

# Effect of the Crosslinking Degree on Curing Kinetics of an Epoxy–Acid Copolymer System

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**ABSTRACT:** The hardening of a commercial epoxy resin (DGEBA) with the cure of high molecular weight acid copolymers was studied using differential scanning calorimetry (DSC). The systems were uncured and partially cured epoxy/poly(acrylic acid–styrene) (SAAS), at different contents of styrene. The conversion degree of the crosslinking of

the systems, examined versus time, temperature of hardening, and styrene contents in the copolymers, were determined. The activation energies of the crosslinking reactions were calculated by the Freeman–Carroll relation and showed a dependence on the state of hardening. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2834–2839, 2003

## INTRODUCTION

Studies on epoxy materials have been extensive in view of their important technical applications. Epoxy resin adhesives have gained wide acceptance by various users. 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> Carboxylic polymers may act as hardeners for such a chemical reaction. The carboxylic acid end groups in acid copolymers are able to react with the oxirane groups of the epoxy resin. The oxirane ring opening, of the epoxy resin by the hydrogen of carboxylic groups, leads to reaction between the macromolecular chains, creating a crosslinked network, insoluble in the usual solvents. The released hydroxyl groups during the crosslinking reaction confer adhesive properties to the formed products. Qualitative and quantitative chemical analyses are necessary to evaluate the optimal conditions of the crosslinking reaction.

## Theory

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

$$d\alpha/dt = k(1 - \alpha)^n \quad (1)$$

where  $\alpha$  is the fractional conversion of reactants consumed after time  $t$ ;  $n$ , the reaction order; and  $k$ , the specific rate constant. A relation such as the following can describe cure reactions that are autocatalyzed:

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

where  $m$  (initiation) and  $n$  (propagation) are the reaction order.

The autocatalyzed systems are characterized by the formation of some intermediate species, which markedly accelerate the crosslinking reaction. Different methods were established in DSC studies<sup>9–11</sup> which evaluated the kinetic parameters.

In this study, the reaction is assumed to follow  $n$ th-order kinetics. The Freeman–Carroll 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 the relation

$$-\frac{\Delta \text{Ln}dH/dt}{\Delta \text{Ln}(\Delta H_T - H)} = n - \frac{E/R \times \Delta 1/T}{\Delta \text{Ln}(\Delta H_T - H)} \quad (3)$$

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

Assuming that the hardening reaction in this case proceeds in accordance with the Arrhenius law, a straight line described by the equation  $y = f(x)$  may represent the relationship (3):

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TABLE I  
Acrylic Acid Content in Copolymers

Polymer references	Percent of acrylic acid
SAAS <sub>1</sub>	8.9
SAAS <sub>2</sub>	29.5
SAAS <sub>3</sub>	63.2
SAAS <sub>4</sub>	79.6

$$y = mx - c$$

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 can be determined.

## EXPERIMENTAL

### Materials

The epoxy resin was a commercial DGEBA (DER 332 from Dow Chemical Co.) with an equivalent epoxy of 174 g. Copolymers of poly(acrylic acid-styrene) (SAAS) at different contents of styrene (Table I), synthesized by free-radical polymerization in solution,<sup>13</sup> were used to cure the epoxy. The resin and copolymers were mixed according to a previous study<sup>13</sup> (Table II) in the presence of triethylamine (15% by weight). For each system, a molar ratio  $r$  ( $r = \text{acid group/equivalent epoxy}$ ) was fixed by a nonisothermal study.<sup>13</sup> The mixture was stirred at room temperature until a clear homogeneous solution was obtained. Samples were enclosed in aluminum differential scanning calorimetry (DSC) pans and introduced in a ventilated dryer at two curing temperatures for different periods of time (20, 30, 60, 90, 120, 180, and 360 min) to obtain different extents of cure.

TABLE II  
Molar Ratio  $r$  for Each System

System	$r^a$
SAAS <sub>1</sub> /DGEBA	0.7
SAAS <sub>2</sub> /DGEBA	0.7
SAAS <sub>3</sub> /DGEBA	1
SAAS <sub>4</sub> /DGEBA	1

<sup>a</sup>  $r$ , acrylic acid group/equivalent epoxy.

### DSC

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 isothermal curing, the sample was quenched to room temperature, introduced in the DSC, equilibrated at 25°C, and then scanned at a heating rate of 10°C/mn 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 degree of reaction completion. The degree of conversion,  $\alpha$ , was calculated by the residual enthalpy of curing:

$$\alpha = \frac{\Delta H_T - \Delta H_R}{\Delta H_T} \quad (4)$$

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

## RESULTS AND DISCUSSION

The total heat of curing ( $\Delta H_T$ ) and the residual heat of curing ( $\Delta H_R$ ) are obtained from DSC curves that are

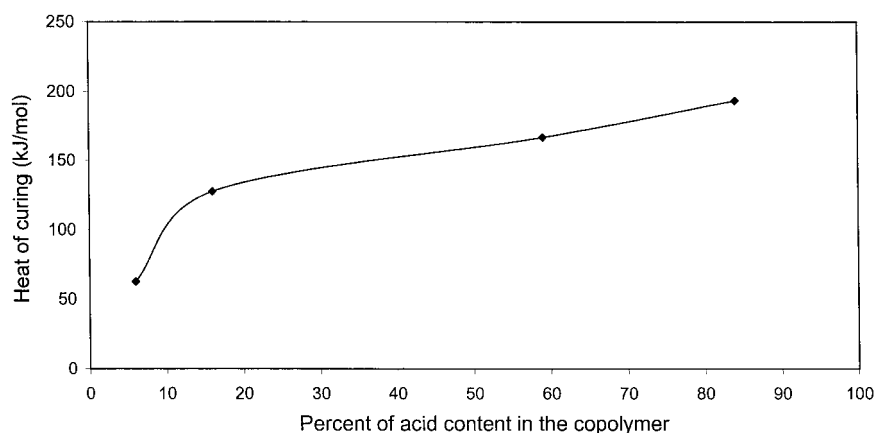


Figure 1 Variation of the heat of curing versus the percent of acid content in the copolymer.

**TABLE III**  
Extent of Cure of Uncured and Partially Cured SAAS1/  
DGEBA System at Different Periods of Curing Time

Time (min)	$T_c = 110^\circ\text{C}$		$T_c = 95^\circ\text{C}$	
	$\Delta H$ (kJ/mol)	$\alpha$	$\Delta H$ (kJ/mol)	$\alpha$
0	62.73	0	62.73	0
20	22.21	0.646	31.30	0.501
30	5.65	0.910	21.70	0.654
60	0	1	11.85	0.811
90			6.27	0.901
120			0	1

**TABLE IV**  
Extent of Cure of Uncured and Partially Cured SAAS2/  
DGEBA at Different Periods of Curing Time

Time (min)	$T_c = 90^\circ\text{C}$		$T_c = 75^\circ\text{C}$	
	$\Delta H$ (kJ/mol)	$\alpha$	$\Delta H$ (kJ/mol)	$\alpha$
0	127.77	0	127.77	0
20	78.51	0.385	103.315	0.252
30	45.87	0.641	64.125	0.398
60	23.51	0.816	47.81	0.698
90	12.43	0.903	27.83	0.781
120	0	1	7.18	0.850
180			0	1

**TABLE V**  
Extent of Cure of Uncured and Partially Cured SAAS3/  
DGEBA System at Different Periods of Curing Time

Time (min)	$T_c = 100^\circ\text{C}$		$T_c = 85^\circ\text{C}$	
	$\Delta H$ (kJ/mol)	$\alpha$	$\Delta H$ (kJ/mol)	$\alpha$
0	167.05	0	167.05	0
20	73.17	0.562	146.50	0.123
30	48.87	0.708	128.30	0.233
60	25.06	0.850	91.88	0.450
90	15.66	0.906	65.15	0.610
120	13.52	0.919	55.84	0.666
180	11.80	0.929	40.78	0.756
360	9.99	0.940	20.98	0.874

**TABLE VI**  
Extent of Cure of Uncured and Partially Cured SAAS4/  
DGEBA System at Different Periods of Curing Time

Time (min)	$T_c = 95^\circ\text{C}$		$T_c = 80^\circ\text{C}$	
	$\Delta H$ (kJ/mol)	$\alpha$	$\Delta H$ (kJ/mol)	$\alpha$
0	193.62	0	193.62	0
20	85.49	0.560	125.40	0.352
30	30.09	0.830	97.78	0.495
60	14.19	0.943	38.34	0.802
90	0	1	17.62	0.909
120			0	1

**TABLE VII**  
Activation Energy and Reaction Order of Uncured and  
Partially Cured SAAS1/DGEBA System for Different  
Curing Times and Temperatures

Time (min)	$T_c = 110^\circ\text{C}$		$T_c = 95^\circ\text{C}$		
	$\alpha$	$E$ (kJ/mol)	$\alpha$	$E$ (kJ/mol)	$n$
0	0	38.52	0	38.52	2.22
20	0.65	41.05	0.501	40.23	2.43
30	0.91	42.05	0.654	40.86	2.57
60			0.811	41.53	2.71
90			0.901	41.90	2.88

**TABLE VIII**  
Activation Energy and Reaction Order of Uncured and  
Partially Cured SAAS2/DGEBA System for Different  
Curing Times and Temperatures

Time (min)	$T_c = 90^\circ\text{C}$		$T_c = 75^\circ\text{C}$		
	$\alpha$	$E$ (kJ/mol)	$\alpha$	$E$ (kJ/mol)	$n$
0	0	35.43	0	35.43	2.00
20	0.385	37.83	0.252	36.55	2.02
30	0.641	39.99	0.398	37.44	2.05
60	0.816	41.56	0.698	39.99	2.15
90	0.903	42.26	0.781	40.68	2.18
120			0.850	41.19	2.20

**TABLE IX**  
Activation Energy and Reaction Order of Uncured and  
Partially Cured SAAS3/DGEBA System for Different  
Curing Times and Temperatures

Time (min)	$T_c = 100^\circ\text{C}$		$T_c = 85^\circ\text{C}$		
	$\alpha$	$E$ (kJ/mol)	$\alpha$	$E$ (kJ/mol)	$n$
0	0	26.74	0	26.74	1.987
20	0.562	27.91	0.123	26.96	1.990
30	0.708	28.32	0.233	27.11	2.00
60	0.850	28.99	0.450	27.55	2.010
90	0.906	29.33	0.610	27.83	2.040
120	0.919	30.28	0.666	28.01	2.090
180	0.929	31.42	0.756	28.61	2.150
360	0.940	32.31	0.874	29.11	2.200

**TABLE X**  
Activation Energy and Reaction Order of Uncured and  
Partially Cured SAAS4/DGEBA System for Different  
Curing Times and Temperatures

Time (min)	$T_c = 95^\circ\text{C}$		$T_c = 80^\circ\text{C}$		
	$\alpha$	$E$ (kJ/mol)	$\alpha$	$E$ (kJ/mol)	$n$
0	0	36.21	0	36.21	2.11
20	0.560	39.61	0.352	38.24	2.14
30	0.83	41.10	0.495	38.99	2.15
60	0.933	41.48	0.802	40.38	2.20
90			0.909	41.10	2.22

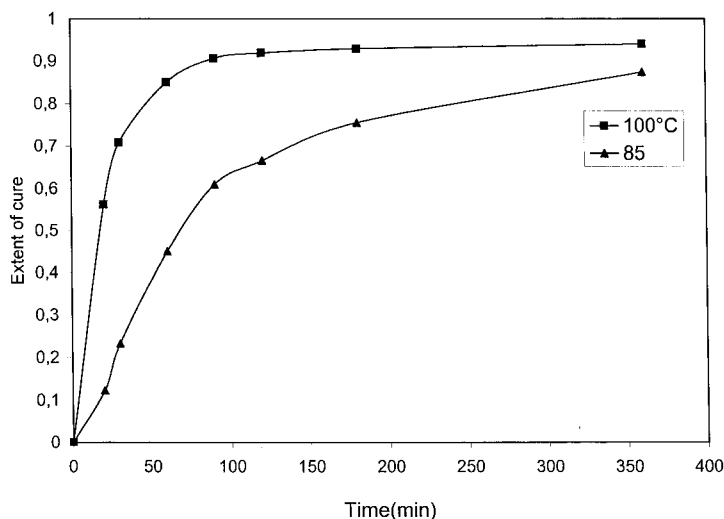


Figure 2 Extent of cure versus time of SAAS<sub>3</sub>/DGEBA system.

also used for kinetic calculations. The exotherms obtained are used to measure the two basic parameters, the partial heat of cure ( $H$ ) at given time  $t$  and the heat flow  $dH/dt$ , which 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  $\Delta \ln dH/dt / \Delta \ln(\Delta H_T - H)$  against  $\Delta(1/T) / \ln(\Delta H_T - H)$ , we obtained the value of  $E/R$ , which is the slope of the straight line; the reaction order  $n$  is the intercept of this curve with the Y-axis.

Figure 1 shows the variation of the heat of curing with the percent of acid content; apart from SAAS<sub>1</sub>/DGEBA, the systems show an elevated heat of curing, leading to good reactivity, which is indicated by the decreasing of the activation energy. The lower reactivity of the SAAS<sub>1</sub>/DGEBA system is explained by its weak acid content.

Tables III–VI give the extent of cure, uncured, and partially cured epoxy resin SAAS systems calculated by the residual heat method for two curing temperatures. Increasing the curing temperature causes a

lower residual heat of reaction ( $\Delta H_R$ ) and a higher conversion degree  $\alpha$ , for a given curing time. Table VII–X indicate the values of the activation energy and the reaction order for different periods of curing time.

Figure 2 illustrates the variation of the extent of cure  $\alpha$ , against time for the system (SAAS<sub>3</sub>/DGEBA) at two different curing temperatures. At the highest temperature (100°C), the extent of cure  $\alpha$  increased rapidly, showing a linear relationship at the beginning of the reaction, and then leveled. At the lower curing temperature (85°C), the trend of variation was similar, but the conversion rate became slower. This phenomenon suggests that the crosslinked spatial structure formed interferes with further reactions according to the mechanism of hardening of epoxy resins with carboxylic polymers.<sup>14</sup> These are interactions between hydroxyl groups formed during the crosslinking reaction, which 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 FTIR deduced that the main reaction of curing is a polyad-

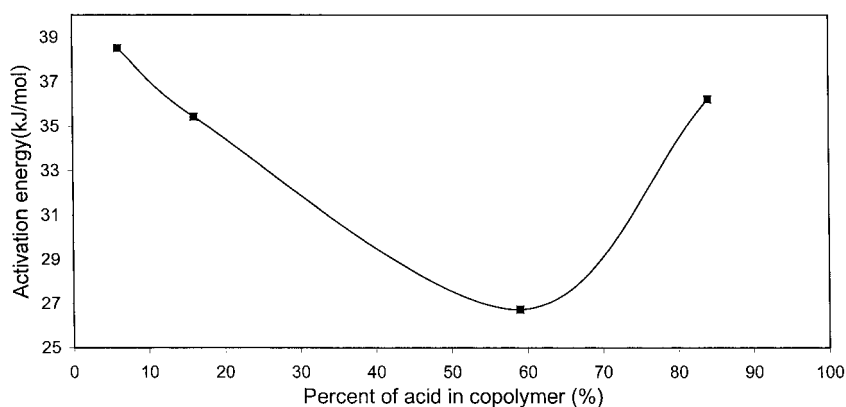


Figure 3 Activation energy versus the percent of acid in the copolymers.

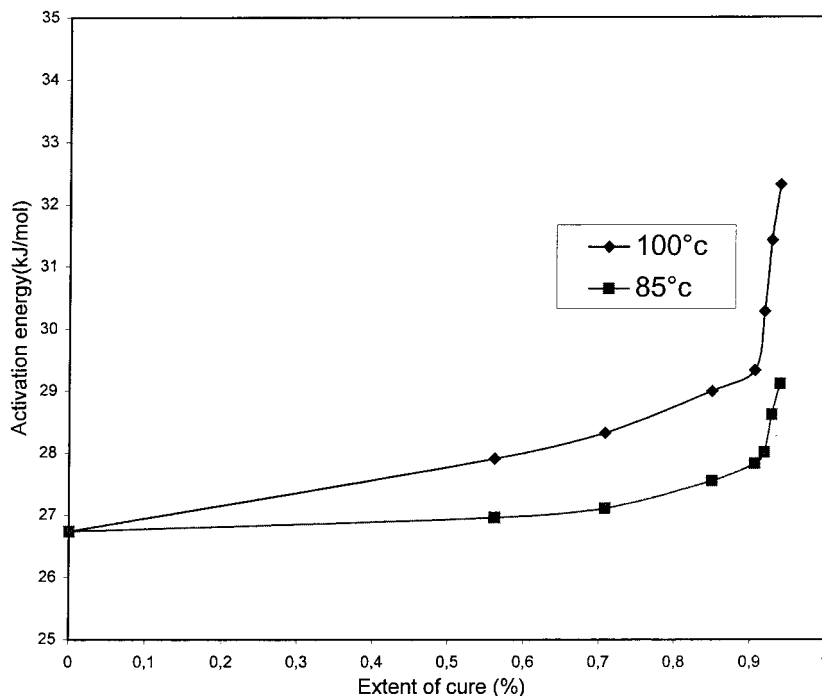


Figure 4 Activation energy versus extent of cure of SAAS3/DGEBA system.

dition esterification reaction followed by an etherification reaction.

Figure 3 gives the variation of the activation energy with the percent of the acid content. The activation energy decreases with the percent of acid content in the copolymer to 60%. The low value of the activation energy indicates a high reactivity. The important presence of styrene segments in the SAAS<sub>1</sub> copolymer generates steric hindrance of acid groups that are trapped. This helps to reduce their reactivity. A higher

activation energy is necessary to relax polymer chains, leading to their reacting.

Additionally, the activation energy tends to increase from a certain acid content (SAAS<sub>4</sub>) due to the presence of inter- and intramolecular hydrogen bonds which reduce the crosslinking reaction. The reaction (acid-epoxy) starts after the rupture of these bonds under a temperature effect.

Figure 4 shows the variation of activation energy with the extent of cure  $\alpha$  (SAAS<sub>3</sub>/DGEBA system), for

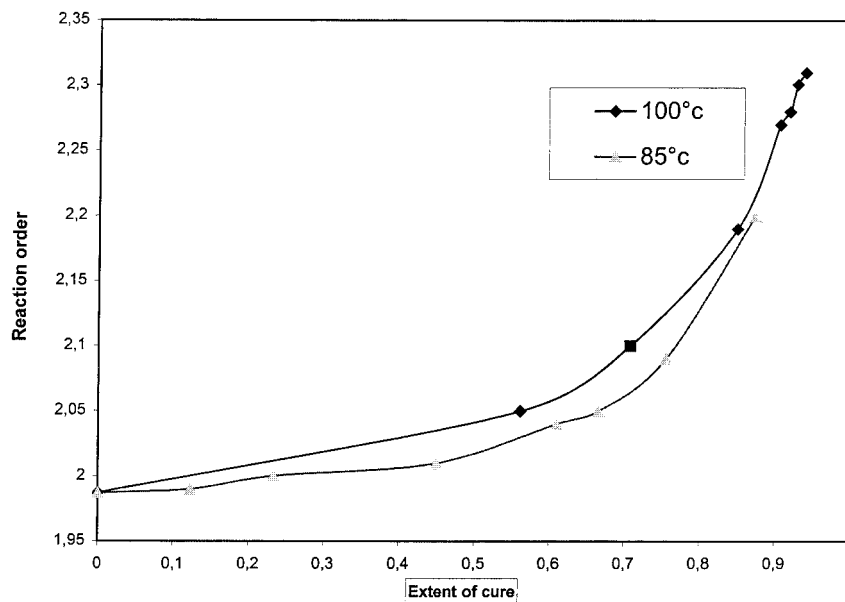


Figure 5 Reaction order versus extent of cure of SAAS3/DGEBA system.

the two curing temperatures (100 and 85°C). We observe 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. During a crosslinking reaction, the first step of the reaction is controlled by successive chemical reactions which give rise to links. With the extent of cure, the system becomes hard; thereafter, the reaction is controlled by the diffusion effect of functional groups through the crosslinked spatial structure formed. At the lower curing temperature,  $E$  is lower. This is likely because, at a lower temperature of cure, the system presents a better regularity of the reactive chemical groups which require a lower activation energy to react than in material cured at higher temperature.

Similar behavior was observed for the reaction order  $n$ , which is illustrated by Figure 5 (SAAS<sub>3</sub>/DGEBA system at 100 and 85°C). The reaction order  $n$  increases with the extent of cure, while the change becomes slower for lower temperature. These results show that the kinetics of the residual curing changes 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 temperature.

### CONCLUSIONS

The cure kinetics of high molecular weight SAAS at different contents of styrene used as a hardener for a

commercial epoxy resin (DGEBA) were studied by the DSC technique. The state of cure was assessed as the residual heat of reaction and was varied by controlling both the time and temperature of the cure. The degree of crosslinking increases while the residual heat of reaction decreases with the time and temperature. Additionally, the activation energy and order of the reaction calculated by the Freeman–Carroll relation increases with the extent of cure of the partially cured epoxy resin.

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