

# The Effect of Bismaleimide Resin on Curing Kinetics of Epoxy–Amine Thermosets

R. CHANDRA,\* L. RAJABI, and R. K. SONI

Department of Polymer Technology and Applied Chemistry, Delhi College of Engineering, Kashmere Gate, Delhi-110006, India

## SYNOPSIS

An analysis of the cure kinetics of several formulations composed of diglycidyl ether of bisphenol-A (DGEBA) and aromatic diamines, methylenedianiline (MDA) and diaminodiphenyl sulfone (DDS), in the absence and presence of 4,4'-bismaleimidodiphenylmethane (BM) was performed. The dynamic differential scanning calorimetry (DSC) thermograms were analyzed with the help of ASTM kinetic software to determine the kinetic parameters of the curing reactions, including the activation energy, preexponential factor, rate constant, and 60 min  $\frac{1}{2}$  life temperature. The effects of substitution of one curing agent for another, their concentration, and the absence and presence of BM resin and its concentration on curing behavior, enthalpy, and kinetic parameters are discussed. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Epoxy resins are widely used as adhesives and as the matrix material for high-performance composites in the aerospace industry. Linear epoxy resins are converted into three-dimensional crosslinked thermoset networks during cure. Various chemical reactions that take place during cure determine the resin morphology, which, in turn, determines the properties of the cured formulation. An understanding of the mechanism and rate (kinetics) of cure is needed to establish processing–morphology–property relationships in thermosets and their composites. An excellent review of the kinetics of cure of thermosetting resins was written by Prime.<sup>1</sup> Various other studies, using different experimental techniques, report efforts to evaluate the rate and mechanism of cure. The cure kinetics have been described by both *n*th order<sup>1–6</sup> and autocatalytic mechanisms.<sup>7–11</sup>

Differential scanning calorimetry (DSC) has been the most commonly used experimental technique for curing studies. The objective of this work was to

study the kinetic parameters obtained from dynamic curing of DGEBA-based thermosets, using different amine curing agents in various concentrations and the effect of the addition of different amounts of bismaleimide resin to the 1 : 1 stoichiometry DGEBA : amine resin systems on the same parameters.

## EXPERIMENTAL

The formulations used in this study are given in Table I. The epoxy resin, diglycidyl ether of bisphenol-A (DGEBA [LY-556]), 4,4'-methylenedianiline (MDA [HT 972]), and 4,4'-diaminodiphenyl sulfone (DDS [HT 976]) were obtained courtesy of Hindustan Ciba Geigy Ltd. and used as such.

### Synthesis and Characterization of BM Resin

4,4'-Bismaleimidodiphenylmethane (BM) was synthesized by the reaction of MDA with maleic anhydride.<sup>12</sup> 4,4'-MDA, 0.5 mol, was dissolved in ( $\cong$  1200 mL) dry acetone in a 2 L reaction kettle equipped with a mechanical stirrer, a nitrogen inlet tube, a condenser, and a solid transfer tube. Maleic

\* To whom correspondence should be addressed.

anhydride (1.10 mol) was added with constant stirring in several portions over a period of 40 min. The solution was refluxed for 3 h in a nitrogen atmosphere. Cyclization of the amic acid intermediate was carried out by treating with fused sodium acetate (65 g)/acetic anhydride (300 mL) mixture and refluxing the solution for another 2–3 h. The solution was then poured into cold water. The precipitates were collected by filtration, repeatedly washed with water, and dried at 70–80°C in an air oven. The product was dissolved in chloroform, passed through a silica gel column, and eluted with chloroform. The solution was concentrated on a rotary evaporator under vacuum, when crystals of bismaleimide (4,4'-bismaleimidodiphenylmethane) separated out. The yield of the product was 70–75%. The melting point of the bismaleimide monomer was 156–158°C, obtained by DSC. The IR spectrum of the bismaleimide was reported in KBr pellets using a Perkin-Elmer infrared spectrophotometer, and the characteristic bands due to imide group (at 1720 cm<sup>-1</sup>), phenyl group (at 1600 and 1490 cm<sup>-1</sup>), and C—N (at 1390 cm<sup>-1</sup>) were observed.

### Cure Kinetics Using Differential Scanning Calorimeter (DSC)

DSC experiments were carried out using DuPont 9900 thermal analyzer, having a 910 DSC module. The curing kinetics of the formulations/resin systems was studied by the ASTM-E-698 kinetic method which is based on the following rate equation:

$$\frac{dC}{dt} = f(C) \left[ Z \exp\left(\frac{-E}{RT}\right) \right]$$

where  $C$  = the fraction reacted,  $t$  = time,  $f(C)$  = any function of  $C$  not involving temperature,  $Z$  = the frequency or preexponential factor (L/min),  $E$  = the activation energy (J/mol),  $R$  = the gas constant (8.314 J/mol K), and  $T$  = temperature.

The blends were prepared by heating the epoxy resin (DGEbPA) to 60°C and adding the other component/components with continuous stirring until a homogeneous/clear solution was obtained (< 5 min). Each freshly prepared sample was poured

**Table I** The Resin Systems Studied by Differential Scanning Calorimetry (DSC)

Sample No.	Resin System <sup>a</sup>	Curing Agent Concn (phr) <sup>b</sup>	Bismaleimide (BM) Concn (Wt %) <sup>c</sup>
1	DGEbPA : MDA	15.38	—
2	DGEbPA : MDA	20.00	—
3	DGEbPA : MDA	30.43	—
4	DGEbPA : MDA	36.34	—
5	DGEbPA : MDA	42.85	—
6	DGEbPA : MDA : BM	30.43	5
7	DGEbPA : MDA : BM		10
8	DGEbPA : MDA : BM		15
9	DGEbPA : MDA : BM		20
10	DGEbPA : MDA : BM		25
11	DGEbPA : DDS	25.00	—
12	DGEbPA : DDS	30.43	—
13	DGEbPA : DDS	36.34	—
14	DGEbPA : DDS	42.85	—
15	DGEbPA : DDS	50.00	—
16	DGEbPA : DDS : BM	36.34	5
17	DGEbPA : DDS : BM		10
18	DGEbPA : DDS : BM		15
19	DGEbPA : DDS : BM		20
20	DGEbPA : DDS : BM		25

<sup>a</sup> DGEbPA (diglycidyl ether of bisphenol-A); MDS (*p,p'*-methylenedianiline), curing agent; DDS (*p,p'*-diaminodiphenyl sulfone), curing agent; BM (4,4'-bismaleimidodiphenylmethane).

<sup>b</sup> Parts per hundred parts of resin (DGEbPA).

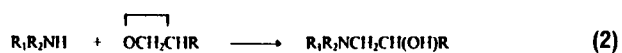
<sup>c</sup> % by wt of the DGEbPA : curing agent system.

in an open aluminum pan, weighed very accurately (ranging from 3–10 mg), and placed inside the DSC cell/oven. Samples aged even a few hours at room temperature gave unreliable results due to the onset of a slow curing reaction. The thermograms of the samples were recorded at three different heating rates, 5, 10, and 15°C/min, in static air. The thermograms were analyzed using a sigmoidal base line. The heat of reaction of each sample specimen was measured against that of the empty reference pan, placed adjacent to it in the heating chamber/cell. The sample temperature was obtained from a thermocouple, which was calibrated for the melting point of indium. The exothermic transition associated with curing reaction could be characterized by defining the following temperatures:  $T_1$ , the onset temperature of curing, was obtained by extrapolating the steepest portion of the front side of the exothermic transition to the base line according to the program of the instrument;  $T_2$ , the temperature for completion of reaction; and  $T_{\text{exo}}$ , the exothermic peak temperature.

## RESULTS AND DISCUSSION

In DSC thermograms of all the formulations of Table I, exothermic transition associated with curing

is observed and, consequently, the reaction rate, being proportional to the rate of heat generation, also passes through a maximum and then decreases (that of 1 : 1 DGEBA : MDA is shown as an example in Fig. 1). Such behavior is characteristic of chemical reactions in which products act as catalysts for the reaction and are referred to as the autocatalytic reactions. These are (in case of epoxide-amine formulations) reactions between the epoxy ring and a primary amine for chain lengthening and a secondary amine for chain branching as shown in Scheme 1, generating some hydroxyl groups which accelerate the rate of the reaction:



However, in the case of DGEBA : MDA/BM and DGEBA : DDS/BM formulations, besides the usual epoxide-amine reactions [reactions (1) and (2)] and reaction (3) (as the case may be) of Scheme 1, the prepolymers/adducts obtained from the Michael-addition reaction<sup>13</sup> of BM/MDA and BM/DDS (Scheme 2) also contribute in the curing of DGEBA. The maleimide double bonds in these

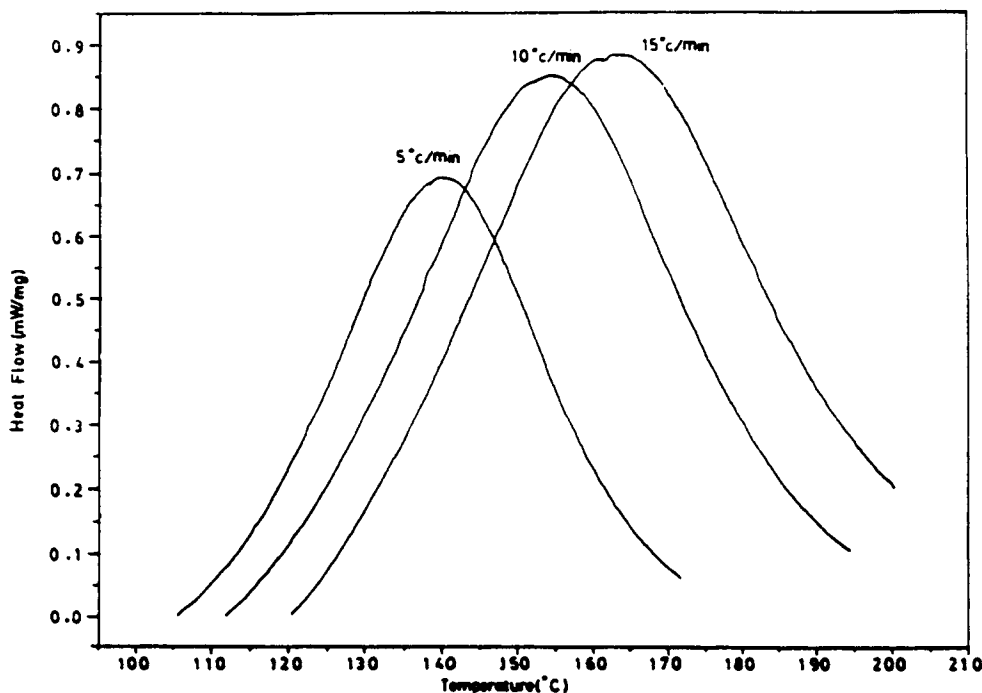
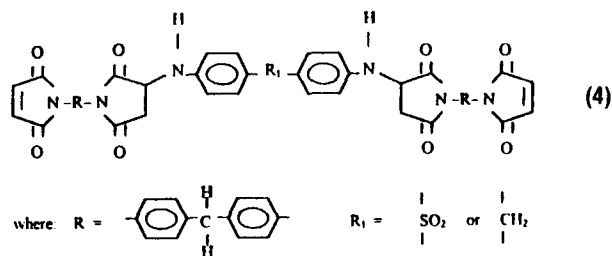


Figure 1 Differential scanning calorimetry of DGEBA : MDA (30.43 phr) system at various heating rates.



Scheme 2

prepolymers/adducts are very electron deficient due to the two adjacent electron-withdrawing carbonyl groups of the maleimide moieties and, thus, are the reactive sites in the thermal polymerization reaction with DGEBA, without the need for a catalyst, involving a free-radical mechanism.<sup>13</sup>

The nearly symmetrical curves recorded for all DSC thermograms suggest that the reactions follow the first-order kinetic which is further supported by the Ozawa plot (Fig. 2) and, hence, the kinetic studies can be made by the ASTM method. The autocatalyzed epoxy is further characterized by maximum heat evolution between 35–50% conversion, depending on the concentration of amine curing agents (in amine-cured systems) and BM resin (in BM-containing resin systems). The exothermic curves of all the formulations of Table I obtained from dynamic DSC experiments were analyzed, using ASTM-E-698 kinetic software with a sigmoidal

horizontal base line, for the calculation of heat of polymerization ( $\Delta H$ ). In all the systems (Table I), the peak exotherm temperature ( $T_{\text{exo}}$ ) varies in a predictable manner with the heating rate. As the concentration of amine curing agent increases in the DGEBA : MDA and DGEBA : DDS systems, the exotherm peak temperature decreases (Tables II and III, respectively), as at higher concentrations of hardners, the availability of primary amine to react with the epoxide in the initial stages of cure is more as a result of which  $T_{\text{exo}}$  is shifted to a lower value; however, the total heat of polymerization ( $\Delta H$ ) increases with increasing the concentration of either of the curing agents, which is due to occurrence of more crosslinking taking place as the amount of hardner increases, although for the formulation 5 of Table I, a slight increase of  $T_{\text{exo}}$  and a decrease of  $\Delta H$  with respect to previous stoichiometry is observed, suggesting larger hydroxyl contributions and less of the epoxide group available to react<sup>14</sup> (Table II).

The BM-containing resin systems include DGEBA : MDA (1 : 1 stoichiometry)/BM and DGEBA : DDS (1 : 1 stoichiometry)/BM, containing five different concentrations (5–25 wt %) of BM each. Addition of varying concentrations of BM to either of these systems does not make any significant change in  $T_{\text{exo}}$ . On increasing the amount of BM (5–25 wt %),  $\Delta H$  decreases in both MDA/BM- and DDS/BM-containing formulations (Tables VI and VII), which may be due to the number

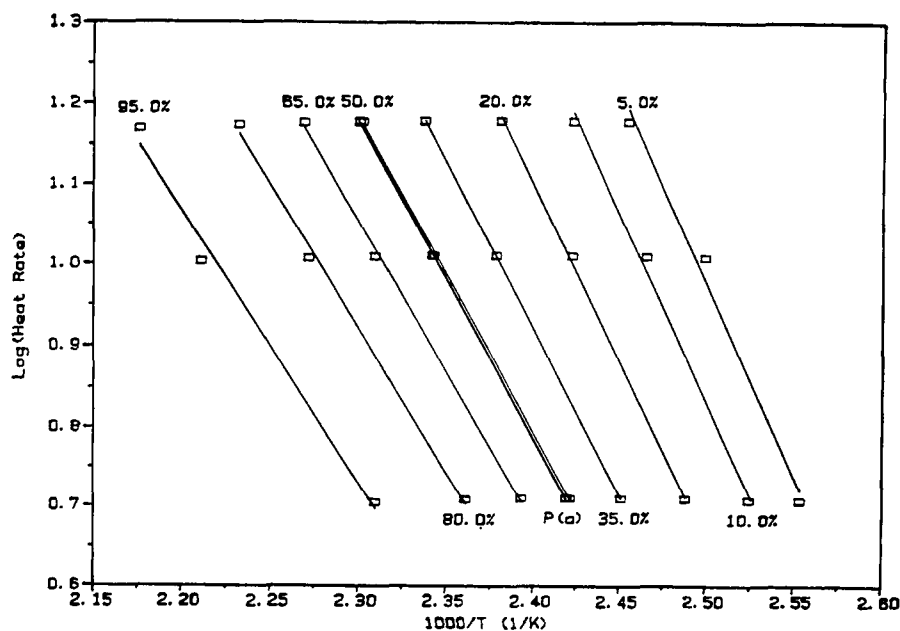


Figure 2 Arrhenius plot of  $\log(\phi)$  vs.  $1/T_{\text{exo}}$  for DGEBA : MDA (30.43 phr) system.

**Table II Kinetic Parameters ( $T_{\text{exo}}$ ,  $\Delta H$ ,  $E_a$ ,  $Z$ , and 60 Min  $\frac{1}{2}$  Life Temperature) from DSC Dynamic Cure Analysis of DGEBA : MDA Systems**

Sample No.	Curing Agent (MDA) Concn (phr)	Heating Rate ( $\phi$ ) ( $^{\circ}\text{C}/\text{min}$ )	$T$ ( $^{\circ}\text{C}$ )	$T_{\text{exo}}$ ( $^{\circ}\text{C}$ )	$T_2$ ( $^{\circ}\text{C}$ )	Heat of Reaction ( $\Delta H$ ) (J/g)	Activation Energy ( $E_a$ ) (kJ/mol)	Log ( $Z$ ) (L/min)	60 Min $\frac{1}{2}$ Life Temp. ( $^{\circ}\text{C}$ )
1	15.38	5	118	152	189	144.2	47.1	4.93	85
		10	137	173	213	101.5			
		15	149	183	224	105.5			
2	20.00	5	112	148	188	184.1	47.4	5.06	81
		10	126	168	221	171.1			
		15	134	179	237	157.7			
3	30.43	5	105	140	172	247.1	68.2	8.01	85
		10	112	154	195	192.7			
		15	120	163	201	133.0			
4	36.34	5	92	133	166	263.1	62.1	7.32	77
		10	97	149	192	234.3			
		15	100	155	205	218.8			
5	42.85	5	98	134	164	229.7	50.9	5.80	70
		10	114	152	187	220.3			
		15	121	162	201	218.6			

of reactions (mentioned earlier) taking place, resulting in the full consumption of epoxide and, therefore, its low availability to react. The DGEBA : MDA/BM systems with 5–15 wt % BM content

show much higher values of  $\Delta H$  (i.e., 266.6, 241.6, and 222.2 J/g, respectively) than that (190.9 J/g) of the resin system without any BM content, suggesting more crosslinking reactions taking place in

**Table III Kinetic Parameters ( $T_{\text{exo}}$ ,  $\Delta H$ ,  $E_a$ ,  $Z$ , and 60 Min  $\frac{1}{2}$  Life Temperature) from DSC Dynamic Cure Analysis of DGEBA : DDS Systems**

Sample No.	Curing Agent (DDS) Concn (phr)	Heating Rate ( $\phi$ ) ( $^{\circ}\text{C}/\text{min}$ )	$T$ ( $^{\circ}\text{C}$ )	$T_{\text{exo}}$ ( $^{\circ}\text{C}$ )	$T_2$ ( $^{\circ}\text{C}$ )	Heat of Reaction ( $\Delta H$ ) (J/g)	Activation Energy ( $E_a$ ) (kJ/mol)	Log ( $Z$ ) (L/min)	60 Min $\frac{1}{2}$ Life Temp. ( $^{\circ}\text{C}$ )
1	25.00	5	168	212	273	122.6	64.9	6.17	145
		10	198	231	285	73.6			
		15	198	243	303	89.4			
2	30.43	5	161	206	245	80.1	62.6	6.10	134
		10	182	225	268	84.1			
		15	186	237	285	107.6			
3	36.34	5	175	205	267	142.5	72.2	7.12	143
		10	186	223	283	133.0			
		15	193	234	297	145.2			
4	42.85	5	153	201	246	183.8	64.9	6.41	133
		10	170	219	268	175.8			
		15	175	230	279	158.4			
5	50.00	5	158	197	234	160.5	62.5	6.17	130
		10	165	218	265	204.6			
		15	181	228	273	216.6			

**Table IV Kinetic Parameters ( $E_a$ ,  $Z$ , and 60 Min  $\frac{1}{2}$  Life Temperature), at Different Conversion Levels from DSC Dynamic Cure Analysis of DGEBA : MDA Systems**

% Conversion	MDA (phr)						60 Min $\frac{1}{2}$ Life Temperature ( $^{\circ}$ C)								
	15.38	20.00	30.43	36.34	42.85	15.38	20.00	30.43	36.34	42.85	15.38	20.00	30.43	36.34	42.85
	Activation Energy ( $E_a$ ) (kJ/mol)						Log ( $Z$ ) (L/min)								
5	46.6	52.4	78.6	106.5	52.1	3.96	4.89	8.77	12.95	5.15	137	127	111	101	111
10	48.1	50.8	78.0	94.9	51.5	4.43	4.90	8.85	11.43	5.28	122	115	105	98	100
20	49.3	47.6	75.7	82.9	50.6	4.81	4.69	8.69	9.87	5.38	108	103	99	93	89
35	50.2	46.1	72.2	73.1	49.6	5.10	4.66	8.35	8.63	5.42	99	92	94	88	79
50	50.8	45.1	69.2	66.6	48.8	5.30	4.64	8.02	7.83	5.43	94	85	90	83	73
65	51.2	43.9	66.5	61.6	48.0	5.44	4.58	7.73	7.23	5.43	90	79	86	78	68
80	51.7	42.5	64.4	56.8	47.1	5.58	4.49	7.51	6.66	5.40	86	73	83	72	62
95	52.2	41.0	63.0	50.8	45.4	5.75	4.40	7.39	5.97	5.31	82	65	79	63	54

**Table V Kinetic Parameters ( $E_a$ ,  $Z$ , and 60 Min  $\frac{1}{2}$  Life Temperature) at Different Conversion Levels from DSC Dynamic Cure Analysis of DGEBA : DDS Systems**

% Conversion	DDS (phr)						60 Min $\frac{1}{2}$ Life Temperature ( $^{\circ}$ C)								
	25.00	30.43	36.34	42.85	50.00	25.00	30.43	36.34	42.85	50.00	25.00	30.43	36.34	42.85	50.00
	Activation Energy, ( $E_a$ ) (kJ/mol)						Log ( $Z$ ) (L/min)								
5	65.1	65.4	93.2	73.6	60.9	5.37	5.65	8.72	6.75	5.23	192	177	184	170	171
10	68.7	63.5	88.9	71.7	61.8	5.99	5.64	8.42	6.70	5.55	179	165	175	160	158
20	72.1	61.5	84.5	69.9	62.7	6.57	5.61	8.09	6.67	5.85	169	153	167	151	147
35	74.3	59.9	81.6	68.5	63.3	6.95	5.59	7.90	6.64	6.08	163	143	160	144	140
50	74.7	59.4	80.9	67.8	63.7	7.08	5.64	7.89	6.64	6.21	159	137	157	140	135
65	76.0	58.7	82.1	67.4	63.8	7.27	5.64	8.04	6.66	6.30	158	132	156	137	131
80	77.8	57.9	83.9	67.5	63.7	7.48	5.62	8.24	6.72	6.35	158	127	158	134	128
95	76.5	56.8	83.1	69.3	63.3	7.36	5.61	8.12	6.96	6.39	157	121	158	134	124

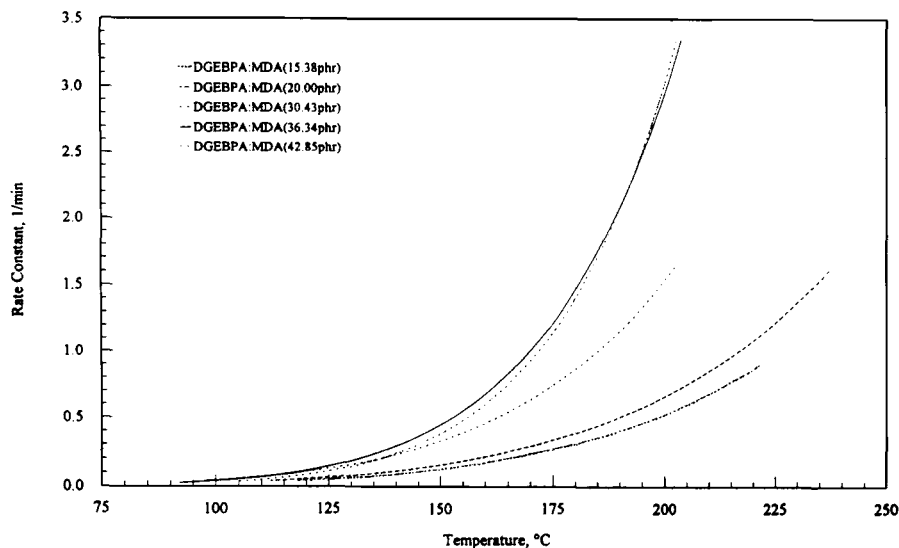


Figure 3 Comparative DSC heating profiles of rate constant of DGEBA : MDA systems.

these systems as a result of the addition of BM, whereas in DGEBA : DDS/BM formulations, only the one with 5 wt % BM content shows a higher value of  $\Delta H$  (150 J/g) than that (140.2 J/g) of the resin system without any BM content.

Kinetic parameters were obtained from dynamic experiments, based on the variation of the exotherm peak temperature ( $T_{\text{exo}}$ ), with respect to the heating rate ( $\phi$ ). Thus, from the set of dynamic profiles obtained at different heating rates (5, 10, and 15°C/min), the activation energy ( $E_a$ ) was obtained from the slope of the linear fit of  $\log(\phi)$  vs.  $1/T_{\text{exo}}$ . The straight curves of the Arrhenius plots (the Arrhenius plot of formulation 3 of Table I is shown as an ex-

ample in Fig. 2), of all the formulations of Table I, represented the best fit of the data to the autocatalytic mechanism and made it easy to compare the slope of the lines at different conversion levels. The linearity of these curves suggest that these curves obey the Arrhenius rate law and the autocatalytic kinetic first-order reactions compare well with the experimentally obtained results. Tables II and III represent the kinetic parameters obtained at the exotherm peak temperature for DGEBA : MDA and DGEBA : DDS resin systems, respectively. As the concentration of MDA increases (15.38–30.43 phr), activation energy ( $E_a$ ) increases. The low values of activation energy in the first two formulations

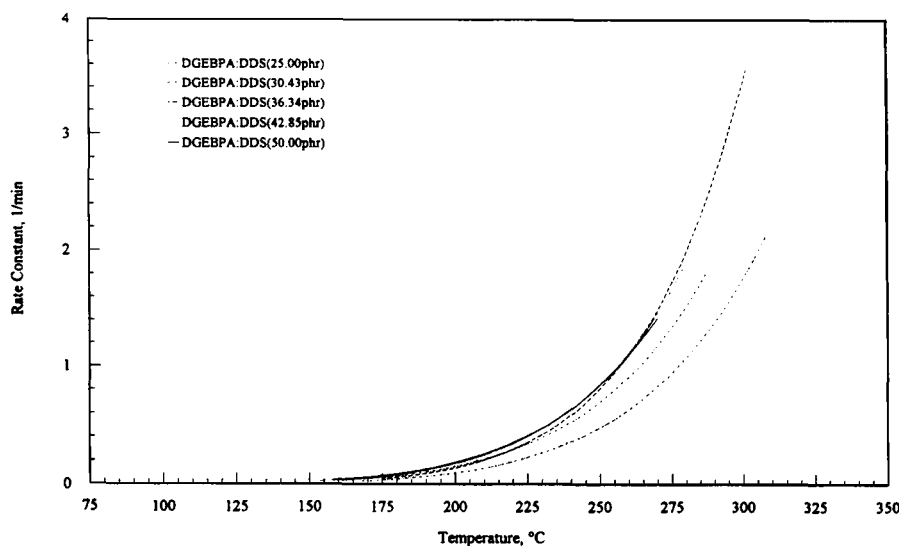


Figure 4 Comparative DSC heating profiles of rate constant of DGEBA : DDS systems.

**Table VI Kinetic Parameters ( $T_{\text{exo}}$ ,  $\Delta H$ ,  $E_a$ ,  $Z$ , and 60 Min  $\frac{1}{2}$  Life Temperature) from DSC Dynamic Cure Analysis of DGEBA : MDA (30.43 phr)/BM Systems Containing Various Concentrations of Bismaleimide (BM)**

Sample No.	Bismaleimide (BM) Conc'n (Wt %)	Heating Rate ( $\phi$ ) ( $^{\circ}\text{C}/\text{min}$ )	$T$ ( $^{\circ}\text{C}$ )	$T_{\text{exo}}$ ( $^{\circ}\text{C}$ )	$T_2$ ( $^{\circ}\text{C}$ )	Heat of Reaction ( $\Delta H$ ) (J/g)	Activation Energy ( $E_a$ ) (kJ/mol)	Log ( $Z$ ) (L/min)	60 Min $\frac{1}{2}$ Life Temp ( $^{\circ}\text{C}$ )
1	5	5	96	140	180	330.2	57.2	6.55	79
		10	106	157	203	240.4			
		15	112	165	215	229.3			
2	10	5	78	138	179	292.2	52.5	5.96	74
		10	99	156	203	213.0			
		15	110	165	218	219.5			
3	15	5	71	139	179	239.2	55.8	6.47	74
		10	88	151	201	203.4			
		15	99	165	215	224.1			
4	20	5	74	136	199	185.0	43.4	4.76	65
		10	91	153	215	199.7			
		15	104	167	237	156.8			
5	25	65	88	138	195	178.0	61.0	7.03	82
		10	92	153	218	193.8			
		15	100	158	231	160.7			

containing lower amounts of MDA than that of 1 : 1 stoichiometry may be due to the low availability of primary and, as a result, secondary amine to react with excess epoxide. On further increasing the con-

centration of MDA from 36.34 to 42.85 phr, the value of the activation energy decreases, probably due to the higher hydroxyl concentration and lower availability of the epoxide group to react. Table III shows

**Table VII Kinetic Parameters ( $T_{\text{exo}}$ ,  $\Delta H$ ,  $E_a$ ,  $Z$ , and 60 Min  $\frac{1}{2}$  Life Temperature) from DSC Dynamic Cure Analysis of DGEBA : DDS (36.34 phr)/BM Containing Various Concentrations of Bismaleimide (BM)**

Sample No.	Bismaleimide (BM) Conc'n (Wt %)	Heating Rate ( $\phi$ ) ( $^{\circ}\text{C}/\text{min}$ )	$T$ ( $^{\circ}\text{C}$ )	$T_{\text{exo}}$ ( $^{\circ}\text{C}$ )	$T_2$ ( $^{\circ}\text{C}$ )	Heat of Reaction ( $\Delta H$ ) (J/g)	Activation Energy ( $E_a$ ) (kJ/mol)	Log ( $Z$ ) (L/min)	60 Min $\frac{1}{2}$ Life Temp ( $^{\circ}\text{C}$ )
1	5	5	150	205	249	204.6	55.1	5.24	127
		10	166	224	271	135.4			
		15	184	237	285	110.0			
2	10	5	164	207	250	125.4	67.3	6.61	138
		10	174	225	270	137.9			
		15	181	237	285	138.1			
3	15	5	161	208	248	109.2	69.8	6.90	140
		10	175	226	264	91.4			
		15	185	237	275	79.1			
4	20	5	165	212	264	103.0	76.1	7.46	150
		10	187	229	278	77.9			
		15	195	241	285	74.6			
5	25	5	165	210	245	69.4	67.8	6.64	140
		10	182	229	263	62.2			
		15	190	240	275	59.4			



**Table VIII Kinetic Parameters ( $E_a$ ,  $Z$ , and 60 Min  $\frac{1}{2}$  Life Temperature) at Different Conversion Levels from DSC Dynamic Cure Analysis of DGEBA : MDA (30.43 phr)/BM Systems Containing Various Concentrations of Bismaleimide (BM)**

% Conversion	BM (Wt %)										60 Min $\frac{1}{2}$ Life Temperature ( $^{\circ}$ C)				
	Log ( $Z$ ) (L/min)														
	5	10	15	20	25	5	10	15	20	25					
	Activation Energy ( $E_a$ ) (kJ/mol)														
5	69.4	40.2	41.1	39.7	73.0	7.60	3.65	3.90	3.58	8.25	107	103	95	103	101
10	67.1	43.0	43.1	41.0	69.9	7.45	4.24	4.36	3.95	7.93	101	91	85	91	97
20	64.0	46.3	45.6	42.0	66.5	7.16	4.86	4.85	4.25	7.55	94	83	78	81	93
35	60.7	48.6	47.5	42.0	64.1	6.83	5.29	5.21	4.38	7.27	88	78	74	74	90
50	58.3	49.2	48.3	41.6	61.6	6.60	5.45	5.39	4.40	6.98	84	75	71	70	88
65	56.3	48.9	48.4	41.3	59.8	6.40	5.48	5.46	4.42	6.76	80	72	69	66	86
80	54.5	48.0	48.3	41.5	58.9	6.22	5.41	5.49	4.49	6.63	76	68	66	64	86
95	53.1	46.8	48.4	44.1	59.2	6.10	5.33	5.56	4.84	6.64	72	63	64	67	88

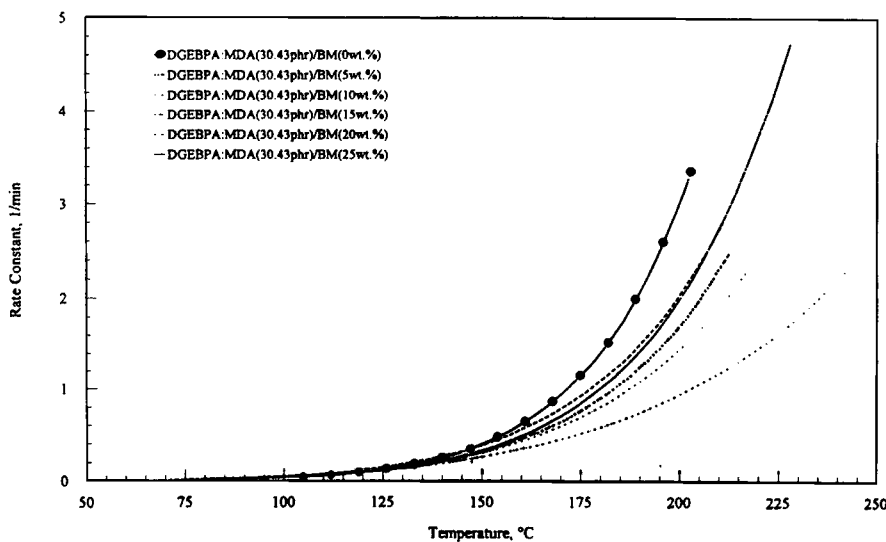
**Table IX Kinetic Parameters ( $E_a$ ,  $Z$ , and 60 Min  $\frac{1}{2}$  Life Temperature) at Different Conversion Levels from DSC Dynamic Cure Analysis of DGEBA : DDS (36.34 phr)/BM Systems Containing Various Concentrations of Bismaleimide (BM)**

% Conversion	BM (Wt %)										60 Min $\frac{1}{2}$ Life Temperature ( $^{\circ}$ C)				
	Log ( $Z$ ) (L/min)														
	5	10	15	20	25	5	10	15	20	25					
	Activation Energy ( $E_a$ ) (kJ/mole)														
5	44.8	83.0	68.3	67.3	72.8	3.26	7.76	6.04	5.72	6.50	177	174	174	186	178
10	47.3	78.1	68.5	72.3	72.0	3.79	7.37	6.26	6.51	6.62	158	165	163	174	166
20	50.4	73.8	69.0	77.5	71.9	4.36	7.04	6.50	7.29	6.79	145	157	154	166	157
35	53.0	70.7	69.6	81.3	72.2	4.82	6.81	6.70	7.84	6.97	136	149	148	161	150
50	54.7	69.3	70.4	84.5	72.7	5.12	6.73	6.87	8.26	7.10	132	144	144	160	147
65	56.1	68.6	71.4	88.8	73.2	5.35	6.71	7.05	8.76	7.24	129	141	142	160	144
80	57.4	68.4	73.2	96.1	74.4	5.57	6.75	7.30	9.56	7.42	126	138	141	164	142
95	59.7	68.6	78.7	112.4	77.2	5.90	6.83	7.96	11.21	7.79	125	136	143	173	141

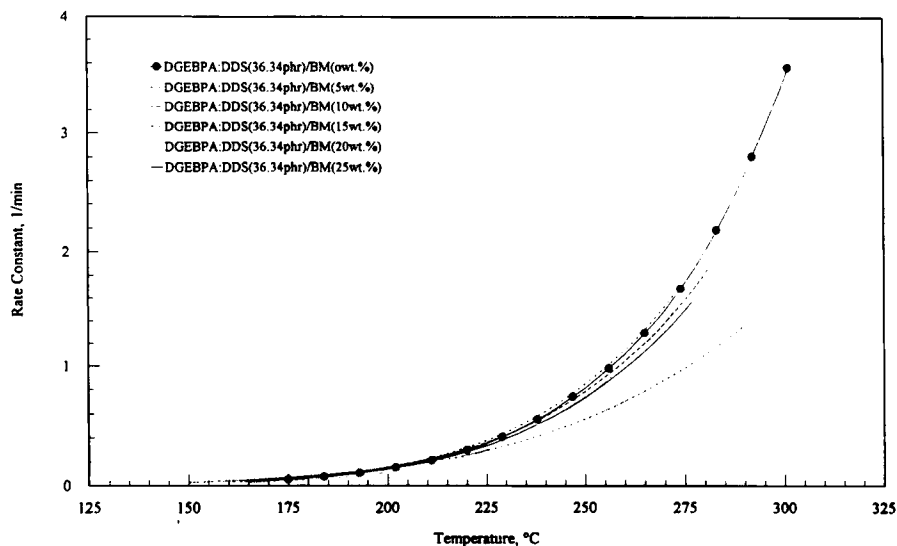
the highest activation energy (72.2 kJ/mol) for the 1 : 1 DGEBA : DDS formulation due to almost complete consumption of epoxides and the respective amines, whereas the first two systems show lower values of activation energy, not only due to less availability of amines (primary and secondary) to react with excess epoxide but also to the probable occurrence of etherification [reaction (3)],<sup>15-17</sup> as usually happens in case of DGEBA : DDS systems with lower concentrations of DDS. Tables IV and V present the variation of kinetic parameters at different conversion levels for MDA- and DDS-cured systems, respectively. Figures 3 and 4 are the comparative plots of rate constant vs. temperature of the five MDA- and DDS-cured systems, respectively. A rapid increase in the rate of amine and epoxide consumption can be induced by the catalytic effect of the hydroxyl groups generated. In both cases, the 1 : 1 stoichiometry formulations (resin systems 3 and 13 of Table I) show the highest rate constant among the amine-cured formulations studied.

The activation energy ( $E_a$ ) at the exothermic peak temperature decreases in DGEBA : MDA/BM formulations as the concentration of BM increases (5–20 wt %) (Table VI), which is also considerably lower than that (68.2 kJ/mol) of the system without any BM content since the formation and chances of the prepolymers formed (Scheme 2), having very active hydrogens of the double bonds in their maleimide moieties to contribute more in curing reactions, exist and probably dominate the

reaction of the secondary amines with DGEBA (secondary amines being formed from the reaction of some primary amines with DGEBA). However, the 25 wt % BM-containing system shows an increase in activation energy probably due to the number of reactions involved during crosslinking as it proceeds, although it is still lower (61 kJ/mol) than that (68.2 kJ/mol) of the reference system. In the case of DGEBA : DDS/BM systems, the overall activation energy ( $E_a$ ) at the peak exotherm temperature increases with increasing the concentration of BM (5–15 wt %), which could be due to the complexity and number of reactions possible with more BM present in the systems, although the activation energy of these systems is still lower than that (72.2 kJ/mol) of the reference system without any BM content, which may be due to the possibility of other reactions such as the epoxide–BM and epoxide–BM/DDS prepolymer taking place besides the epoxide–secondary amine reaction which is slow and needs higher temperatures (>150°C) to proceed. The 20 wt % BM content system shows the highest (76.1 kJ/mol) activation energy among the five DDS : BM-cured formulations, which is also higher than that (72.2 kJ/mol) of the reference system. The variation of kinetic parameters at different % conversions for the MDA/BM- and DDS/BM-cured formulations are given in Tables VIII and IX, respectively. The comparative plots of rate constant vs. temperature of the above-mentioned systems are shown in Figures 5 and 6, respectively.



**Figure 5** Comparative DSC heating profiles of rate constant of DGEBA : MDA/BM systems.



**Figure 6** Comparative DSC heating profiles of rate constant of DGEBA : DDS/BM systems.

## CONCLUSIONS

The curing kinetics of the BM-containing resin systems studied follow the autocatalytic kinetic first-order reactions. Addition of bismaleimide resin to the epoxy-amine formulations has certain effects on the kinetics of curing due to the possible additional reactions (the complexity of reactions) that could take place as a result of the presence of BM.

## REFERENCES

1. R. B. Prime, *Thermal Characteristics of Polymeric Materials*, E. Turi, Ed., Academic Press, New York, 1982, Chap. 5.
2. M. A. Acitelli, R. B. Prime, and E. Scalt, *Polymer*, **12**, 335 (1971).
3. T. Donellan and D. Roylance, *Polym. Eng. Sci.*, **22**(13), 821 (1982).
4. N. S. Schneider, J. F. Sprouse, G. L. Hagnauer, and J. K. Gillham, *Polym. Eng. Sci.*, **19**, 304 (1979).
5. R. B. Prime, *Anal. Calorim.*, **2**, 201 (1970).
6. R. B. Prime, *Polym. Eng. Sci.*, **13**, 453 (1973).
7. K. Horie, H. Hiura, M. Sawada, I. Mita, and H. Kambe, *J. Polym. Sci. A-1*, **8**, 1357 (1970).
8. S. Sourour and M. R. Kamal, *Thermochim. Acta*, **14**, 41 (1976).
9. M. E. Ryan and A. Dutta, *Polymer*, **20**, 203 (1979).
10. C. C. Riccardi, H. E. Adabbo, and R. R. J. Williams, *J. Appl. Polym. Sci.*, **29**, 2481 (1984).
11. J. Mijovic, J. Kim, and J. Slaby, *J. Appl. Polym. Sci.*, **29**, 1449 (1984).
12. I. K. Varma, Sangita, and D. S. Varma, *J. Appl. Polym. Sci.*, **28**, 191 (1983).
13. H. Stenzenberger, in *Polyimides*, D. Wilson, H. D. Stenzenberger, and P. M. Hergenrother, Eds., 1990, p. 79. John Wiley & Sons, New York.
14. D. K. Hadad, in *Epoxy Resins, Chemistry and Technology*, C. A. May, Ed., 1988, p. 1089. Marcel Dekker, New York.
15. C. C. Riccardi and R. J. J. Williams, *Polymer*, **27**, 913 (1986).
16. K. Dusek, M. Bleha, and S. Lunak, *J. Polym. Chem. Ed.*, **15**, 2393 (1977).
17. U. M. Bokare and K. S. Gandhi, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 857 (1980).

Received November 28, 1995

Accepted March 12, 1996