

DYNAMIC DSC CHARACTERIZATION OF EPOXY RESIN BY MEANS OF THE AVRAMI EQUATION

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Abstract

A phenomenological approach was used to characterize the cure processes of epoxy resins (a diglycidyl ether of bisphenol A and its modifier CTBN) from dynamic experiments by DSC. Various kinetic parameters were obtained by using a modified Avrami expression. The resulting overall activation energies for the two systems agreed very well with the published data in the whole cure temperature range. In contrast with the isothermal results and the general dynamic models, a change in the exponent and the non-linear temperature dependence of the rate constant were also observed.

Keywords: Avrami expression, CTBN, cure kinetics, epoxy

Introduction

The cure kinetics of epoxy and unsaturated polyester resins under isothermal conditions analysed by Avrami theory was earlier reported and discussed [1, 3]. The results obtained were in good agreement with the experimental data. The attractive feature of isothermal experiments is that the rate constants at each temperature are better defined and the constants obtained at different temperatures permit determination of the activation energy associated with the cure reactions [4, 5]. However, the nature of the reactions and the final products may differ at different temperatures, and the kinetic parameters thus obtained are not without ambiguity [6].

Dynamic experiments conducted at a specified heating rate with the use of DSC will yield conversion–time–temperature data that are comprehensive enough to permit direct evaluations of the kinetic parameters. A single dynamic run gives as much information as do several isothermal runs. Furthermore, dynamic measurements can provide kinetic information over a larger temperature range and there are no precure problems, as is the case with isothermal experiments in which the sample must first be heated to the isothermal hold temperature, during which cure reactions may take

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place. It is valuable as a precursor to isothermal studies and is often the only means of analysing the cure kinetics of systems with multiple exotherms [7]. One shortcoming of this method based on the mechanistic model is the requirement of an assumed reaction order.

In comparison with the isothermal method, the case of a dynamic cure is theoretically more difficult as regards the phenomenological kinetic model, due to the complex temperature dependence of the rate constant and the peculiar feature of the cure, although it is a case which more closely simulates the fabrication process [8].

In this work, the dynamic cure behaviour of epoxy resin systems was studied. The kinetic parameters were obtained by using the modified Avrami equation and a comparison with isothermal results was also made.

Experimental

Materials

The epoxy resin systems used in this study consisted of a diglycidyl ether of bisphenol A (DGEBA) (Shell Chemicals, Epon 828), 4,4'-methylene dianiline (MDA; Fluka Chemie Co.) and a low molecular mass carboxyl-terminated butadiene-acrylonitrile (26%) copolymer (CTBN) (Kukdo Chemical Co.). These materials were used as supplied, without further purification. The epoxide equivalent mass of the resin was taken as 184 and the concentration of CTBN was 10%.

The resin was cured by employing stoichiometric quantities of diamine. The two systems are referred to as DGEBA-MDA and DGEBA-CTBN-MDA. The epoxy resin was mixed with CTBN and melted MDA under efficient stirring at about 80°C, and then cooled rapidly to room temperature. The resulting material was kept under desiccation in a freezer at -20°C prior to use. Caution had to be taken to avoid overheating the materials, especially for the epoxy system containing the CTBN oligomer, in which the fast cure reaction will take place at higher temperature.

Dynamic characterization

Samples consisting of 3–6 mg mixture were placed in aluminium DSC pans and run on a Seiko I-5000 series instrument. Dynamic scans were conducted at heating rates of 5, 10, 15 or 20°C min⁻¹, and were used to determine the heat relating to the curing process and the reaction kinetics. The carrier gas was nitrogen at a flow of 50 ml min⁻¹.

The DSC curves were analysed on the basis of the following assumptions: The area under the curves is proportional to the extent of reaction, and the extent of reaction during the mixing of the epoxy resin and the hardener may be neglected. The extent of cure α at any time is defined as

$$\alpha = \frac{\Delta H}{\Delta H_0} \quad (1)$$

where ΔH is the heat of reaction determined from the partial area under the DSC curve up to the point of interest. ΔH_0 is the ultimate heat of cure.

Results and discussion

Typical dynamic DSC curves at four heating rates for the DGEBA–MDA system are shown in Fig. 1. It is seen that the cure exotherm shifts to higher temperatures with increasing heating rate.

The area under the exotherm is related to the curing heat, ΔH , as discussed above in the Experimental section. The extent of cure can be calculated from the heat of cure. Figures 2 and 3 reveal that the extent of cure decreases correspondingly at the given cure temperature when the heating rates are increased for these two systems. A comparison of Figs 2 and 3 demonstrates that there is a higher extent of cure at the same cure temperature for the DGEBA–CTBN–MDA system. This is consistent with the result obtained from the isothermal experiment. It can be attributed to the accelerating influence of CTBN due to the incompatibility between the epoxy and the CTBN oligomer [1].

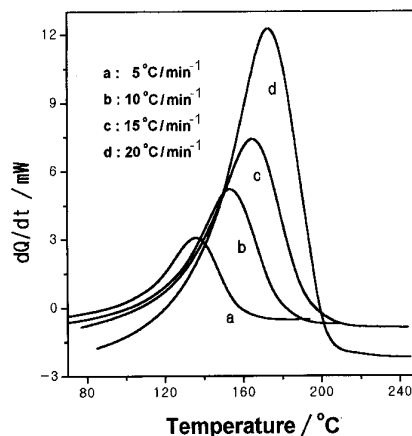


Fig. 1 Dynamic DSC curves at different heating rates for DGEBA–MDA

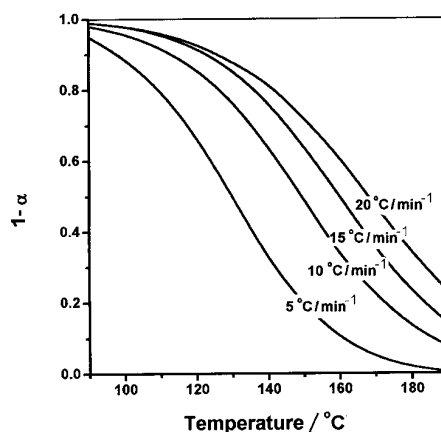


Fig. 2 Temperature dependence of uncured fraction at different heating rates for the DGEBA–MDA system

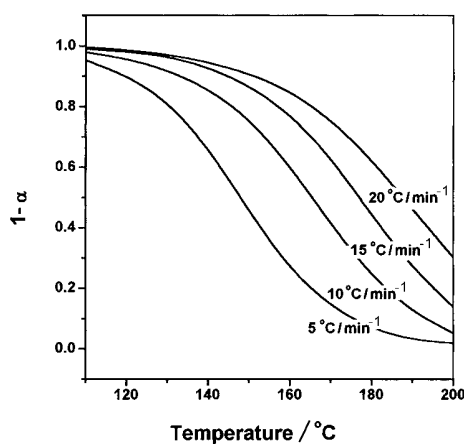


Fig. 3 Temperature dependence of uncured fraction at different heating rates for the DGEBA-CTBN-MDA system

The classical Avrami equation

$$\alpha(t) = 1 - \exp(-k't^n) \quad (2)$$

where $\alpha(t)$ is the extent of cure at time t , k' is the Avrami rate constant, and n is known as the Avrami exponent, describing the isothermal cure, can be extended to the non-isothermal process.

In the present work, the Ozawa method is adopted to describe the cure process of epoxy resin at a constant heating rate [9]. At a given temperature, n is constant, the untransformed volume fraction can be written as

$$1 - \alpha = \exp(-k''R^{-n}) \quad (3)$$

where α is a function of temperature, R is the heating rate, and $R = dT/dt$. k'' is a function of the temperature of the process.

From Eq. (3), the modified Avrami equation is given by

$$\log[-\ln(1 - \alpha)] = \log k'' - n \log R \quad (4)$$

Equation (4) can be used to obtain the kinetic parameters from the observation of the cure process at different heating rates. A plot of $\log[-\ln(1 - \alpha)]$ vs. $\log R$ at a given temperature should yield a straight line with a slope of $-n$ and an intercept of $\log k''$.

A typical plot of the above equation for the dynamic cure behaviour of the epoxy resin is given in Fig. 4. A similar result can be obtained for the DGEBA-MDA system. The values of the rate constant and exponent at the different temperatures are listed in Table 1. The unit of the rate constant, corresponding to that in the isothermal result, min^{-1} , is $\text{min}^n \text{K}^{-n}$.

The plots in Fig. 4 exhibit the good linear reactions for the whole cure temperature range. These results confirm that the modified Avrami equation appropriately

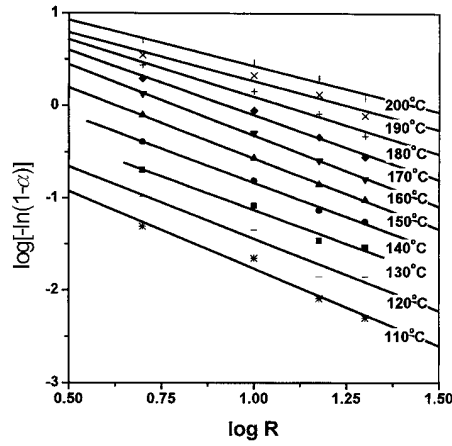


Fig. 4 Avrami plots of dynamic cure of DGEBA-MDA at various temperatures

Table 1 Kinetic parameters obtained from Eq. (4) at different temperatures under dynamic conditions for two epoxy systems

Temperature/°C	DGEBA-MDA		DGEBA-CTBN-MDA	
	$k''/\text{min}^n \text{K}^{-n}$	n	$k''/\text{min}^n \text{K}^{-n}$	n
90	–	–	0.37	1.26
100	–	–	0.96	1.35
110	1.23	1.65	1.76	1.31
120	1.34	1.56	2.99	1.28
130	2.13	1.46	4.98	1.26
140	4.38	1.48	8.65	1.27
150	9.21	1.53	10.79	1.18
160	16.38	1.54	13.85	1.11
170	19.97	1.35	15.39	1.00
180	20.76	1.21	17.99	0.94
190	21.54	1.05	21.39	0.90
200	24.95	1.02	–	–

describes the dynamic cure process for both systems. It is also found that the Avrami rate constant is sensitive to temperature, increasing with rising temperature, as would be expected. However, it is interesting to note that the values of the exponent decrease when the cure temperature is over 140°C for the DGEBA-CTBN-MDA system, and over 160°C for the DGEBA-MDA system, and there is a transition point, depending upon the cure temperature. The Avrami exponent is known to pro-

vide qualitative information on the nature of the nucleation and the growth process in the crystallization of a polymer and can change; in fact, n often decreases as nucleation stops, and only the growth of nuclei continues in the later stage of the reaction kinetics. This fact of change in n may imply that a change occurs in the cure mechanism when the cure temperature reaches this point, although the formation and growth of microgels is essentially different from those of crystals. It is possible that the growth of the microgel particles formed is predominantly diffusion-controlled in one direction in the higher temperature range, as the retardation of viscosity. A similar result was obtained when the data were analysed by a mechanistic model described as a diffusion-controlled process.

With the calculation of the rate constants, we assume an Arrhenius temperature dependence to obtain the values of the activation energy and frequency factor, i.e.:

$$k = A \exp \frac{-E_a}{R_o T} \quad (5)$$

where E_a is the overall activation energy, A is an overall frequency factor; and R_o is the universal gas constant. This is a common method of analysis of non-isothermal data. If the Arrhenius relation is obeyed, the overall activation energy and frequency factor can be determined from the slope and intercept, respectively, of the best-fit line.

Figure 5 depicts a plot of $\ln k$ vs. $1/T$. If we do not consider the change in slope of the lines and only give an overall activation energy and an overall frequency factor, an actual balance in nucleation and growth over the entire cure process, the activation energies reported in Table 2 are in very good agreement with data published on similar epoxy systems. Typical values of 58.5–67 kJ mol⁻¹ were reported by Gough and Smith [10] and Kil *et al.* [11] from gel time measurements, and of 50–58 kJ mol⁻¹ by Prime [12], and Horie *et al.* [13] from reaction rate measurements (DSC). However, it can be seen that the Arrhenius plots are not straight lines for the whole $1/T$ range, but display a marked change in slope at around 140°C for the DGEBA–CTBN–MDA system and around 160°C for the DGEBA–MDA system. Since the

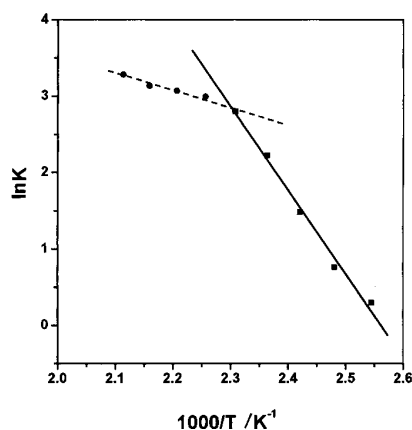


Fig. 5 Temperature dependence of rate constant for the DGEBA–MDA system

slope is a measure of the activation energy, the results indicate marked changes in the energies of nucleation and growth. It is clear that such changes reflect the exponent change described previously.

To describe the data better, a further analysis was carried out separately in the different temperature ranges. As shown in Table 2 and Fig. 5, the activation energy falls

Table 2 Overall activation energy given by different analytical methods for DGEBA–MDA and DGEBA–CTBN–MDA, kJ mol^{-1}

System	$E(0)$	$E(1)$	$E(2)$	$E(I)$	$E(D)$	$E(K)$
DGEBA–MDA	55.1	71.0	24.3	64.4	54.5	47.7
DGEBA–CTBN–MDA	54.8	75.5	26.7	66.8	56.9	48.4

$E(0)$, $E(1)$ and $E(2)$ are the activation energy values for the balanced, primary and second section, respectively. $E(I)$, $E(D)$, and $E(K)$ are the values for the isothermal, Doyle model and Kissinger expressions

to approximately one-third of the value observed in the lower cure temperature range. Such a decrease in apparent activation energy is commonly observed in heterogeneous reactions, especially when diffusion limitations set in [2, 14, 15]. It occurs at around 85% conversion for the DGEBA–MDA system, and 91% conversion for the rubber modified epoxy. The present results may therefore be interpreted to imply that the diffusion factors become significant in the late stage of the curing of epoxy systems. This means phenomenologically that the number of microgel particles dispersed in the low molecular weight prepolymer (continuous phase) increases during the course of the cure reaction. When the higher temperature is reached, a mass dispersion limitation eventually sets in, the particles are forced to impinge on one another, and phase inversion may occur.

The activation energy in the lower temperature range closely agrees with that observed in the isothermal experiments. This may show that there is a similar cure mechanism under isothermal conditions and in the primary stage of the dynamic cure for both systems, in which the cure process is kinetic-controlled.

In fact, the amount of liquid transformed into microgel particles in a given time or at a given temperature depends on the rate of growth of existing microgel particles and the rate of nucleation of new ones. The growth rate is zero at T_{c0} (T_c below which no significant reaction of the uncured resin mixture occurs), and then rises to a maximum with the advance of the cure reaction. The propagation of primary chains, intramolecular cyclization and crosslinking predominate in this temperature range, decreasing as the rising viscosity and intermolecular crosslinking inhibit growth. The use of Eq. (4) may therefore be appropriate only when growth is completed before T rises to the temperature of the maximum growth rate [16].

To evaluate the kinetic parameters, the effectively modified derivation mode of Eq. (6) [17] and the Kissinger expression, a mechanistic model [18], are applied here. The apparent activation energy values are listed in Table 2.

For the derivative model proposed by Doyle [17], the relationship between the heating rate and scanning temperature can be expressed as

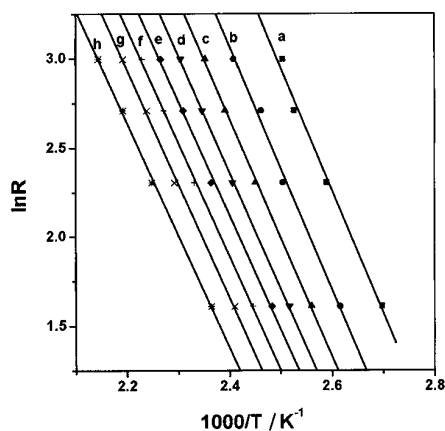


Fig. 6 Arrhenius plots of DGEBA-CTBN-MDA at different heating rates and different extents of cure; Extent of cure: a - 0.1; b - 0.2; c - 0.3; d - 0.4; e - 0.5; f - 0.6; g - 0.7; h - 0.8

$$\ln R = X - 1.0516 \frac{E}{R_0 T_R(\alpha)} \quad (6)$$

where X is a constant, and $T_R(\alpha)$ is the temperature at which a given extent of reaction is reached. Plots for different heating rates at different extents of cure are shown in Fig. 6. The activation energy values obtained from the slopes are seen to be very consistent with those observed from Fig. 5 and reported in the literature.

The Kissinger expression gives

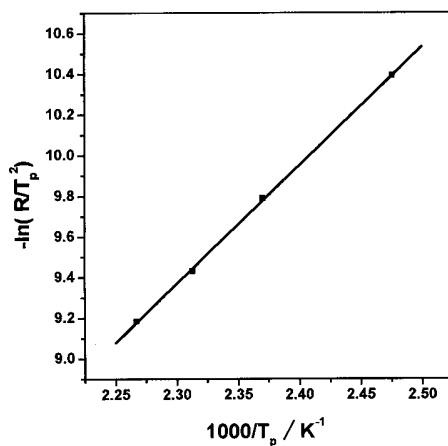


Fig. 7 Plot of $-\ln(R/T_p^2)$ vs. T_p^{-1} for DGEBA-CTBN-MDA

$$-\ln\left(\frac{R}{T_p^2}\right) = \frac{E}{R_o T_p} - \ln\frac{AR_o}{E} \quad (7)$$

where T_p is the temperature at which the maximum conversion rate occurs in the DSC curve. The activation energy values obtained from the slopes of the $-\ln(R/T_p^2)$ vs. $1/T_p$ plots for both systems are also in good agreement with the published data [19] (Fig. 7).

The results observed from the phenomenological model described by the Avrami expression are therefore reliable for dynamic cure conditions. In contrast with the isothermal experiments, the diffusion-controlled cure process is described in the late stage of curing, which was not the case for the general dynamic models.

Conclusions

In contrast with the isothermal results, the cure behaviour of these epoxy systems under dynamic conditions reveals two different sections, depending on the cure temperature. The kinetic parameters can be determined either from the whole cure process or separately from each section. The activation energy obtained from the first slope closely agrees with that obtained under isothermal conditions, and the balance value, for a combination of the two sections, is a reflection of the overall cure process.

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