matrix takes place, i.e., its viscosity increases with filling time. High performance composite parts require high fiber fractions and long flow paths, which results in large flow resistance and long filling times. Since the number of reported works in the literature taking into account the influence of chemical reaction in the mold filling is quite limited, most of the work has been conducted on the simulation of the mold filling in RTM and to understand the influence of processing conditions,

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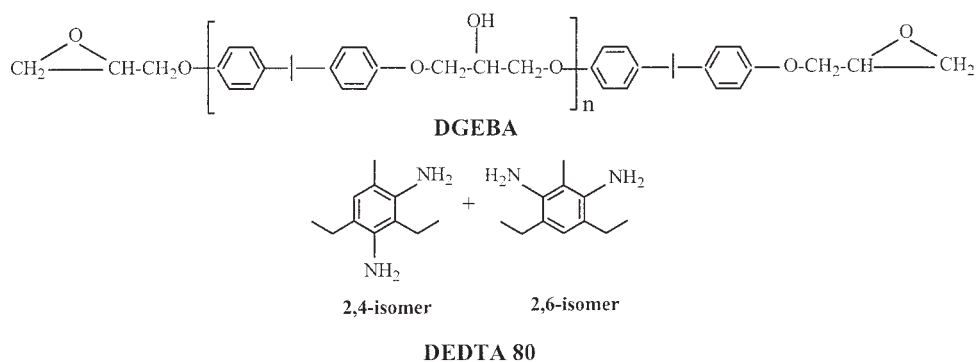


Figure 1 Chemical formulas of the epoxy prepolymer DGEBA, and the liquid aromatic diamine DETDA 80.

material properties, and flow variables on performance of the composites. However, only limited information can be found relating the cure reaction and viscosity change of the epoxy resin during the filling stage of RTM process.^{11–16} The successful production of epoxy composite parts via RTM process requires good knowledge of the kinetic and rheological properties of the epoxy/amine systems. The ability to predict and monitor the kinetic and viscosity changes of the reactive system during the impregnation of fibers plays a key role in the development and the control of RTM processes.

In the case of epoxy/amine systems that are frequently used in RTM, an autocatalytic kinetic model is often employed for predicting the curing of epoxy thermosets in autoclave processing of composite materials.^{17–20} A variety of kinetic models have been also used to relate the rate of the chemical reactions to the time, temperature, and extent of cure.^{11–16,21–25} Moreover, different events such as phase separation, gelation, vitrification, etc. take place during the cure reaction which makes the kinetics modeling more complicated.

The other essential feature to predict is the viscosity change. The rheological characterization of thermosetting is complicated since the rheology of the reactive mixture depends on a variety of variables such as time, temperature, shear rate, pressure, nature of reactants, etc.²⁶ The change of viscosity during the impregnation phase due to curing reaction is the main factor affecting the processing of RTM parts.^{27,28} The combination of the previous kinetic model and the rheological measurements enables a chemorheological model to be established. Extensive work in the literature has focused on the determination of the cure effects on the viscosity of thermosetting resin, and a summary of various chemorheological models can be found in these reviews.^{19,20,29}

The objective of the present work is to investigate the cure kinetics and viscosity behavior of an epoxy prepolymer (DGEBA) cured with a liquid aromatic diamine (DETDA 80) for an RTM use. A kinetic model is used to describe the cure of DGEBA/DETDA 80 resin

in the temperature range 100–150°C. A chemorheological model is developed for this system, focusing on low extents of cure, i.e., the important region for the mold filling stage. This study will provide information for optimizing the curing conditions for RTM process. Work to extend the use of DGEBA/DETDA 80 modified by a thermoplastic for RTM formulations is reported in another publication.³⁰

EXPERIMENTAL

Materials

The epoxy resin used in this work was D.E.R 330 (DGEBA, Dow Chem Deutschland, Rheinmuster, Germany), with $n = 0.15$ and a molar mass of 383.1 g/mol, kindly supplied by Dow Chemical Co. The liquid aromatic hardener (DETDA 80) was a mixture of two diethyltoluene diamine isomers (77–81% 3,5-diethyltoluene-2,4-diamine and 18–22% 3,5-diethyltoluene-2,6-diamine), manufactured by Lonza (Switzerland) and had a molar mass of 178.28 g/mol. The chemical formulas of the epoxy and amine comonomers are shown in Figure 1. The epoxy/liquid aromatic diamine system was prepared in a stoichiometric ratio (weight ratio 100:23). This formulation is characterized with a lower reactivity than that obtained typically for epoxy/cycloaliphatic amine systems, and is perfectly well suited for our further purpose.³⁰

Differential scanning calorimetry

A Mettler TA 3000 differential scanning calorimeter equipped with a DSC-30 oven and a Perkin-Elmer DSC7 instrument were used to analyze the reaction kinetics of DGEBA/DETDA 80 by assuming proportionality between the heat evolved during the cure and the extent of reaction or conversion (x). The calibration was regularly made using Indium standards on each experiment being performed.

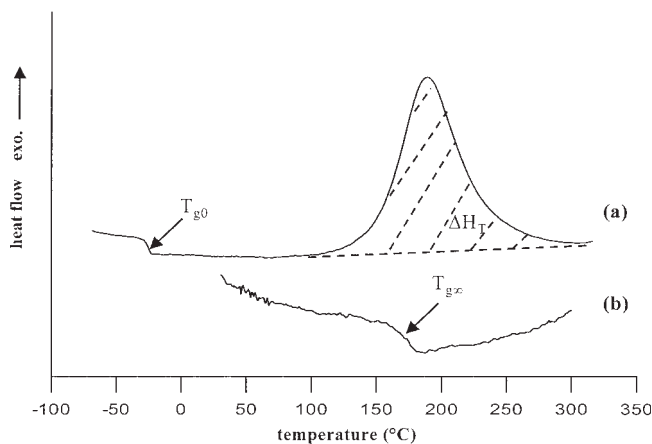


Figure 2 Dynamic thermograms obtained at a heating rate of 5°C/min from the unreacted DGEBA/DETDA 80 system: (a) 1st scan, (b) 2nd scan.

For dynamic DSC scans, samples of 20–25 mg weight were sealed in aluminum pans and heated under argon atmosphere. The first heating was performed at rates of 2, 5, 10, 15, and 20°C/min in a temperature interval from –80 to 350°C to measure the values of T_{g0} , i.e., for $x = 0$, and ΔH_T , i.e., total heat of reaction corresponding to $x = 1$. The value of $T_{g\infty}$, i.e., for a full conversion, was determined during the second scan after rapid cooling.

Isothermal DSC experiments were conducted at four temperatures ranging from 100 to 150°C under nitrogen atmosphere. Cure was performed in aluminum pans, with sample weights between 5 and 10 mg. The time required to attain the maximum reaction extent at the temperature considered was determined from the thermograms when they leveled off at the base line close to the initial base line. The areas of the peak under the isothermal curve were used to calculate the extent of reaction at various times. The extent of reaction, x , at a time t was defined as $x = \Delta H_t / \Delta H_T$, where ΔH_t is the heat of cure at time t and ΔH_T is the total heat of cure. In this study, the total heat of cure has been obtained from dynamic DSC experiments.

Rheological measurements

A rheometric dynamic analyzer (RDAII) was used to measure the complex viscosity changes with cure time. Measurements were performed during the isothermal cures in the temperature range of 100–150°C. Parallel plate geometry with a diameter of 40 mm and a gap of about 1 mm is subjected to forced oscillations with frequency from 1 to 100 rad/s. An initial strain amplitude of 100% at the edge of the plate is reduced during reaction down to 1% to ensure a linear viscoelastic response. The evolution of the viscosity, storage shear modulus (G'), loss

shear modulus (G''), and loss factor ($\tan \delta$) were recorded as a function of both reaction time and frequency. The gelation of the samples was assumed to be at the point at which $\tan \delta$ is nondependent on frequency.^{31,32}

RESULTS AND DISCUSSION

Kinetic analysis

To determine the total heat of reaction, the DGEBA/DETDA 80 system was heated from –80 to 320°C with a rate of 5°C/min as shown in Figure 2. The step in the heat flow at –26°C indicates the glass transition of the unreacted system (T_{g0}). The reaction starts at about 100°C, with a exothermic peak maximum located at 189°C. By integration of the area under the thermogram, a heat of 394 J/g could be obtained, which was taken to be the total heat of reaction generated to reach full conversion. This value corresponds to a reaction enthalpy normalized to the number of epoxy groups (epoxy equivalent, ee) of 93 kJ/ee, which is typical for epoxy/amine reactions.^{33,34} The consecutive heating scan shows a step in the heat flow at 172°C related to the glass transition of the fully reacted system. These values from DSC dynamic scan, i.e., ΔH_T and $T_{g\infty}$, have been verified varying the heating rates from 2 to 20°C/min. Based on the dynamic DSC results, the isothermal DSC measurements of the epoxy-liquid aromatic diamine were conducted between 100 and 150°C, which is the temperature range suitable for the mold filling of the RTM process (Fig. 3).

The phenomenological model developed by Kamal and Sourour was used for isothermal kinetic analysis.^{17,18} The epoxy/amine reaction was found to be autocatalytic in nature. In fact, the reaction is catalyzed by a proton donor like hydroxyl groups

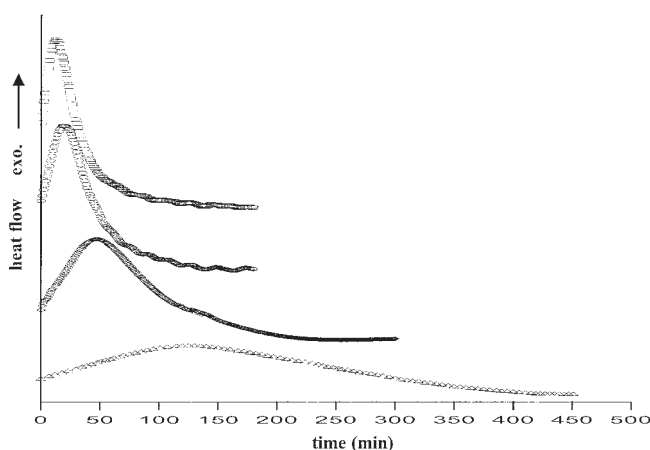


Figure 3 Isothermal thermograms obtained at curing temperatures of (Δ) 100°C, (◇) 120°C, (○) 140°C, and (□) 150°C.

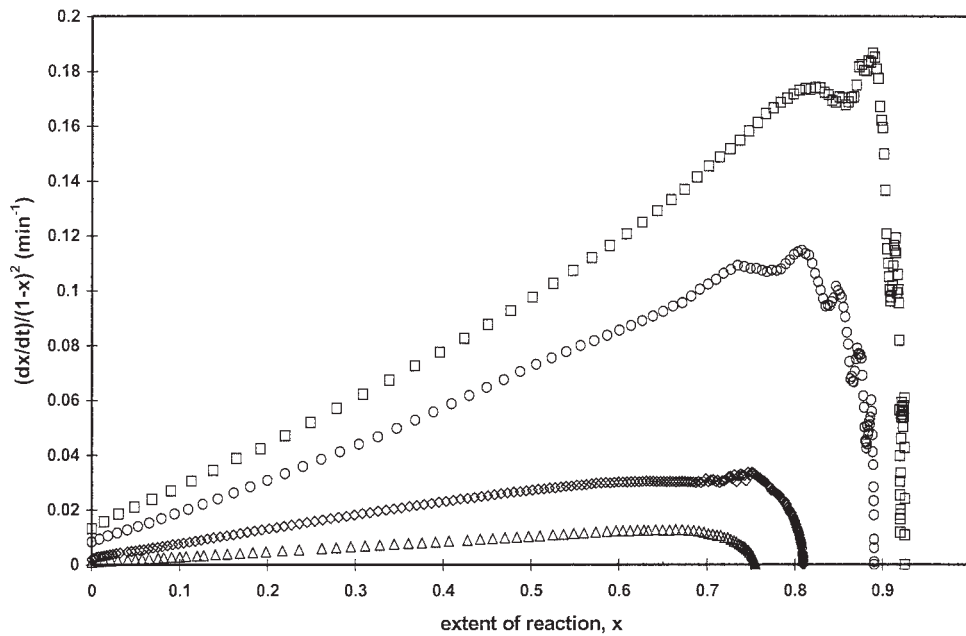


Figure 4 Reduced reaction rate $[(dx/dt)/(1-x)^2]$ versus x at curing temperatures of (Δ) 100°C, (\diamond) 120°C, (\circ) 140°C, and (\square) 150°C.

already present or the ones that are produced during cure. The general equation assumed for the curing reaction of an epoxy/amine system is given below.

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

where k_1 and k_2 are the apparent rate constants for the reaction catalyzed by proton donors initially present in the system and proton donors that are produced during cure respectively. m and n are the kinetic exponents of the reaction and $m + n$ gives the overall reaction order. Equation (1) considers only the chemical kinetics whereas the influence of diffusion is not taken into account. Assuming equal reactivity of all the amino hydrogens, the reaction rate for a stoichiometric mixture of epoxy and amine can be described using $m = 1$ and $n = 2$, as it is normally the case in epoxy/amine systems.^{35,36} In our case, a plot of $(dx/dt)/(1-x)^2$ versus x gives a straight line, at least in the conversion range between 0 and 40%, with intercept k_1 and slope k_2 (Fig. 4). The results obtained for our data justify the assumption of the values of kinetic exponents m and n . Values of these constants, at various temperatures used in our isothermal experiments, are listed in Table I. The linear regions of the curves are followed by maxima and sharp declines towards zero. This deviation from eq. (1) is attributed to vitrification, i.e., the time at which T_g of the reactive system reached the cure temperature.³⁷

The kinetic constants k_1 and k_2 depend on temperature according to Arrhenius law:

$$k_i = A_i \exp\left(\frac{E_{ai}}{RT}\right) \quad (2)$$

where A_i is the pre-exponential constant, E_{ai} is the activation energy, R is the gas constant, and T is the absolute temperature. Plotting $\ln(k_i)$ versus $1/T$ gives straight lines of slope $-E_{ai}/R$ and intercept $\ln(A_i)$. These plots are shown in Figure 5.

The values of E_{a1} and E_{a2} obtained in this study for the DGEBA/DETDA 80 system (59.6 and 59.2 kJ/mol, respectively) are close to each other, suggesting that a unique activation energy could represent the overall curing reaction. Thus, the rate of the reaction dx/dt for this epoxy/liquid aromatic diamine system can be given by the following form:

$$\frac{dx}{dt} = \left[2.45 \times 10^5 \exp\left(\frac{7177.4}{T}\right) + 3.75 \right] \times 10^6 \exp\left(\frac{7129.3}{T}\right) x [1-x]^2 \quad (3)$$

TABLE I
Kinetic Parameters for DGEBA/DETDA 80 Cure Process

T (°C)	k_1 (min ⁻¹)	k_2 (min ⁻¹)
100	1.10×10^{-3}	1.87×10^{-2}
120	2.90×10^{-3}	4.97×10^{-2}
140	6.40×10^{-3}	1.29×10^{-1}
150	1.13×10^{-2}	1.71×10^{-1}
A_i (min ⁻¹)	2.45×10^5	3.75×10^6
E_{ai} (kJ/mol)	59.6	59.2

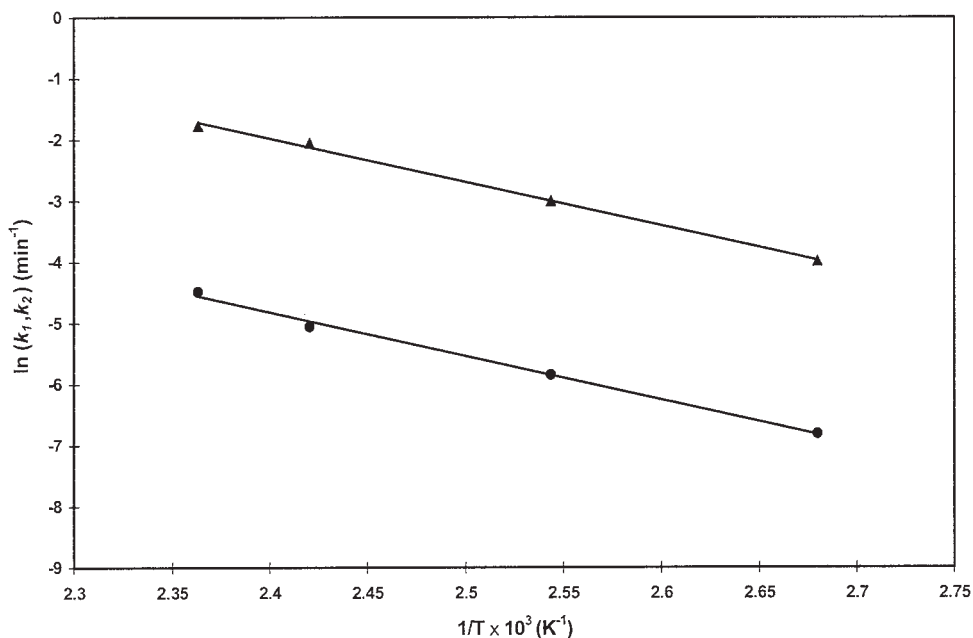


Figure 5 Arrhenius plots of rate constants, k_1 and k_2 from eq. (2): (●) k_1 , (▲) k_2 .

In Figures 6 and 7, the experimental data of extent of reaction (x) and the corresponding rate of reaction dx/dt versus time are compared with the values of model predictions described by eq. (3) at different cure temperatures. The calculated data were solved with a four-order Runge Kutta integration technique. A good correlation is observed over the temperature range of 100–150°C. The experimental data agree well with the model predictions during a large stage

of cure. However, at high conversions, the values predicted by the model are too high compared with the experimental data due to the vitrification. This means that the cure reaction is controlled by diffusion during the later stages. The deviations from experimental data were greater at lower cure temperatures, where the reaction becomes diffusion controlled earlier. Figure 8 shows the experimental and theoretical data of dx/dt versus x at different cure

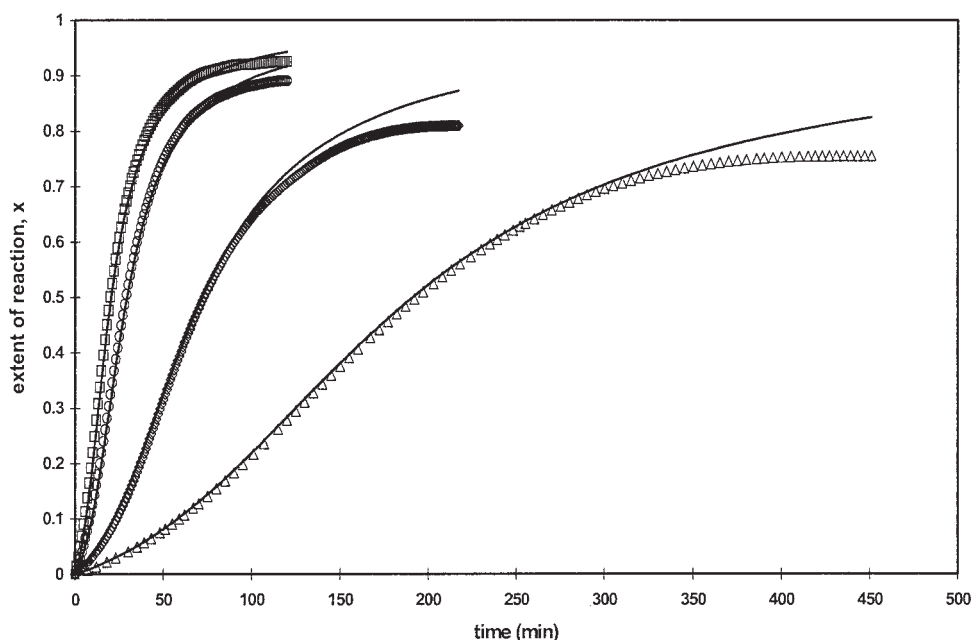


Figure 6 Comparison of the experimental data with (—) kinetic model predictions: x versus time at curing temperatures of (Δ) 100°C, (◇) 120°C, (○) 140°C, and (□) 150°C.

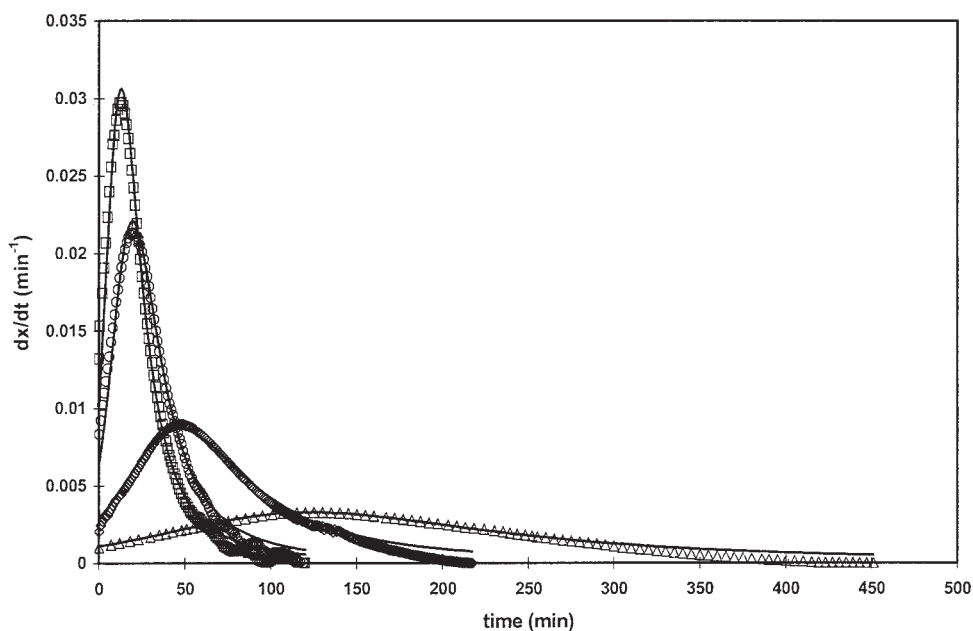


Figure 7 Comparison of the experimental data with (—) kinetic model predictions: dx/dt versus time at curing temperatures of (Δ) 100°C, (\diamond) 120°C, (\circ) 140°C, and (\square) 150°C.

temperatures. A maximum of rate of reaction is observed at conversions around 30% as a consequence of the autocatalytic behavior of this epoxy/amine reaction.

Rheological analysis

A numerical simulation of the RTM mold filling requires relations between rheological variables, reac-

tion kinetics, and processing conditions. The objective is to optimize the processing parameters, obtain high quality parts and minimize the experimental work required to establish an adequate cure cycle. However, one major difficulty is to take into account the influence of thermal history in the chemorheological models. In fact, as soon as the calorimetric and rheological data are combined, conversion and viscosity may be immediately affected by parameters such as

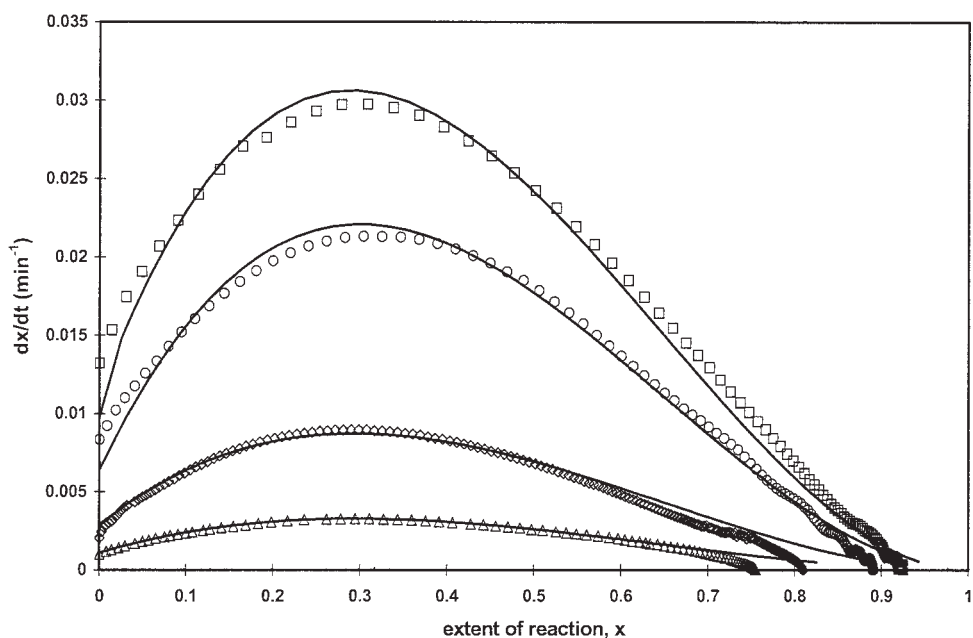


Figure 8 Comparison of experimental data with (—) kinetic model predictions: dx/dt versus x at curing temperatures of (Δ) 100°C, (\diamond) 120°C, (\circ) 140°C, and (\square) 150°C.

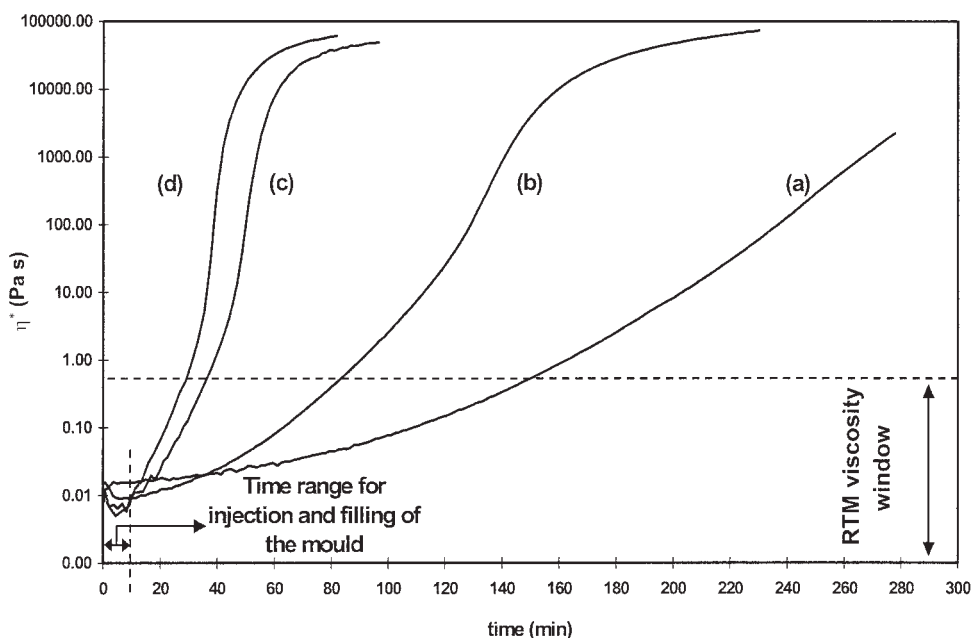


Figure 9 Complex viscosity, η^* , versus the time at curing temperatures of (a) 100°C, (b) 120°C, (c) 140°C, and (d) 150°C: frequency rate = 10 rad/s.

the sample volume, atmosphere, and the time to reach the thermal equilibrium in each technique.^{38,39} The aim of the second part of this work is to use a model able to describe the evolutive rheological behavior of our system, focusing on low conversions of cure.

Figure 9 shows the complex viscosity evolution with reaction time for the DGEBA/DETDA 80 system over a range of processing temperatures. As

expected, the initial complex viscosity varies inversely with temperature in the early stage of cure, causing the viscosity to be initially lower at higher temperatures. As cure occurs, the viscosity curves crossover due to a higher reaction rate at higher temperature. The increase of cure temperature will facilitate the impregnation of fibers by the resin, and it is shown that the viscosity remains below 0.5 Pa s (i.e., the suitable viscosity value for RTM process)

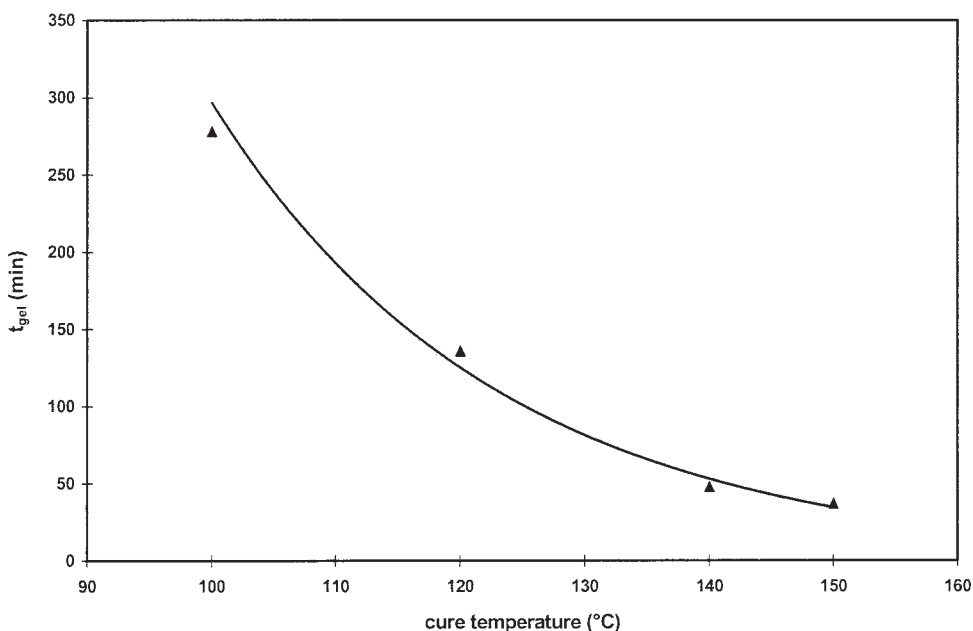


Figure 10 Gelation time-temperature correlation according to an Arrhenius model.

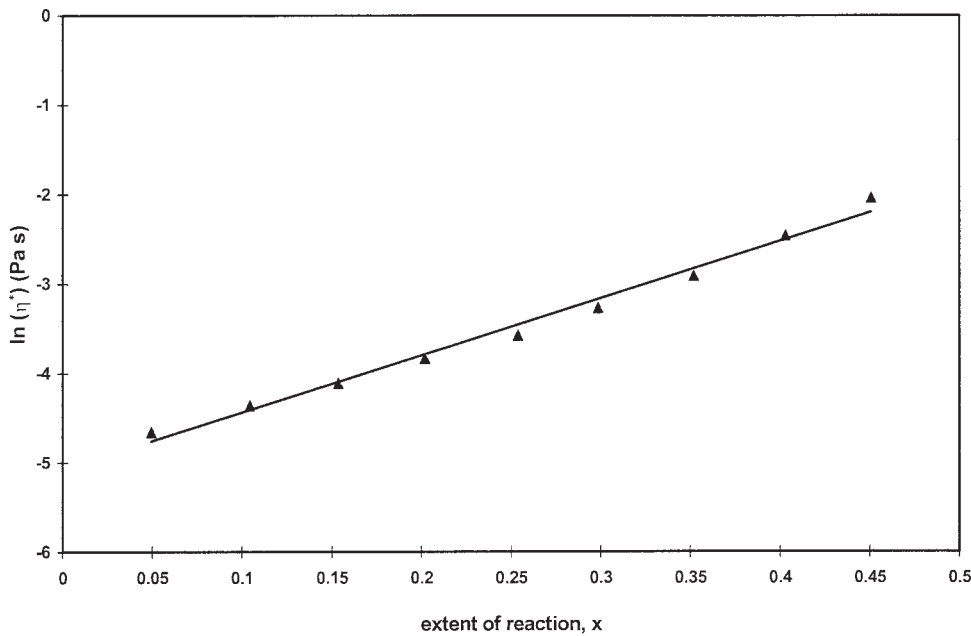


Figure 11 $\ln(\eta^*)$ versus x at a curing temperature of 120°C.

for a long period of time.^{40,41} It is generally believed that if the viscosity is higher than 0.5 Pa s, a high injection pressure and expensive molds would be required. In addition, a high injection pressure can lead to fiber displacements, i.e., preform buckling, in the mold cavity.

The variation of $\tan \delta$ as a function of the frequency is commonly used to calculate the gelation time of epoxy/amine system.^{31,32} The gelation times (t_{gel}) of the DGEBA/DETDA 80 system at different temperatures are represented in Figure 10. The relation between the gelation time and temperature is found to obey an Arrhenius law, according to the following relation:

$$t_{gel} = 5.82 \times 10^{-6} \exp\left(\frac{6619.4}{T}\right) \quad (4)$$

The apparent activation energy was obtained from the linear regression of the $\ln(t_{gel})$ versus $1/T$ and a value was 55.1 kJ/mol was calculated.

Different models have been presented for the viscosity evolution of epoxy resins during the RTM process.^{11,13,16,19,29,42} The models utilize the degree of cure as a parameter to predict the viscosity of the resin. Another approach was proposed by Fontana.⁴³ In his model, the viscosity data are used directly to simulate the viscosity behavior with the normalization of the data by a shifting function for which determination of the cure kinetics is not required. However, it is difficult to determine the shifting factors that are used in the simulations, and the model assumes that they are not dependent on temperature and cure state, limiting the applicability of the approach.

In the case of an isothermal cure, the predominant empirical model has the following form:

$$\eta^*(T, x) = \eta_0 \exp\left(\frac{U}{RT} + kx\right) \quad (5)$$

where η_0 and k are constants, U is the activation energy of viscous flow, R is the gas constant, and T is the absolute temperature. To obtain the constant η_0 and k , eq. (5) is modified to give the following:

$$\ln(\eta^*) = P + kx \quad (6)$$

where P is a parameter associated with rheological properties of uncured system and is expressed as

$$P = \ln(\eta_0) + \left(\frac{U}{R}\right) \frac{1}{T} \quad (7)$$

Figure 11 shows the experimental values of viscosity in logarithmic scale versus the extent of reaction (x) at a curing temperature of 120°C. Linearity is shown if the $\ln(\eta^*)$ is plotted at low conversions, with slope and intercept allowing estimation of the constants k and P , respectively. The apparent calculated value of k was found to be dependent on the cure temperature as reported in Table II. Similar proce-

TABLE II
Temperature Dependence of the Constant k in eq. (6)

Constant	T (°C)			
	100 °C	120 °C	140°C	150 °C
k	10.713	6.389	5.918	5.251

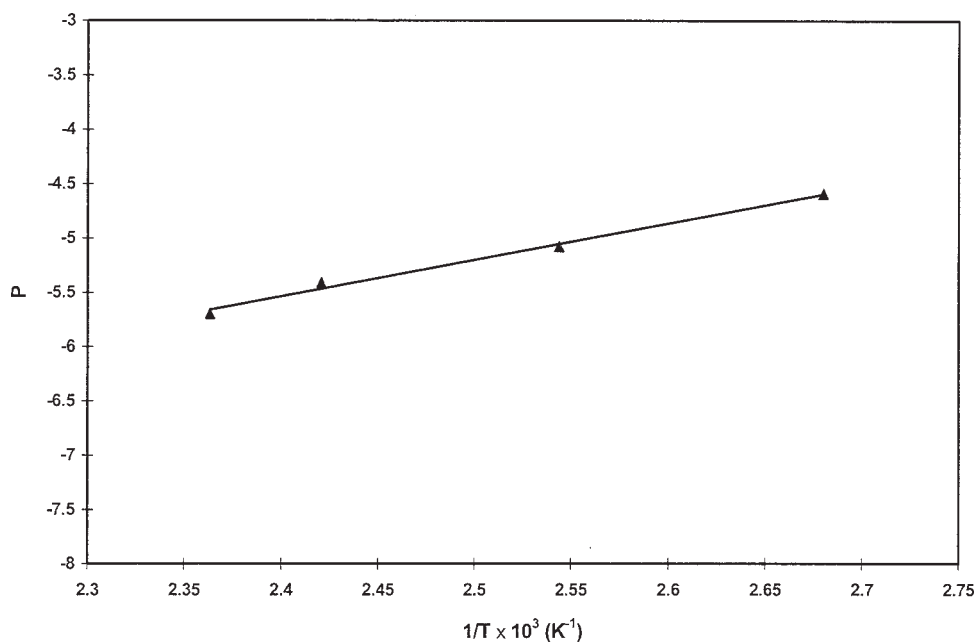


Figure 12 Plot of the parameter P in eq. (7) versus inverse of absolute temperature.

dures are employed to estimate η_0 and U from the linear relationship between P and $1/T$, as shown in Figure 12. The apparent constant parameters are found to be $\eta_0 = 1.26 \times 10^{-6}$ Pa s, $k = 47.923 - 0.102 \times T$ (K), and $U = 27.9$ kJ/mol.

Thus, the viscosity of the DGEBA/DETDA 80 system can be obtained by the following expression:

$$\eta^*(T, x) = 1.24 \times 10^{-6} \exp \left[\frac{3359.2}{T} + \left(47.923 - \frac{0.102}{T} \right) x \right] \quad (8)$$

Figure 13 shows the results for DGEBA/DETDA 80 system over the RTM processing temperature range, where plots of experimental values of viscosity versus extent of reaction are compared with those calculated by the chemorheological model represented by eq. (8). The predicted viscosity curves agrees well with the experimental data up to the extent of reaction of 0.45, simulating the initial curing stage of the RTM process. Thus, this chemorheological model enables us to describe the viscosity behavior in a period of time comprising of the mold filling, fiber

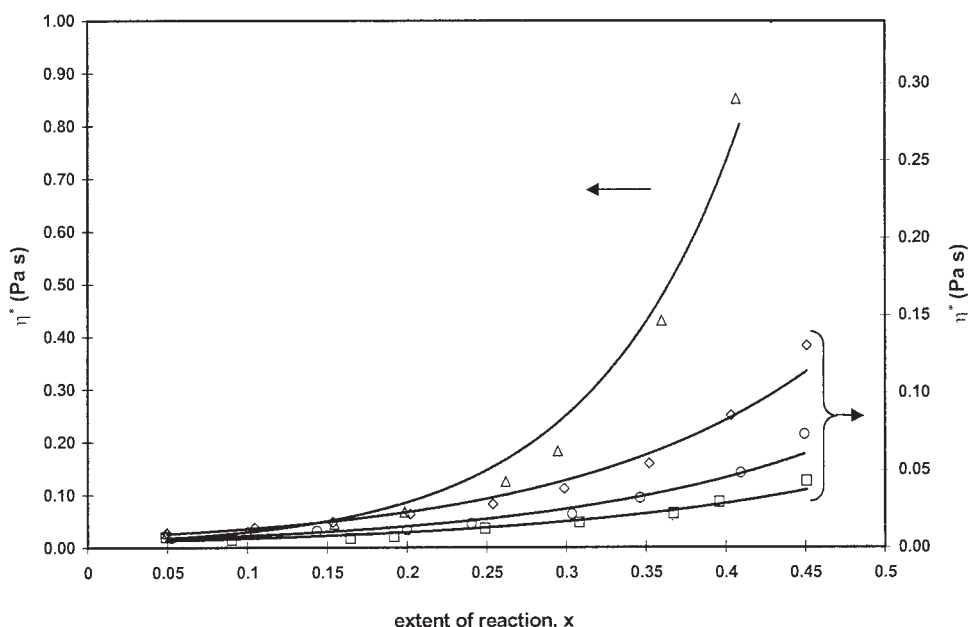


Figure 13 Comparison of the experimental data with (—) empirical model predictions: viscosity η^* versus x at curing temperatures of (Δ) 100°C, (\diamond) 120°C, (\circ) 140°C, and (\square) 150°C.

impregnation, and the first stages of reaction, thus defining a model applying in a large RTM viscosity window of this epoxy/liquid aromatic diamine (Fig. 9).

CONCLUSIONS

In this work, the kinetics of an epoxy/liquid aromatic diamine reactive system was studied by the use of dynamic and isothermal DSC experiments in the injection temperature range of the RTM process. The epoxy resin system used is a mixture of diglycidylether of bisphenol-A (DGEBA) and a liquid aromatic diamine (DETDA 80), hitherto not previously studied from kinetic viewpoint. The results were fitted with a well-known phenomenological model based on two rate constants, k_1 and k_2 , and a two reaction order, viz., 1 and 2, providing a good description of the cure kinetics up to the point of vitrification. The constants of reaction, k_1 and k_2 , showed an excellent Arrhenius fit to temperature, yielding a unique value of about 59 kJ/mol for the apparent activation energy. The maximum rate of reaction was observed for conversions of about 30%. The rheological analysis of DGEBA/DETDA 80 system shows excellent ability to be processed by RTM and it displays low viscosity and a long pot life at the injection temperature. An empirical model was formulated for the advancement of the viscosity during cure at conversions up to 0.45, which is of significance during mold-filling stage in RTM. A reasonably good agreement between predicted and measured values of viscosity was obtained and allows simulation of the chemorheological behavior during RTM processing. This work was carried out to design in a next step advanced composites based on thermoset/thermoplastic blends.

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