# Effect of the Crosslinking Degree on Curing Kinetics of an Epoxy-Anhydride Styrene Copolymer System

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ABSTRACT: The cure kinetics of a high molecular weight acid copolymer used as a hardener for a commercial epoxy resin (DGEBA) was studied by DSC. The systems were uncured and partially cured epoxy poly(maleic anhydride-*alt*-styrene) (PAMS) at different periods of time. The state of cure was assessed as the residual heat of reaction and was varied by controlling both the time and temperature of cure. The conversion degree of crosslinking increased with time and temperature. Additionally, the activation energy and reaction order were calculated by the Freeman–Carrol relation and showed a dependence on the conversion degree of crosslinking. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2089–2094, 1999

**Key words:** maleic anhydride–styrene copolymer; diglycidyl ether of bisphenol A; curing; DSC

## **INTRODUCTION**

Because of their strength, versatility, and excellent adhesion to a variety of surfaces, epoxy resin adhesives gained wide acceptance by various users. They revolutionized joining and fastening technology in some industries. The epoxy resin cohesion is obtained during the crosslinking reaction in the presence of crosslinking agents known as hardeners. The crosslinking agents are labile hydrogen compounds such as acids,<sup>1</sup> anhydrides,<sup>2</sup> and amines.<sup>3</sup> The crosslinking reaction leads to the formation of a tridimensional system insoluble in the usual solvents.

The kinetics of the epoxy-anhydride system was studied through phenomenological models of the nth-order reaction and the autocatalytic model.

The cure of epoxy resins was studied by differential scanning calorimetry (DSC) by Fava<sup>4</sup> and Barton.<sup>5</sup> This technique gives a quantitative measurement of the residual amount of reaction and also allows determination of the glassy rubber transition temperature  $(T_g)$ . Other authors<sup>6,7</sup> studied the cure kinetics of the epoxy-anhydride systems using various nonisothermal DSC scans, which allow the calculation of the activation energy.

The objective of the present work is to study the cure kinetics of an epoxy resin diglycidyl ether of bisphenol A (DGEBA) cured by a copolymer, poly(maleic anhydride-*alt*-styrene) (PAMS), used as an adhesive.<sup>8</sup> The styrene gives to the adhesive the properties of mechanical resistance, whereas the anhydride component provides for the crosslinking reaction.

## Theory

For thermosets which follow the *n*th-order kinetics, the rate of conversion,  $d\alpha/dt$ , is proportional to the fraction of unreacted material. This can be expressed in the classical expression as:

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Temperature (°C)

**Figure 1** DSC curves of uncured and partially cured epoxy/PAMS for different curing times at 85°C (a) = 0; (b) = 20 min; (c) = 30 min; (d) = 60 min; (e) = 90 min; (f) = 120 min; (g) = 180 min; (h) = 360 min.

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

where  $\alpha$  is the fractional conversion of reactants consumed after time t, n is the reaction order, and k is the specific rate constant.

Cure reactions that are autocatalyzed can be described by a relation such as:

$$d\alpha/dt = k\alpha^m (1-\alpha)^n \tag{2}$$

where m is also a reaction order.

The autocatalyzed systems are characterized by the formation of some intermediate species that markedly accelerates the crosslinking reaction. Different methods are established resulting in DSC studies<sup>9–11</sup> that permit the evaluation of kinetic parameters.

In this study, the reaction is supposed to be following *n*th-order kinetics. The Freeman–Carrol relation<sup>12</sup> is applicable to many epoxy cure reactions and offers a rapid and simple technique. The activation energy and reaction order were calculated from this relation:

$$\frac{\Delta \ln dH/dt}{\Delta \ln (\Delta H - H)} = n - \frac{\frac{E}{R} * \Delta \frac{1}{T}}{\Delta \ln (\Delta H - H)}$$
(3)

where dH/dt is the heat flow, generated in the curing reaction (w/g);  $\Delta H$  is the total heat of curing (KJ/mol); n is the reaction order; E is the activation energy; R is the constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>); and T is the absolute temperature (K).

On assuming that the hardening reaction in this case proceeds in accordance with the Arrhenius law, the relationship (3) may be represented by a straight line described by the equation

$$Y = mx - c$$

	$T_C = 8$	$T_C = 85^{\circ}\mathrm{C}$		$T_C = 75^{\circ}\text{C}$	
Time (min)	$\Delta H_R$	α	$\Delta H_R$	α	
0	196.000	0.000	196.000	0.000	
20	128.350	0.363	177.800	0.117	
30	108.395	0.462	154.300	0.234	
60	76.345	0.621	135.650	0.326	
90	65.345	0.676	122.600	0.391	
120	58.370	0.710	93.680	0.535	
180	56.630	0.719	63.270	0.686	
360	41.080	0.796	49.360	0.755	

Table IExtent of Cure of Uncured andPartially Cured DGEBA/PAMS System atDifferent Periods of Curing Time

where m = E/R and c = n. From the slope of the straight line, the activation energy was calculated, and from a knowledge of the intercept c, the order of reaction was determined.

### **EXPERIMENTAL**

#### **Materials**

The epoxy resin was a commercial DGEBA (Dow Chemical Co.; DER332) with an equivalent epoxy of 174 g. A hardener, a copolymer PAMS, synthesized by free radical polymerization in solution, was used to cure the resin. Resin and copolymer were mixed in 0.7 mol acid/mol epoxy proportion fixed in a previous study<sup>13</sup> in the presence of a tertiary amine. The mixture was stirred at room temperature until a clear homogeneous solution was obtained. Samples were enclosed in aluminum DSC pans and introduced in a ventilated dryer at the curing temperatures (85 and 75°C) for different periods of time (20, 30, 60, 90, 120, 180, 360 min) to obtain different extents of cure.

#### **Differential Scanning Calorimetry**

Calorimetric measurements were performed with a DSC 930 Dupont instrument equipped with a DSC model 912 with two cells connected to an IBM 2100 microprocessor. The calorimeter was previously calibrated with an indium standard. The sample weights were 10 mg. After the isothermal curing, the sample was guenched to room temperature, introduced in the DSC, equilibrated at 25°C, and then scanned at a heating rate of 10°C/min from 25 to 250°C. The cure of an epoxy resin is an exothermic process and the heat evolved can be detected quantitatively by the DSC, thus giving a measurement of the amount of reaction remaining in the sample. The degree of conversion  $\alpha$  was calculated by the residual enthalpy of curing:

$$\alpha = \frac{\Delta H_T - \Delta H_R}{\Delta H_T}$$

where  $\Delta H_T$  is the total heat of curing obtained by nonisothermal DSC scan of fresh sample, and  $\Delta H_R$  is the residual heat of curing of a sample isothermally cured at 85 or 75°C during a specified period of time.

## **RESULTS AND DISCUSSION**

Figure 1 shows the DSC curves of the uncured epoxy resin and partially cured resins at a heat-

 $T_C = 75^{\circ}\text{C}$  $T_C = 85^{\circ}\text{C}$ Time (min) E (kcal/mol) E (kcal/mol) α п α п 0.000 0.000 1.90 0 28.7801.928.780200.363 30.886 2.030.11728.780 2.0030 0.462 31.870 2.430.234 29.750 2.0060 0.62132.680 2.60.326 30.780 2.0690 0.676 32.900 2.750.391 31.1002.09120 0.71036.600 3.020.53532.5002.60180 0.74042.7603.320.686 32.900 2.60360 0.7960 45.926 3.600.75537.190 3.02

Table IIActivation Energy Values and Order Reaction of Uncured and Partially CuredDGEBA/PAMS System for Different Curing Times and Temperatures



**Figure 2** Conversion degree ( $\alpha$ ) versus time of the system DGEBA/PAMS at (a) = 85°C and (b) = 75°C.

ing rate of 10°C/min. These curves give the total heat of curing  $(\Delta H_T)$  and the residual heat of curing  $(\Delta H_R)$  and are used for kinetic calculations. The exotherms obtained are used to measure the two basic parameters, the partial heat of cure (*H*), and the heat flow at some time *t*; *dH/dt* is measured by the displacement of the cure exotherm from the baseline at any time. A minimum of 10 values of *H* and *dH/dt* were tabulated for each exotherm. By plotting  $\Delta \ln dH/dt/\Delta \ln(\Delta H$ - H) against  $\Delta(1/T)/\ln(\Delta H - H)$ , we obtained the value of *E/R*, which is the slope of the straight line; the order reaction, *n*, is the intersection of this curve with the *Y* axis.

Table I gives the extent of cure, uncured, and partially cured epoxy resin PAMS system calculated by the residual heat method for two curing temperatures (85 and 75°C). The effect of increasing curing temperature causes a lower residual heat of reaction  $(\Delta H_R)$  and a higher conversion degree  $\alpha$ , for a required curing time.

Table II indicates the values of activation energy and the order reaction for different periods of curing time.



**Figure 3** Activation energy (*E*) versus degree of conversion of the system DGEBA/PAMS at (a) =  $85^{\circ}$ C; (b) =  $75^{\circ}$ C.



**Figure 4** Reaction order (*n*) versus degree of conversion of the system DGEBA/PAMS at (a) =  $85^{\circ}$ C; (b) =  $75^{\circ}$ C.

Figure 2 illustrates the variation of the degree of conversion  $\alpha$  against time of the system at 85 and 75°C curing temperatures. At 85°C, the conversion degree  $\alpha$  increased rapidly for the first hour, showing a linear relationship between  $\alpha$ and time, and then leveled. At the lower curing temperature, the trend of variation was similar, but the conversion rate became slower. This phenomenon suggests that the crosslinked spatial structure formed interferes with further reaction according to the mechanism of hardening of epoxy resins with acid anhydrides proposed by Fish and Hofman.<sup>14</sup> These are reactions of anhydride groups with resin hydroxyl groups and carboxy groups formed by their successive reaction with resin groups and could lead to complex formations that would hamper the mobility of the system, resulting in a slower conversion rate. A recent study<sup>15</sup> by Fourier Transform Infrared Spectroscopy (FTIR) showed that total conversion is obtained after several hours of postcure at 96°C.

The different processes that occur in curing the epoxy/PAMS system may also lie by observing that the features of the corresponding exothermic peak change with increasing  $\alpha$ . The shape of the peak becomes progressively more regular and symmetric (see Fig. 1).

Figure 3 shows the variation of activation energy with the extent of cure  $\alpha$  for the two curing temperatures. We observed an increase of E with the extent of cure and the mobility of the reactive groups decreases with the extent of cure, which in turn produces an increase of the activation energy of the system. At 75°C curing time, E is lower than that of 85°C. This is likely because at lower temperatures of cure, the system presents a better regularity of the reactive chemical groups that require a lower activation energy to react than in material cured at higher temperatures.

Similar behavior was observed for the order reaction n, which is illustrated by Figure 4. At 85°C curing temperature, n increases with the extent of cure, while the change becomes slower for 75°C. These results show that the kinetics of the residual curing change from the uncured resin to the partially cured.<sup>16</sup> This change of the kinetic parameters is probably due to secondary reactions which are favored by higher temperatures.

## **CONCLUSION**

The cure kinetics of a high molecular weight PAMS used as hardener for commercial epoxy resin (DGEBA) was studied by DSC. The state of cure was assessed as the residual heat of reaction and was varied by controlling both the time and temperature of cure. The degree of crosslinking increases, whereas the residual heat of reaction decreases with time and temperature. Additionally, the activation energy and order of reaction calculated by the Freeman–Carrol relation increase with the extent of cure of the partially cured epoxy resin.

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