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KINETICS OF CURING REACTION OF A DIGLYCIDYL ETHER OF BISPHENOL A/1,3-BISAMINOMETHYL-CYCLOHEXANE (DGEBA/1,3-BAC) EPOXY RESIN SYSTEM

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Abstract

By employing differential scanning calorimetry (DSC) we have studied the kinetic of the cure reaction for a system containing a diglycidyl ether of bisphenol A (DGEBA) and 1,3-bisaminomethylcyclohexane (1,3-BAC) as a curing agent, using an isothermal approach over the temperature range of 60–110°C.

We have determined the reached conversions at several cure temperatures and the reaction rates. The results showed that this cure reaction is autocatalytic. The experimental data were compared with the autocatalytic model proposed by Kamal, which includes two rate constants and two reaction orders. This model gives a good description of cure kinetics up to vitrification point. The activation energies for these rate constants were 44–57 kJ mol^{-1}.

From the gel time measurements the value obtained for the overall activation energy was 49.5 kJ mol^{-1}.

Keywords: cure kinetics, DSC, epoxy resins, gelation

Introduction

The properties of a thermosetting polymer depend on the extent of reaction. The understanding of the mechanism and kinetics of cure is essential for a better knowledge of structure property relationships and for the usage of these materials as reinforced composites.

Cure kinetic models are generally developed by analyzing experimental results obtained by different thermal analysis techniques. Excellent reviews on these topics are available [1, 2]. Differential scanning calorimetry (DSC) has been used extensively to characterize cure kinetics of thermosetting systems for a wide variety of applications regarding shelf-life predictions and optimization of processing conditions.

Two important aspects of the curing reactions of thermoset resins are gelation and vitrification. Gelation corresponds to the incipient formation of an in-

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finite network during the epoxy curing reaction and the vitrification is related to the transformation from liquid state to glassy state as a result of increase in molecular weight. Therefore, the cure kinetics of the thermoset resins is complicated by the relative interaction between the chemical kinetics and the changing of physical properties [3].

The work described here was part of a larger study of the curing characteristics and structure property relationships of DGEBA/1,3-BAC epoxy system [4]. The objective of this part of the project was to study the cure reaction of this system.

Experimental

The epoxy resin used was a diglycidyl ether of bisphenol A (DGEBA), Epikote 828 of Shell and the curing agent was 1,3-bisaminomethylcyclohexane (1,3-BAC) manufactured by Mitsubishi Gas Chem. Co. Both components were commercial products, and were used as received without purification. The formulation is 100 g DGEBA for 18.5 g 1,3-BAC. Mixture was stirred at room temperature no more than one minute and then samples were enclosed in aluminium capsules. DSC measurements were performed with a Perkin Elmer DSC-7 supported by a Perkin Elmer Computer.

Isothermal and dynamic-heating experiments were conducted under a nitrogen flow of 40 ml min^{-1} using samples about 5–6 mg size. For isothermal experiments, the instrument was stabilized at –10°C, then the sample pan was placed in the DSC cell and heated at high rate to experimental temperature, ranging from 60 to 110°C with a 10°C temperature increment.

For dynamic heating experiments, four different heating rates were investigated: 2.5, 5, 7.5 and 10°C min^{-1} from –10 to 200°C.

Gelation times were measured by curing samples at five different temperatures: 60, 70, 80, 90 and 100°C and determining the solubility in tetrahydrofuran (THF). Gelation was ascribed to the incipient formation of an insoluble fraction.

Results and discussion

Kinetics of the cure

If the cure reaction is the only thermal event, then the reaction rate $d\alpha/dt$ is equal to the heat flow, dH/dt, divided by the overall heat of reaction ΔH_o

$$\frac{d\alpha}{dt}=\frac{dH/dt}{\Delta H_o} \tag{1}$$

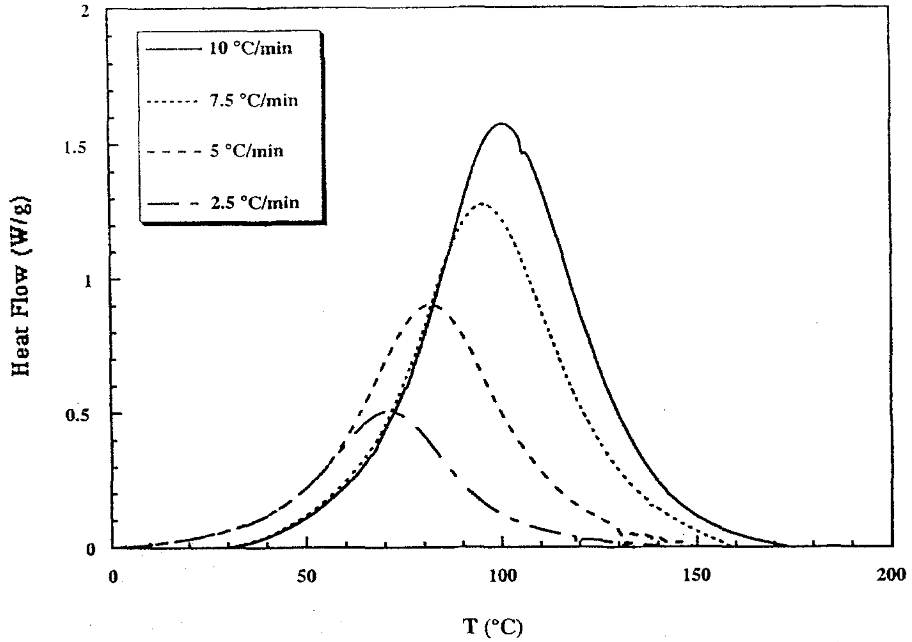

Fig. 1 DSC curves in the dynamic mode at different heating rates

Figure 1 shows the DSC curves characterizing the reaction at various heating rates. The overall heat evolved in the reaction has been determined as the average value of heat calculated in each thermogram. The corresponding value found for the DGEBA/1,3-BAC system was $\Delta H_o=495.5$ J g^{-1}.

Isothermal DSC curves are shown in Fig. 2. The position of the peaks at $t > 0$ characterizes all the experimental curves, suggesting an autocatalytic kinetic behaviour.

If one assumes that the extent of reaction, α, is proportional to the heat generated during reaction, the reaction rate can be expressed as a function of conversion and temperature:

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha) \tag{2}$$

where $k(T)$ is the Arrhenius rate constant and $f(\alpha)$ is a function that depends on the reaction mechanism. The Arrhenius rate constant has been described by

$$k(T) = A \exp\left(\frac{E}{RT}\right) \tag{3}$$

being A the pre-exponential factor, E the activation energy, T the absolute temperature and R the gas constant.

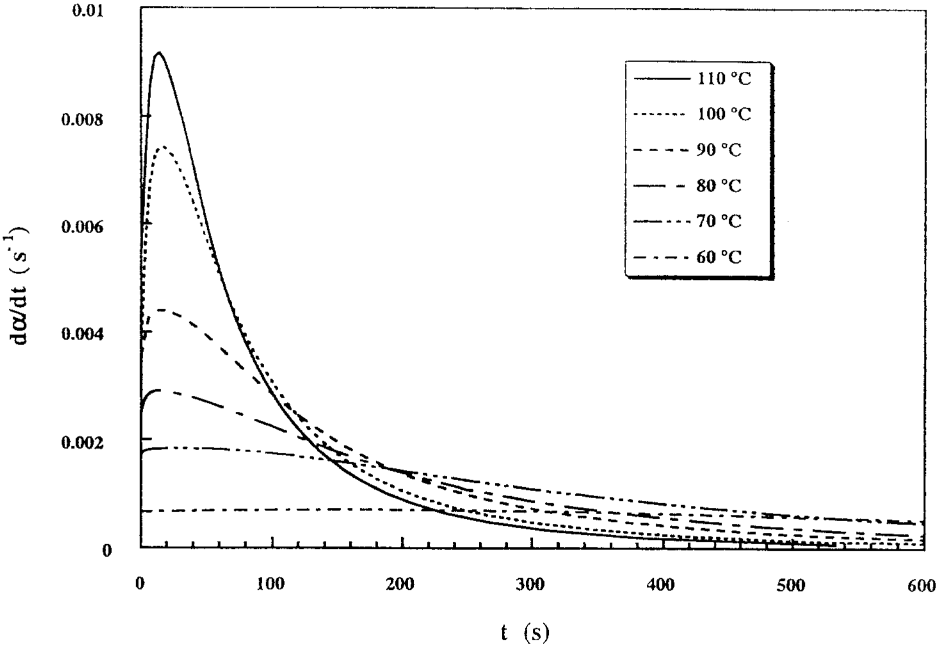

Fig. 2 Reaction rate dα/d*t*, *vs.* time curves for different cure temperatures

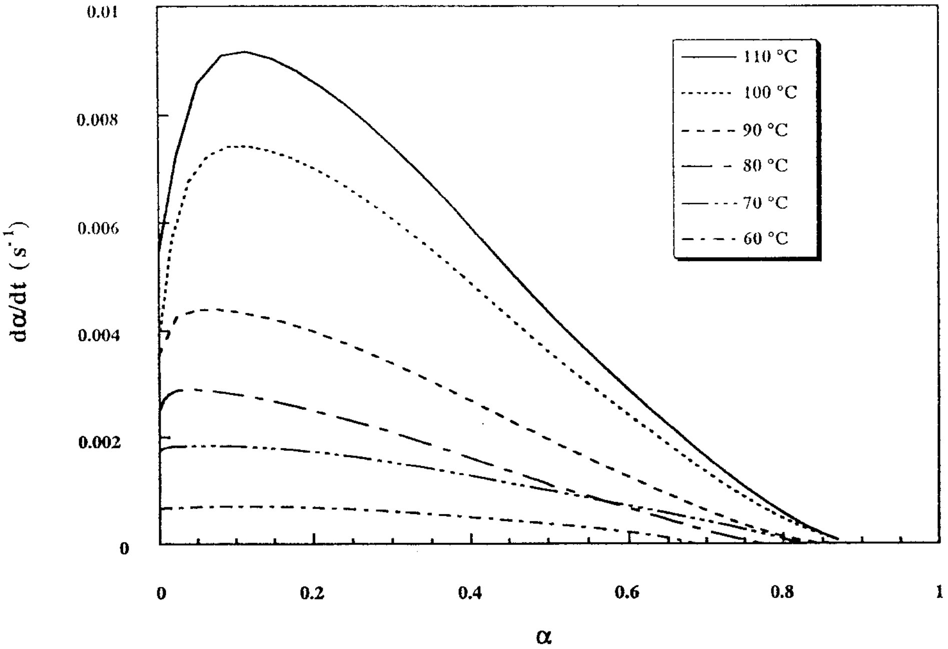

Fig. 3 Reaction rate dα/d*t*, *vs.* conversion, α, curves at different temperatures

To model the kinetics, it has been applied the so-called autocatalytic model with two kinetic constants, K_1, K_2 and two reaction orders, m and n, which embodies the experimental observations (Fig. 2) that the peak in the exotherms occur at some $t > 0$ and that the rate of reaction at $t=0$ is nonzero,

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \tag{4}$$

The introduction of four parameter, K_1, K_2, m and n makes it possible to obtain a good fit to experimental data, and the equation has found successful application for similar epoxy systems [5–8].

Figure 3 shows DSC data on the DGEBA/1,3-BAC system plotted as $d\alpha/dt$ *vs.* α at different temperatures. Curves were fitted to the autocatalytic model using a least squares method up to 30–50 % of the conversion depending on the curing temperature (Fig. 4a) to estimate the kinetic parameters during the first portion of the cure because in this study it is assumed that diffusion is the limiting factor in the later portions of the cure and the reaction rate mechanism subsequently changes. Typical comparison between experimental data and predictions of the autocatalyzed model (Eq. 4) are shown in Fig. 4b.

A good agreement is observed up to 45% conversion, after which significant deviations are observed due to the onset of gelation. Values of model parameters are present in Table 1. From the data in this table, the obtained values for activation energies of the rate constants were 44 and 57 kJ mol^{-1}, in good agreement with values obtained by other authors for similar systems [9–11]. The orders of reaction m and n, lightly change with temperature but their sum is in the range 2.5–3.

Table 1 Kinetic parameters of the autocatalytic model

T/°C	K_1/s^{-1}	K_2/s^{-1}	m	n
60	0.00066	0.0021	0.98	2.1
70	0.00120	0.0021	0.72	2.0
80	0.00250	0.0034	0.52	2.1
90	0.00360	0.0071	0.57	2.1
100	0.00380	0.0160	0.49	2.1
110	0.00540	0.0240	0.59	2.3

Gelation

Gel times, t_{gel}, were defined as the cure time at constant temperature leading to an incipient gel in tetrahydrofuran. Figure 5 shows Arrhenius plots of experimental values of t_{gel} *vs.* $10^3/T$. An activation energy equal to E=49.5 kJ mol^{-1} resulted, in excellent agreement with the activation energies of the rate constants.

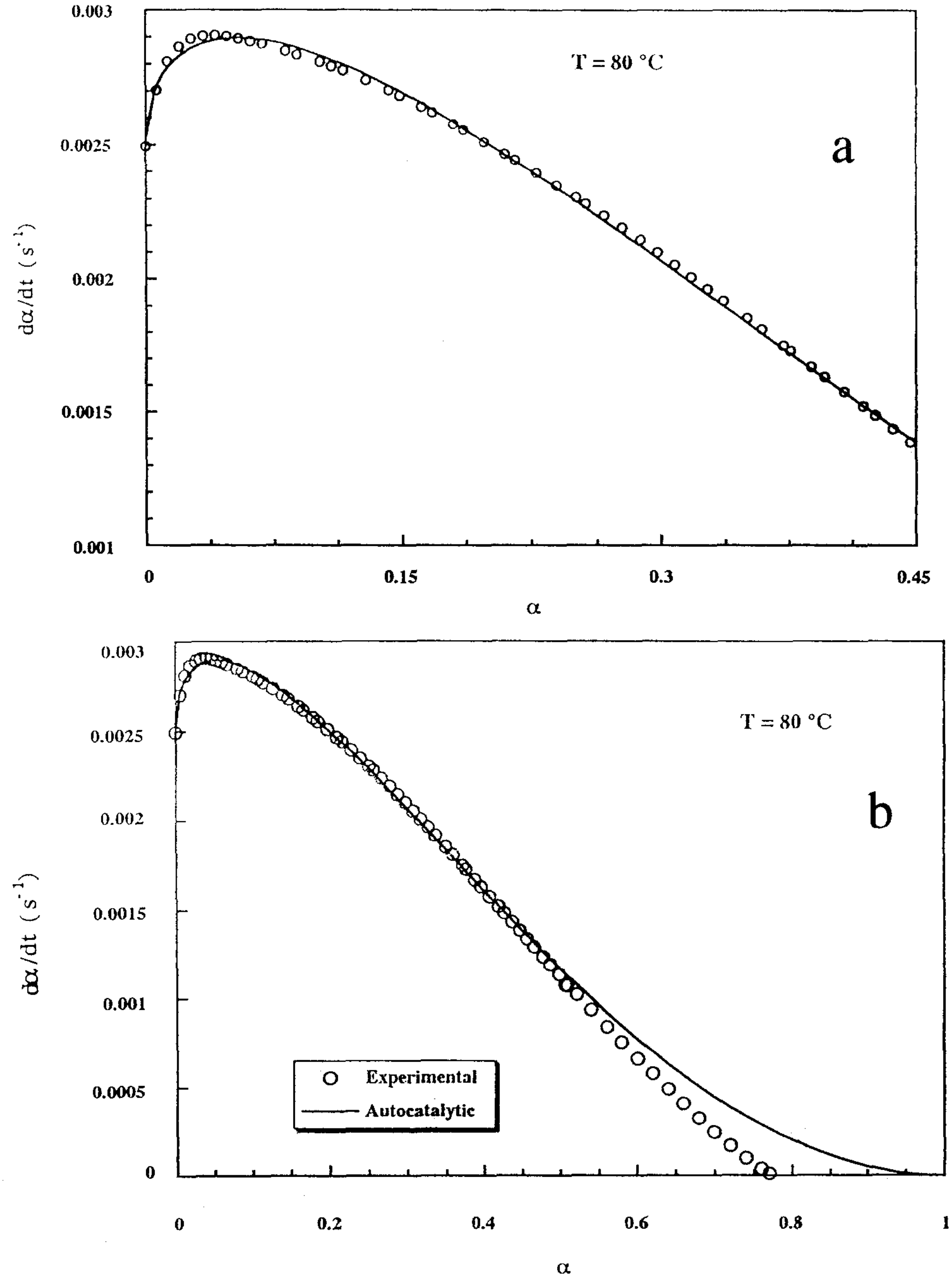

Fig. 4 Typical isothermal experiment at the cure temperature of 80°C. (a) Experimental data fitted to the autocatalytic model up to 45% of the conversion. (b) Comparison between experimental data and predictions of the autocatalyzed model over the entire range of conversion

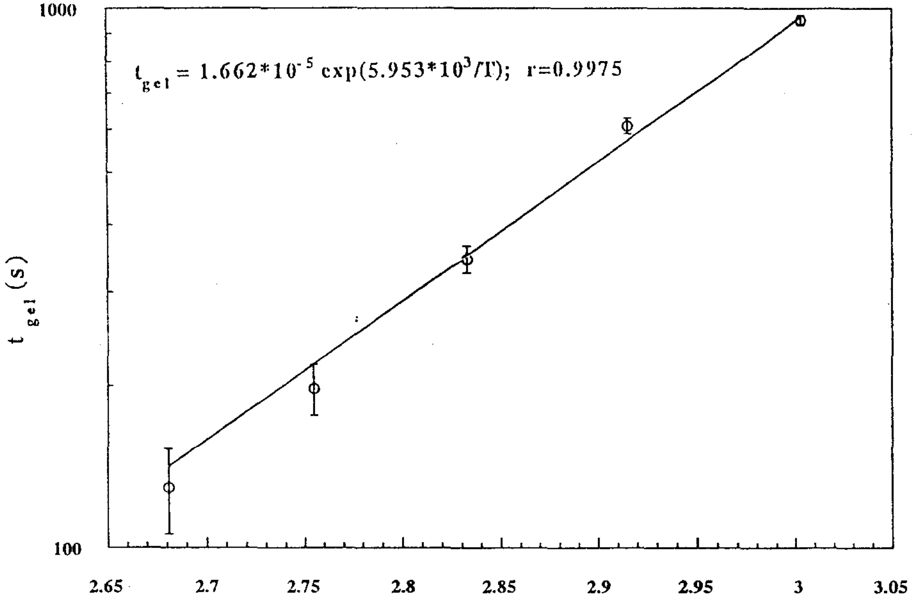

Fig. 5 Arrhenius plot of the gel times

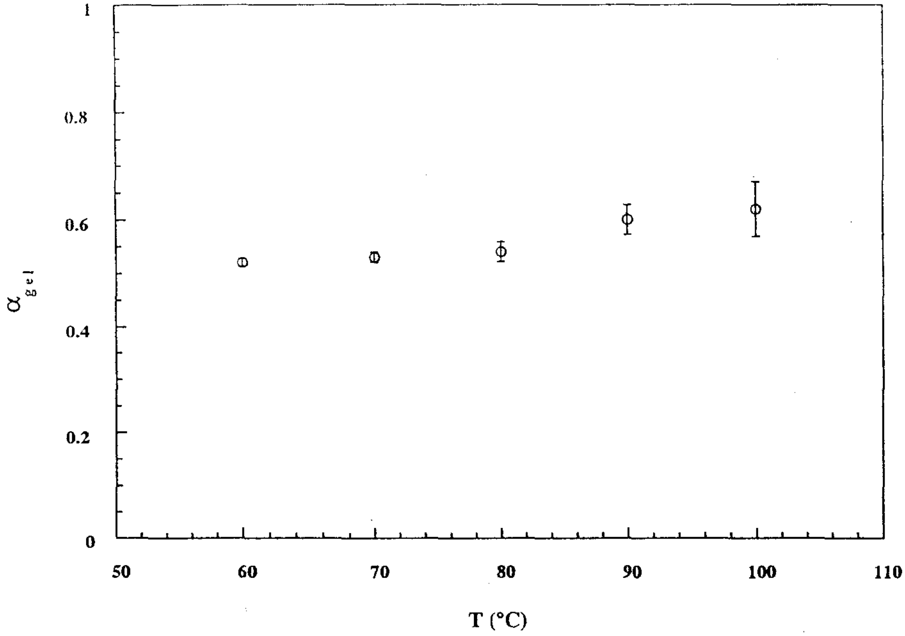

Fig. 6 Conversion at gelation *vs.* temperature

For stoichiometric blends the theoretical conversion at gelation may be calculated according to the expression [12].

$$\alpha_{gel} = \frac{1}{\sqrt{(f_a - 1)(f_e - 1)}} \tag{5}$$

where α_{gel} is the fractional conversion of epoxide at gelation and f_a and f_e are the functionalities of the amine and epoxide respectively. In our case α_{gel} is 0.58. By combining the gel time measurements and DSC data results the experimental values for fractional conversion at gelation were obtained and there are shown in Fig. 6. It can be seen that α_{gel} increases lightly with temperature but the Arrhenius plot for gelation showed a good linearity indicating that a point of constant conversion was being measured. Experimental values obtained differ more and more from the value predicted by gelation theory when increasing temperature. It could be due to the different sizes of the samples used both in DSC and gel time measurements [13].

Conclusions

A phenomenological kinetic model has been used in this work to describe the cure kinetics of DGEBA/1,3-BAC epoxy system over the temperature range of 60–110°C.

We have determined the reached conversions at several cure temperatures and the reaction rates. The experimental data, showing an autocatalytic behaviour were compared with the model proposed by Kamal. This model gives a good description of cure kinetics up to the onset of vitrification. The values for activation energies of the rate constants were 44–57 kJ mol^{-1}.

The value for the overall activation energy calculated from gel time measurements was 49.5 kJ mol^{-1} in excellent agreement with the activation energies of the rate constants.

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