

# Effect of Oxirane Groups on Curing Behavior and Thermal Stability of Vinyl Ester Resins

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**ABSTRACT:** The effects of oxirane groups in vinyl ester (VE) resin and reactive diluent on curing characteristics and thermal behavior of cured resins are described. Stoichiometric (0.5:1, sample A) as well as nonstoichiometric (0.5:0.85, sample B) ratios of the diglycidyl ether of bisphenol-A (DGEBA) and methacrylic acid (MA) were used for the synthesis of VE resins. Resin sample B had more residual epoxy groups because of the stoichiometric imbalance of the reactants. VE resins thus obtained were diluted with methyl methacrylate (MMA; 1:1, w/w), and controlled quantities of epoxy groups were introduced by partial replacement of MMA with glycidyl methacrylate (GMA), keeping the overall ratio of resin and reactive diluent constant. Increase of GMA content in resin A or B resulted in a decrease in gel time, indicating that the curing reaction is facilitated by the presence of epoxy groups. An increase in initiator content also reduced the gel time. In the differential scanning calorimetry (DSC) scans, a sharp curing exotherm was observed in the temperature range  $107 \pm 3$ – $150 \pm 1$  °C. The onset temperature ( $T_{\text{onset}}$ ) and peak exotherm temperature ( $T_{\text{exo}}$ ) decreased with increase in GMA content. Heat of curing ( $\Delta H$ ) also increased with increase in GMA content. A broad exotherm was observed after the initial sharp exotherm that was attributed to the etherification reaction. Cured VE resins were stable up to 250–260 °C, and started losing weight above this temperature. Rapid decomposition was observed in the temperature range 400–500 °C. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 416–423, 2001

**Key words:** vinyl ester resins; glycidyl methacrylate (GMA); methyl methacrylate (MMA); curing; thermal behavior; diglycidyl ether of bisphenol-A (DGEBA)

## INTRODUCTION

Since their successful commercialization in mid-1960s, the bismethacryloxy derivatives of diglycidyl ether of bisphenol-A [DGEBA; vinyl ester (VE) resins] have been the subject of intense research. These resins are easily synthesized by reacting 1 mol of DGEBA with 2 mol of methacrylic acid (MA) in presence of suitable catalysts (such as

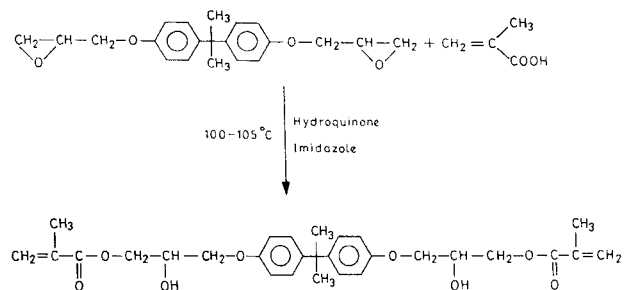
imidazole or quaternary ammonium salts) according to the reaction shown in Scheme 1.

Because the viscosity of neat resins is considerably high ( $10^5$  cPs), reactive diluents have been used in the resin formulations.<sup>1–5</sup> In addition to reducing the viscosity (100–500 P), these diluents control the crosslink density and affect strength, percent elongation, hardness, chemical resistance, scratch resistance, and surface finish.

Styrene is the most commonly used reactive diluent because of its low cost, high compatibility, and reactivity. Styrene imparts good mechanical properties and heat distortion resistance to cured resins. The styrene content in these resin formu-

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Scheme 1

lations ranges from 30 to 60%. The effect of styrene content on the properties of VE resin has been reported in the literature.<sup>2</sup> Substitution of styrene by small quantities of  $\alpha$ -methyl styrene in VE resins acts as an exotherm peak depressant and increases curing time.<sup>6-8</sup> Other reactive diluents used in these resin formulations are methyl methacrylate (MMA), ethyl methacrylate, acrylonitrile, vinyl toluene, dicyclopentadiene diacrylate,<sup>9</sup> etc.

No systematic studies on use of functional vinyl monomers [such as, glycidyl methacrylate (GMA)] as reactive diluents have been reported in the literature. However, studies on copolymerization of GMA and MMA using free radical as well as group transfer polymerization have been reported,<sup>10</sup> and functionalized polymers based on GMA have been developed. Copolymerization of GMA and VE resin through a vinyl double bond will yield a repeating unit containing pendant epoxide groups.

To develop functionalized resins, we have recently reported partial replacement of MMA by GMA in VE resin formulations.<sup>11</sup> GMA is a versatile bidentate monomer capable of imparting oxirane functionality to VE resins containing MMA or other vinyl monomers.

Oxirane functionality can also be imparted to VE resins during synthesis by varying the molar ratios of DGEBA and MA. It was, therefore, considered of interest to synthesize VE resins using stoichiometric as well as nonstoichiometric ratios of DGEBA and MA. Here we report the effect of structural variations of VE resin and reactive diluent on curing characteristics and thermal behavior of cured resins.

## EXPERIMENTAL

### Materials

Diglycidyl ether of bisphenol-A (DGEBA; epoxy equivalent, 180), manufactured by CIBATUL un-

der the trade name Araldite LY 556 (Ciba Giegy, was used for the synthesis of VE resin. Methacrylic acid (MA; Merck), hydroquinone (Sarabhai M. Chemicals), imidazole (Loba Chemie Indo Australan Company), methyl methacrylate (MMA; Merck), glycidyl methacrylate (GMA; Fluka), methanol (BDH), and *N,N*-dimethyl aniline were used as received. Benzoyl peroxide (BPO; CDH) was recrystallized using chloroform.

### Synthesis of VE Resin

VE resin was prepared by reacting both stoichiometric (0.5:1, sample A) and nonstoichiometric (0.5:0.85, sample B) amounts of DGEBA with MA in air atmosphere at 100–120 °C, using imidazole as a catalyst and hydroquinone as an inhibitor. Sample A was prepared by reacting 180 g of DGEBA with 84 mL of MA (molar ratio, 0.5:1) containing 0.25 g of hydroquinone and 0.42 g of imidazole in a four-necked reaction kettle equipped with a mechanical stirrer and condenser. Sample B was prepared by the same procedure just described for Sample A, with the exception of using 72 mL of MA (molar ratio of DGEBA and MA, 0.5:0.85). The progress of the reaction was monitored by determining the acid number at regular time intervals. The reaction was allowed to continue until the acid number reached a value <10 (~3–4 h). No attempt was made to remove the remaining catalyst or its fragments from the reaction medium. The amber-colored resin was then cooled and stored at low temperature.

### Reactive Diluents

MMA and GMA were used as reactive diluents for VE resins (1:1 ratio w/w; i.e., 100 g of VE resin and 100 g of reactive diluent). Samples with 100:0, 80:20, 60:40, 40:60, 20:80, and 0:100 g ratios of MMA to GMA were designated as G-0, G-1, G-2, G-3, G-4, and G-5, respectively. Prefix A or B was added to specify the VE resin used in these formulations.

### Characterization of VE Resin

To characterize the DGEBA and VE resin, the epoxy equivalent weight, which is defined as the weight of resin that contains 1 g equiv of epoxy, was determined volumetrically by the HCl/dioxane method. Structural characterization of the VE resin was done by Fourier transform infrared

spectroscopy (FTIR) with a Digilab Bio-Rad FTS 40 spectrometer.

### Curing Studies

Differential scanning calorimetry (DSC) and gel time measurement techniques were used to investigate the curing behavior. Gel time was determined by taking 10 g of VE resin (Sample A or B) in a test tube and keeping it in a constant-temperature water bath. As soon as the resin in the test tube acquired the temperature of water bath (i.e.,  $45 \pm 1$  °C in sample A and  $40 \pm 1$  °C in sample B), 0.2 g of BPO (initiator), and 0.05 g of *N,N*-dimethylaniline (promoter) were added. The initiator and promoter were mixed thoroughly with the resin. After mixing, the temperature of resin was recorded at regular time intervals. An increase in temperature was observed with increase in duration of reaction. The time taken to reach the highest temperature was taken as the gel time. To investigate the effect of initiator on gel time, curing of sample B using 6% each of BPO and *N,N*-dimethylaniline was also carried out.

The curing of VE/MMA/GMA formulations in the presence of 2 or 4% BPO was monitored by recording DSC scans in static air atmosphere. This technique is a useful method for direct measurement of the rate of exothermic polymerization. A DuPont 2100 thermal analyzer with a 910 DSC module was used for this purpose. A heating rate of 10 °C/min and a sample weight of  $5 \pm 1$  mg was used for recording DSC scans in static air atmosphere.

The exothermic transition associated with curing reaction was characterized by noting the following parameters:  $T_{\text{initial}}$ , temperature at which exotherm begins;  $T_{\text{onset}}$ , obtained by extrapolation of steepest portion of the exotherm;  $T_{\text{final}}$ , temperature of the end of exotherm (obtained by extrapolation);  $T_{\text{exo}}$ , exothermic peak temperature;  $\Delta H$ , heat of curing (calculated by measuring the area under the exothermic transition).

### Thermal Stability

A DuPont 2100 thermal analyzer with a 951 TG module was used for recording thermogravimetric/differential thermogravimetric (TGA/DTGA) traces in nitrogen atmosphere (flow rate, 60 cm<sup>3</sup>/min). A heating rate of 20 °C/min and sample weight of  $10 \pm 1$  mg was used in each experiment. Cured resin samples were obtained by heating VE/MMA/GMA resins at 80 °C in a nitrogen at-

mosphere for 2 h and then at 120 °C for another 2 h in the presence of 2% BPO for sample A and 6% BPO for sample B. Sample AG-5 was also cured with 6% BPO. The relative thermal stability of the resins was evaluated by comparing initial decomposition temperature ( $T_i$ ), temperature of maximum rate of weight loss ( $T_{\text{max}}$ ), final decomposition temperature ( $T_f$ ), and char residue at 600 °C.

## RESULTS AND DISCUSSION

### Characterization of VE Resin

The epoxy equivalent weights of samples A and B were 497 and 464, respectively. These values indicate that a different proportion of epoxy groups are present in sample A and sample B.

In the IR spectrum of the VE resin, strong absorptions due to the carbonyl groups of the ester linkages were observed at 1720 and 1180 cm<sup>-1</sup>. The carbonyl stretching at 1700 cm<sup>-1</sup> was absent, indicating that the reaction of the acid with the epoxy group was complete. The absorption bands at 1636 cm<sup>-1</sup> is due to the double bond stretching of vinyl esters.

The Brookfield viscosity of VE resin (sample B)/MMA (1:1 w/w), determined with a Brookfield synchroelectric viscometer at  $30 \pm 1$  °C (spindle LV-2 at 10 rpm) was 16–20 cps. No significant change in viscosity was observed on partial substitution of MMA by GMA.

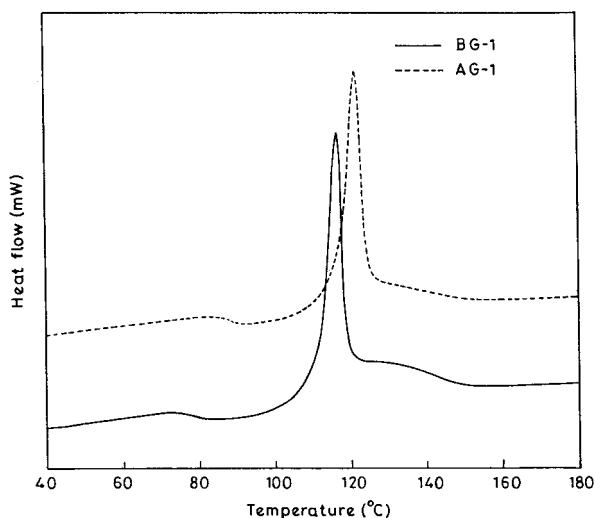
### Curing of VE Resins

The structure of the crosslinked network obtained after curing will depend on the structure of VE resin, reactive diluents, and initiator concentration. The effect of these parameters on curing is described in the following text.

### Effect of Structure of VE Resin

Samples A and B of VE resin contained different proportions of residual epoxy groups. In Figure 1, the DSC traces of samples AG-1 and BG-1 are given. The exotherm peak position as well as heat of curing ( $\Delta H$ ) was higher in BG-1. The curing of VE resins proceeds by free radical polymerization of olefinic groups of reactive diluent and VE resin. The observed sharp exotherm in DSC may be attributed to such vinyl polymerization.

One point that can be noted from Figure 1 is that immediately after the sharp exotherm, a



**Figure 1** DSC traces of samples AG-1 and BG-1.

broad exothermic transition is observed in sample BG-1. The difference in curing behavior of samples A and B, which contain similar amounts of GMA, may be attributed to the variation in the concentration of unreacted epoxy groups in these resins. The residual epoxy groups may react with pendant hydroxyl groups of VE resin, leading to the formation of ether linkages. Such etherification reactions have been reported in epoxy resins at high temperatures.<sup>12</sup>

Comparative data giving characteristic curing temperatures and gel times for samples AG-5 and BG-5 are given in Table I. The heat of curing as well as gel time for sample BG-5 was higher than that of sample AG-5.

#### Effect of Reactive Diluents

To investigate the effect of reactive diluents on curing behavior (1:1 w/w), resin formulations containing different weight % of MMA/GMA were prepared. In the DSC traces of these samples, a sharp exotherm was observed in the temperature range  $107 \pm 3$ – $150 \pm 1$  °C. The onset temperature ( $T_{\text{onset}}$ ) of curing as well as peak exothermic temperature ( $T_{\text{exo}}$ ) decreased significantly on replacement of MMA by GMA (up to 60 wt %; sample AG-3; Figure 2). Further increase in GMA only marginally affected the characteristic temperatures of curing. The overall heat of curing increased with increase in GMA concentration (Table II). These results thus indicate that overall heat of curing increased with increase in oxirane groups in the VE resin formulations. These oxirane groups may be present in reactive diluents

or VE resins. The broad exothermic transition after the sharp exotherm was more prominent in samples containing higher amounts of GMA.

To qualitatively assess the contribution of the broad exotherm to the overall curing reaction, the area of this region was determined manually and heat of curing ( $\Delta H_1$ ) was calculated. The ratio of  $\Delta H_1$  to overall  $\Delta H$  value represents the fraction of heat liberated during etherification (i.e., reaction of pendant hydroxyl groups with epoxy groups). These results are also given in Table II. Surprisingly similar values were observed in samples A/BG2–G5. These results are understandable on the basis of availability of pendant hydroxyl groups and the diffusion-controlled nature of reaction at later stages of curing.

Gel times of samples A and B are given in Table III. The gel times were higher in sample B irrespective of GMA content. Because the gel time of sample A in the presence of 2% BPO was much lower, studies using higher BPO concentration (6%) were not carried out.

#### Effect of Initiator Concentration

The gel time of sample B using 2% BPO with 0.5% *N,N*-dimethylaniline was higher than that of the sample containing 6% BPO with 6% *N,N*-dimethylaniline. This result may be because of the availability of more number of radicals that initiate polymerization and hence lead to faster curing. Comparative data of gel time of sample B cured with 2% and 6% BPO are given in Table III.

#### Activation Energy of Curing

To determine the activation energy ( $E_a$ ) of the curing reaction, the multiple heating rate method of Ozawa<sup>13</sup> was used. The assumptions made in this method are that the peak maximum repre-

**Table I** Curing Characteristics of Vinyl Ester Resins (Samples A & B) Containing GMA as Reactive Diluent (1:1 w/w)

Curing Characteristics/ Sample Designation	AG-5	BG-5
$T_{\text{initial}}$ (°C)	97.6	100.0
$T_{\text{onset}}$ (°C)	110.8	114.1
$T_{\text{exo}}$ (°C)	116.6	121.5
$T_{\text{final}}$ (°C)	156.3	157.6
$\Delta H$ (J/g)	127.2	190.9
$T_{\text{gel}}$ (s)	120.0	180.0

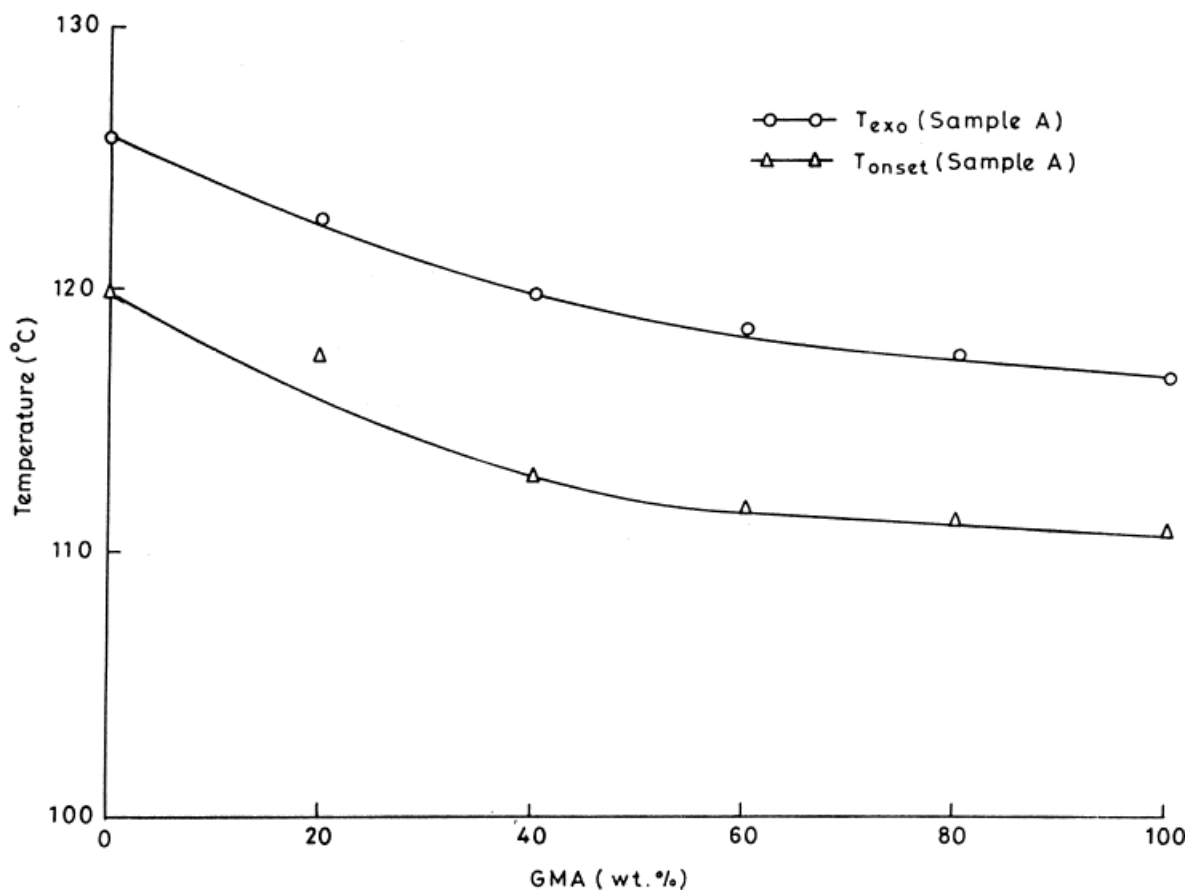


Figure 2 Effect of GMA concentration on  $T_{\text{onset}}$  and  $T_{\text{exo}}$ .

sents a point of constant conversion for each heating rate and that the temperature dependence of the reaction rate constant obeys the Arrhenius equation. DSC scans were recorded at four different heating rates (5, 10, 15, and 20 °C/min) of VE

resin diluted with varying amounts of MMA or GMA. DSC scans of sample AG-2 recorded at four different heating rates are shown in Figure 3.

The peak exotherm temperature ( $T_{\text{exo}}$ ) shifted to higher temperatures with increasing scan

Table II Effect of Structure of Resin/Diluent on Heat of Curing (2% BPO)

Reactive Diluent MMA/GMA (wt %)	$\Delta H$ Value of VE Resin Containing MMA/GMA as Reactive Diluents (1:1 w/w)	
	Sample A	Sample B
100/0	75.7 (0.19)	—
80/20	83.9 (0.24)	115.3 (0.32)
60/40	97.6 (0.31)	128.9 (0.30)
40/60	113.3 (0.32)	151.8 (0.31)
20/80	116.1 (0.32)	158.9 (0.34)
0/100	127.2 (0.31)	190.9 (0.30)

Figures in parenthesis indicate ratio of area under broad exotherm to the overall heat of curing reaction ( $\Delta H_1/\Delta H$ ).

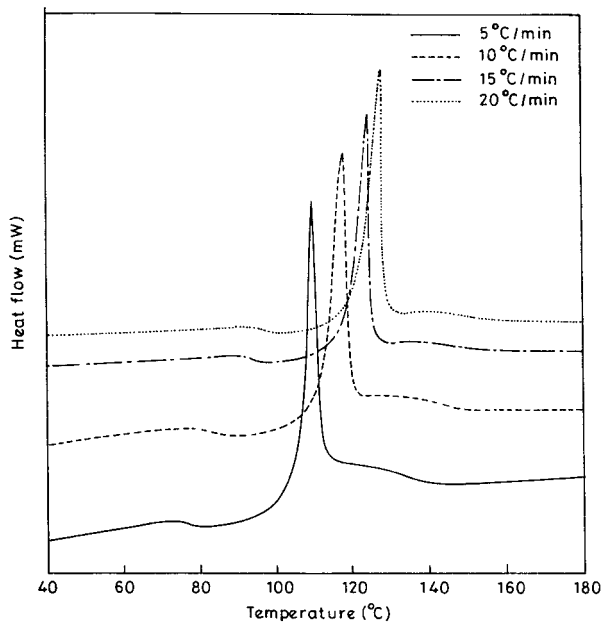
Table III Effect of Reactive Diluent/Initiator Concentration on Gel Time

Reactive Diluent MMA/GMA (wt %)	$T_{\text{gel}}$ of VE Resin (s)		
	Sample A <sup>a</sup>	Sample B <sup>b</sup>	Sample B <sup>c</sup>
100/0	> 7200	> 7200	> 7200
80/20	> 7200	> 7200	> 1980
60/40	420	630	300
40/60	270	540	210
20/80	210	360	105
0/100	120	180	45

<sup>a</sup> Curing done at  $45 \pm 1^\circ\text{C}$  using 2% BPO and 0.5% *N,N*-dimethyl aniline.

<sup>b</sup> Curing done at  $40 \pm 1^\circ\text{C}$  using 2% BPO and 0.5% *N,N*-dimethyl aniline.

<sup>c</sup> Curing done at  $40 \pm 1^\circ\text{C}$  using 6% BPO and 6% *N,N*-dimethyl aniline.

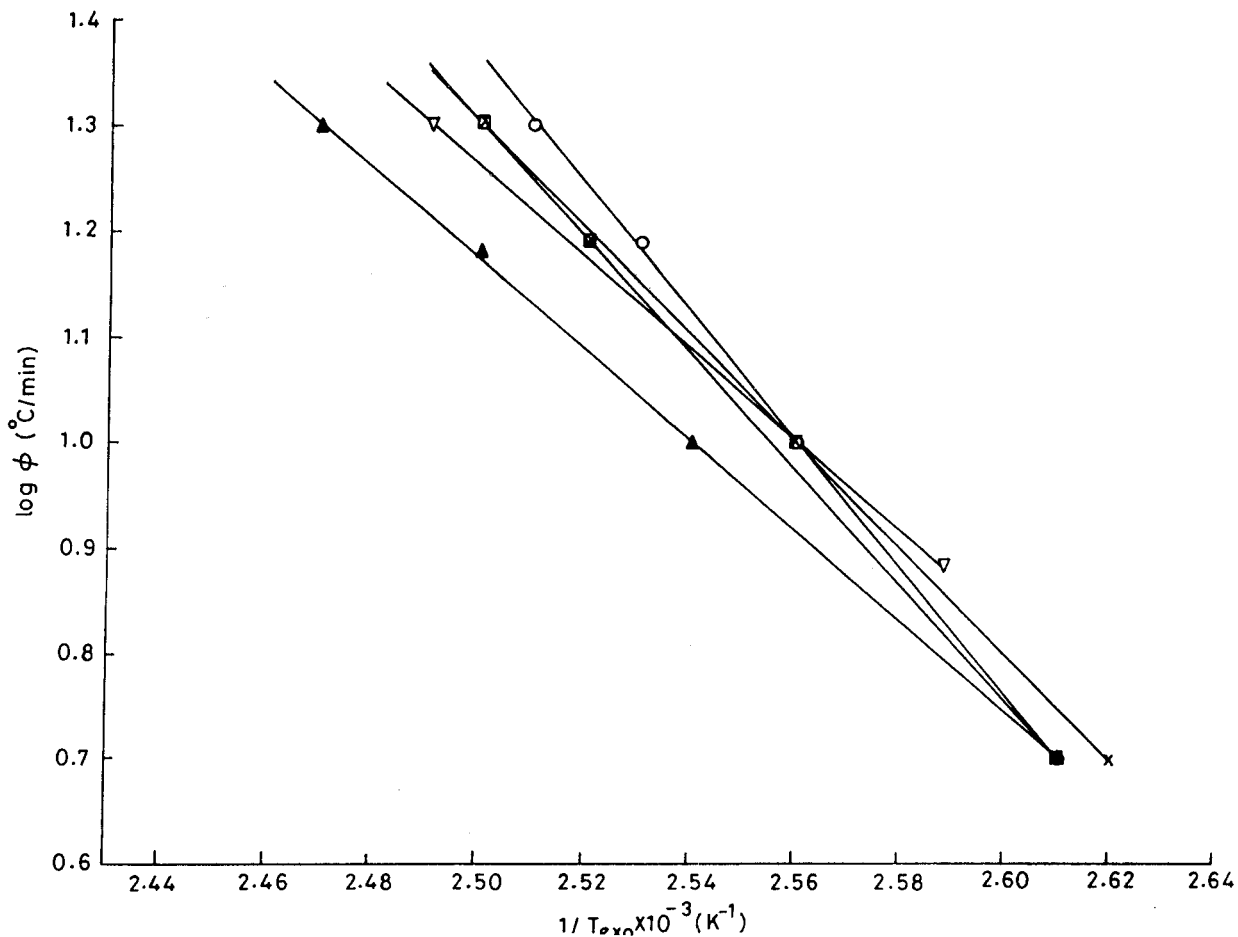


**Figure 3** DSC scans of sample AG-2 recorded at four different heating rates.

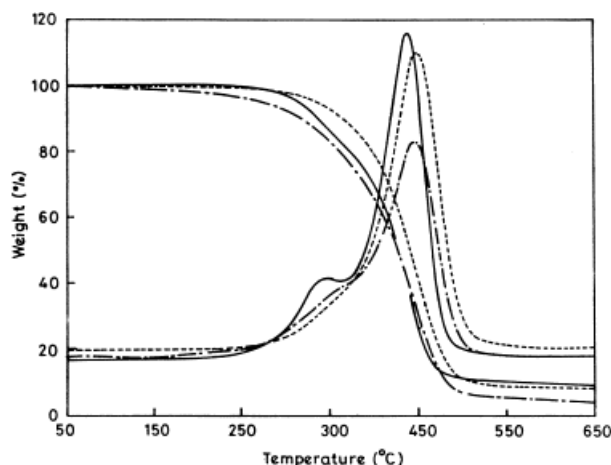
**Table IV** Effect of Reactive Diluent Concentration on Activation Energy of Curing

MMA/GMA Content (wt %)	Activation Energy of Curing (kJ/mol)	
	Sample A	Sample B
100/0	107.5	108.1
80/20	—	105.0
60/40	98.2	98.1
40/60	—	97.6
20/80	—	91.1
0/100	76.9	77.5

rates. A plot of log of heating rate ( $\log \phi$ ) versus  $1/T_{\text{exo}}$  for different samples is shown in Figure 4, and activation energy for various VE/MMA/GMA resin formulations is tabulated in Table IV. The  $E_a$  values for samples A and B were almost the



**Figure 4** Plot of  $\log \phi$  versus  $1/T_{\text{exo}}$  for samples with varying amounts of GMA: (○) BG-1; (×) BG-2; (□) BG-3; (▽) BG-4; (▲) BG-5.



**Figure 5** TGA/DTGA trace of cured resin samples. Key: (---) AG-5, cured using 2% BPO; (- · - ·) AG-5, cured using 6% BPO; and (—) BG-5, cured with 6% BPO.

same. This result indicates that the structure of resin does not affect activation energy of samples:  $E_a$  decreased with increasing amounts of reactive diluent GMA.

#### Thermogravimetric Analysis

Thermal stability of isothermally cured resins was determined in nitrogen atmosphere by TGA. A multistep decomposition was observed in VE resin containing MMA as a reactive diluent. Cured resin samples containing GMA/MMA as the reactive diluent were stable up to 250–260 °C, and started losing weight above this temperature.

Rapid decomposition was observed in the temperature range 400–500 °C.

Thermal behavior of cured resins was evaluated by TGA in a nitrogen atmosphere. The TGA/DTGA traces of samples AG-5 and BG-5 cured with 6% BPO are shown in Figure 5. The TGA trace of AG-5 cured with 2% BPO is also shown in this figure. The results of TGA are summarized in Table V. All AG samples that were cured with 2% BPO showed a single-step decomposition, whereas BG samples with higher amounts of GMA (samples BG-3 to BG-5) that were cured with 6% BPO showed two-step degradation. A two-step degradation was also indicated in the TGA trace of AG-5, which was cured with 6% BPO. Thus, the amount of initiator used for curing and excess of oxirane groups in the VE resin formulations influence the thermal stability of the cured resin. The first step of decomposition (temperature range 259 ± 6–355 ± 7 °C) in these samples may be due to end-group-initiated degradation. The higher concentration of initiator residues in these samples may be responsible for onset of degradation at a lower temperature. All the samples showed a weight loss of 92 ± 2% up to 600 °C.

#### CONCLUSIONS

The oxirane content of VE resin was varied by changing the structure of the resin or by adding a reactive diluent (GMA) in VE resin formulations.

**Table V** Results of Thermogravimetric Analysis of Cured VE Resin Sample B (Sample A)

Sample Designation	Characteristic Temperatures (°C) & Weight Loss (%)			
	$T_i$	$T_{max}$	$T_f$	Wt Loss (%)
BG-0	109.4	240.6	294.0	15.4
	294.0	—	384.0	20.9
	384.0 (282.6)	422.0 (447.8)	505.0 (573.9)	54.4 (92.1)
BG-1	243.7 (275.8)	427.3 (444.8)	503.0 (555.2)	85.3 (94.1)
BG-2	262.5 (287.7)	435.4 (435.1)	518.7 (547.3)	90.7 (93.8)
BG-3	253.0	—	347.0	13.6
	359.4 (272.4)	434.0 (437.9)	500.0 (541.3)	77.4 (92.6)
	265.6	—	362.5	13.6
BG-4	362.5 (266.6)	430.7 (435.1)	537.5 (543.8)	78.1 (92.1)
BG-5	253.0	337.0	359.3	17.3
	360.0 (269.5)	438.0 (447.8)	503.0 (565.2)	72.4 (92.6)

Resin B was cured using 6% BPO; Values in parenthesis represents the characteristic temperatures for sample A cured using 2% BPO.

The effect of the oxirane content on properties of VE resins was evaluated, and the following conclusions may be drawn from the results.

1. The gel time of resin decreased by an increase in oxirane content of the resin.
2. The heat of curing increased with increase in oxirane content.
3. The temperature dependence of curing (measured by activation energy determination) was unaffected by slight differences in oxirane content of the resin (e.g., resins A and B). However, when the oxirane content of the resin was increased significantly (by using GMA as a reactive diluent), a decrease in activation energy of curing reaction from 108 to 77.5 kJ/mol was observed.
4. Thermal stability of cured resins depended on the concentration of the curing agent. An increase in the concentration of BPO from 2 to 6% resulted in a two—three-step decomposition.

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