

# Viscoelastic Behavior of Anhydride-Cured Epoxy System Initiated by Thermal Latent Catalyst

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**ABSTRACT:** The thermal latency and viscoelastic behavior during the cure of a new catalytic (*N*-benzylpyrazinium hexafluoroantimonate) anhydride-cured epoxy system were studied with differential scanning calorimetry and a rheometer under isothermal conditions. The gelation time was obtained from the evaluation of the storage modulus, loss modulus, and damping factor. The temperature dependence on the reaction time was described by the Arrhenius expression, and the crosslinking activation energy was determined from the Arrhenius plot based on the gelation time and reaction temperature. The gelation time and crosslinking activation energy characterized from rheological behaviors increased with increasing anhydride composition and showed a maximum value with a mixing ratio of 0.65, which was due to the compact crosslinking network without a side reaction in the ratio. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 646–653, 2001

**Key words:** *N*-benzylpyrazinium hexafluoroantimonate; latent property; viscoelastic behavior; gel point; crosslinking activation energy

## INTRODUCTION

In the development of high-performance polymeric composites, the physical and mechanical improvements of the polymeric matrix play an important role in the resulting composite behavior.<sup>1</sup> Epoxy resins are used extensively as matrixes in composite material systems.<sup>2</sup> Anhydride-cured epoxy resins are thermosetting resins that are used as matrixes for many advanced materials in the aerospace and electronic industries, and they generally exhibit improved high-temperature stability and good physical and electrical properties.<sup>3</sup>

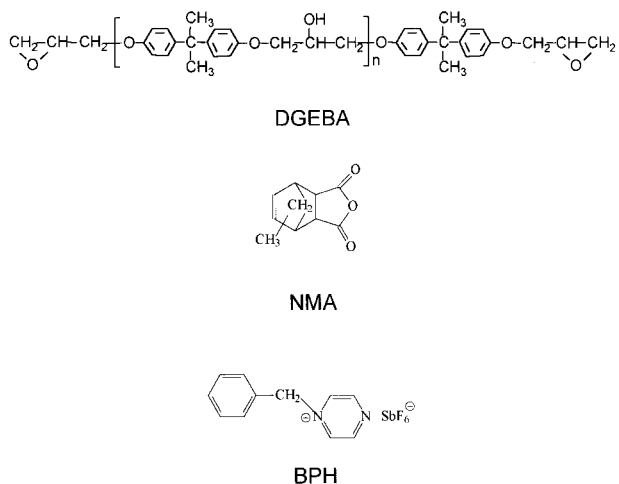
Tertiary amines have been widely used as catalysts because anhydrides do not directly react

with the epoxy group.<sup>2</sup> Meanwhile, the catalyst used for enhancement of anhydride reactivity produces toxicity, low heat resistance, and prompt vitrification. The *N*-benzylpyrazinium salt used in this work as a thermal latent catalyst overcomes the disadvantages of current catalysts, such as excessively rapid gelation, high hygroscopicity, and light instability. In addition, it exhibits a long pot-life, excellent thermal latency, and reasonable thermal stability because the initiator activity of the *N*-benzylpyrazinium salts can be enhanced by decreasing the nucleophilicity of the counterion ( $\text{SbF}_6^-$ ) and introducing an electron-donating substituent on the phenyl ring of the benzyl group.<sup>4</sup>

Rheological properties such as the viscosity and the dynamic modulus can be directly correlated to the evaluation of the physical and mechanical properties of the system during cure.<sup>5</sup> Studies of the dynamic properties of gelling systems using

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**Scheme 1** The chemical structures of DGEBA, NMA, and BPH.

dynamic light scattering<sup>6</sup> and rheological measurements<sup>7,8</sup> revealed that critical gels exhibited a continuous power law relaxation time spectrum. Measurements on critical gels of epoxy,<sup>9</sup> siloxane,<sup>10</sup> and polyurethane,<sup>11</sup> clearly showed the application of this power law behavior. The characterization of the network buildup is very useful from the theoretical and practical points of view. Furthermore, viscoelastic studies of the crosslinking process on the epoxy resin are essential for optimization of the processing cycle.

The present work concerns the characterization of viscoelastic properties as a function of the reaction time during epoxy gel formation, and we attempt to correlate the gelation time with its crosslinking activation energy. The effects of the rheological characteristics including the temperature effect on the crosslinking reaction, the ratio of anhydride, the complex viscosity, and the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) are investigated.

## EXPERIMENTAL

### Materials

The epoxy resin system consisted of commercial diglycidyl ether of bisphenol A (DGEBA, YD-128, Kukdo Chem. Inc.) with methylbicyclo-[2,2,1]heptene-2,3-dicarboxylic acid anhydride (NMA, Aldrich) as a curing agent. The thermal latent catalyst was *N*-benzylpyrazinium hexafluoroantimonate (BPH), which was synthesized according

to recent work.<sup>4</sup> Scheme 1 shows the structures of DGEBA, NMA, and BPH.

The BPH was added to the DGEBA and they were mixed with 25, 45, 65, 85, and 105 wt % NMA. Their compositions are listed in Table I.

### Evaluation of Latent Properties

The thermal latency was studied by the investigation of the conversion as a function of reaction time using isothermal differential scanning calorimetry (DSC) performed on a DuPont DSC910 supported by a DuPont thermal analyzer at 200 and 50°C.

### Rheological Experiments

There are two different stages of curing.<sup>5</sup> In the beginning, the sample is dealt with as a liquid; after the gel point it loses its fluidity and becomes a solid. Thus, in the initial part, the rheological kinetics are followed by a viscometric method; then the cure can be monitored by measuring the rheological properties such as the  $G'$ , the  $G''$ , and the loss tangent ( $\tan \delta$ ). The rheological factors were measured using a Physica Rheolab MC100 spectrometer with parallel-plate geometry in a standard frequency on the order of 5 Hz. The plate diameter was 40 mm and the gap size was 0.5 mm.

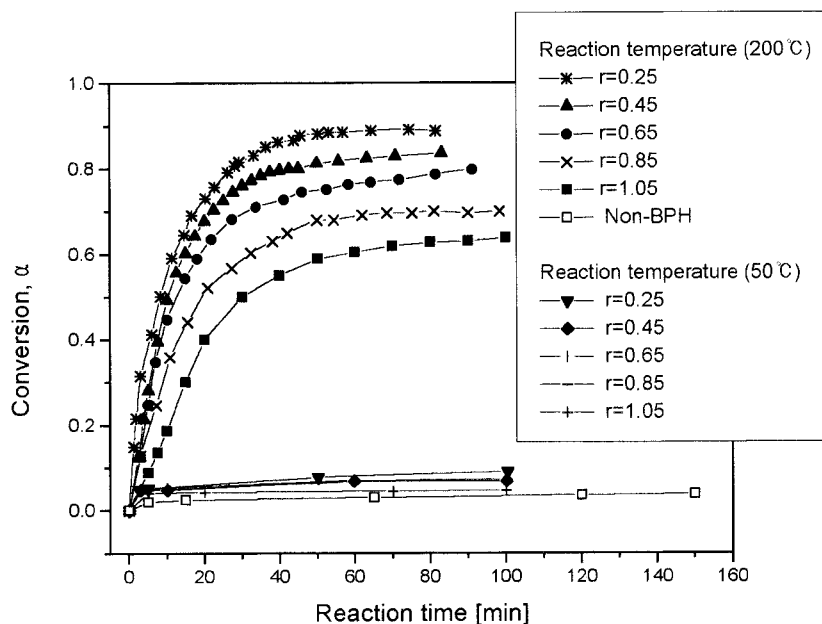
## RESULTS AND DISCUSSION

### Thermal Latent Properties

Figure 1 shows the conversion as a function of the curing time as determined by isothermal DSC for the different compositions of the system made with 1 wt % BPH catalyst. As the reaction time proceeded, the conversion decreased when the anhydride content was increased at 200°C. For the epoxy resin cure the anhydrides were generally

**Table I** Composition of DGEBA/NMA/BPH System

Mixing Ratio	DGEBA/NMA/BPH (wt %)
0.25	100/25/1
0.45	100/45/1
0.65	100/65/1
0.85	100/85/1
1.05	100/105/1



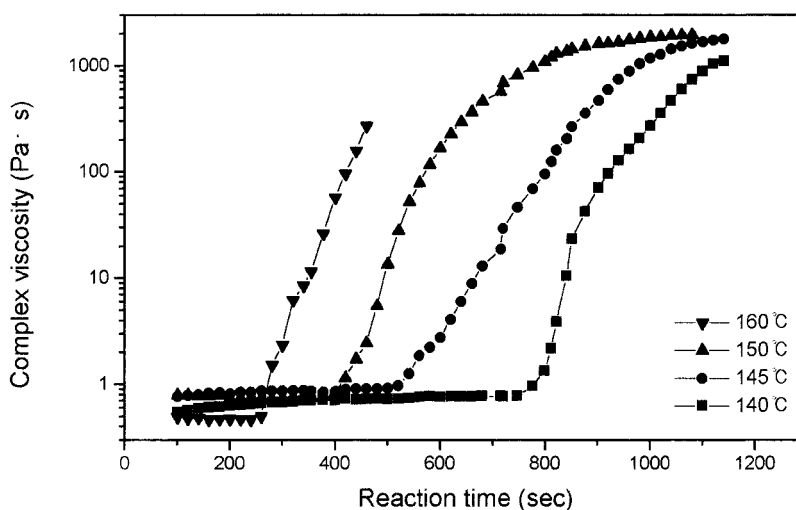
**Figure 1** Time-conversion curves of the DGEBA/NMA/BPH system measured at 200 and 50°C by isothermal DSC.

selected to provide low viscosity and long shelf life.<sup>2</sup> Thus, the low conversion was due to the poor reactivity of the anhydride. The conversion with the 50°C reaction temperature presented no significant change as the reaction time increased. This was a consequence of the low temperature, which had become a limiting factor prohibiting the activity of the catalyst. The addition of BPH used as the catalyst in this system showed a fast reverse reaction; therefore, the low stability of the

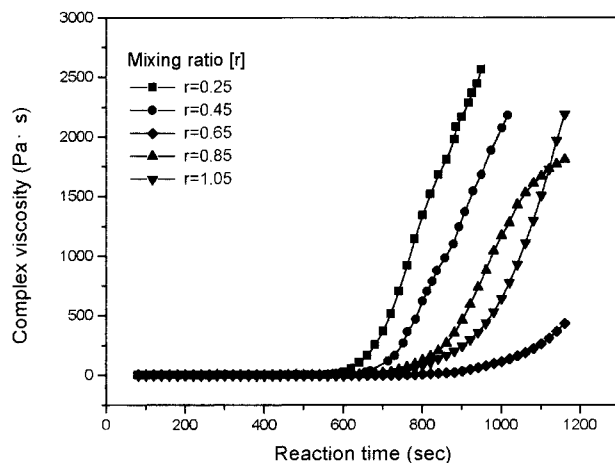
benzyl cation limited the initiator activity to some extent of the initiation temperature.<sup>12</sup>

### Viscosity Profiles

During cure the epoxy was transformed from an oligomer to a branched network. In this process the viscosity dramatically increased with increasing reaction time at 140, 145, 150, and 160°C, as shown in Figure 2. In the initial stage of gelation



**Figure 2** Viscosity profiles for a mixing ratio of 0.65 obtained at 140, 145, 150, and 160°C.



**Figure 3** The composition dependence of the complex viscosity at different contents of anhydride.

the molecular weight slowly increased as a consequence of the chain growth of the mixture with the reaction time. As the crosslinking went on there was a suddenly increase of the viscosity of the system because of the progressive formation of a tridimensional polymeric network.

Figure 3 shows the composition dependence of the complex viscosity at different contents of anhydride on the reaction time that was used for determining the gelation process. The time obtained from the intersection of the last trace of the linear fraction increased when increasing the anhydride content and showed a maximum value with a mixing ratio of 0.65 in this system. This was a consequence of the structure–reactivity relationship, which was fundamental for optimizing the process condition. As shown in Figure 3, the reaction time could be directly correlated with the cure reactivity.<sup>5</sup> If the cure reactivity is too fast before vitrification, the system cannot form a well-developed network structure. Therefore, the 0.65 mixing ratio was the optimum condition to make a well-developed crosslinking structure without rapid vitrification or steric hindrance in this system.

### Viscoelastic Criterion for Gel Point

Studies of the rheological properties of a gelation system using dynamic light scattering<sup>13</sup> and rheological measurements<sup>14</sup> revealed that incipient or critical gels exhibit a continuous power law relaxation time spectrum.<sup>15</sup> A theoretical model<sup>16,17</sup> of the evolution of the viscoelastic properties characterized by the complex shear modulus ( $G^* = G'$

+  $iG''$ ) is classically described by the following relation:

$$G^* = G_0 \gamma^n f(i\omega/\omega^*) \quad (1)$$

where  $\lambda = (p_c - p)/p_c$  is the relative distance to the gel point,  $p$  is the reaction extent,  $p_c$  is the reaction extent at the gel point,  $\omega^* = \omega_0 \lambda^{s+n}$  is the characteristic frequency associated with the slowest relaxation process, and  $s$  and  $n$  are the exponents that govern the power law behaviors of the steady-state viscoelastic properties.

In the case of  $\omega^* > \omega$  and before the gel point ( $p < p_c$ ), the system behaves as a viscous liquid and we have  $f(i\omega/\omega^*) = (i\omega/\omega^*) + (\omega/\omega^*)^2 + \dots$ , which leads to<sup>17</sup>

$$G^* = (G_0/\omega_0^2) \gamma^{-2s+n} \omega^2 + i(G_0/\omega_0) \gamma^{-s} \omega \quad (2)$$

In this state, the polymer is called sol because it is soluble in good solvents and there are well known relationships between the modulus and frequency, such as  $G' \propto \omega^2$ ,  $G'' \propto \omega$ .

After the gel point ( $p > p_c$ ), we have  $f(i\omega/\omega^*) = 1 + (i\omega/\omega^*) + \dots$ , which leads to

$$G^* = G_0 \gamma^n + i(G_0/\omega_0) \gamma^{-s} \omega \quad (3)$$

At this stage the cure system behaves like an elastic medium with a  $G'$ , which is frequency independent, while  $G''$  keeps the same frequency dependence (i.e.,  $G'' \propto \omega$ ). The polymer beyond the gel point is called a gel, and it is not soluble even in a good solvent.

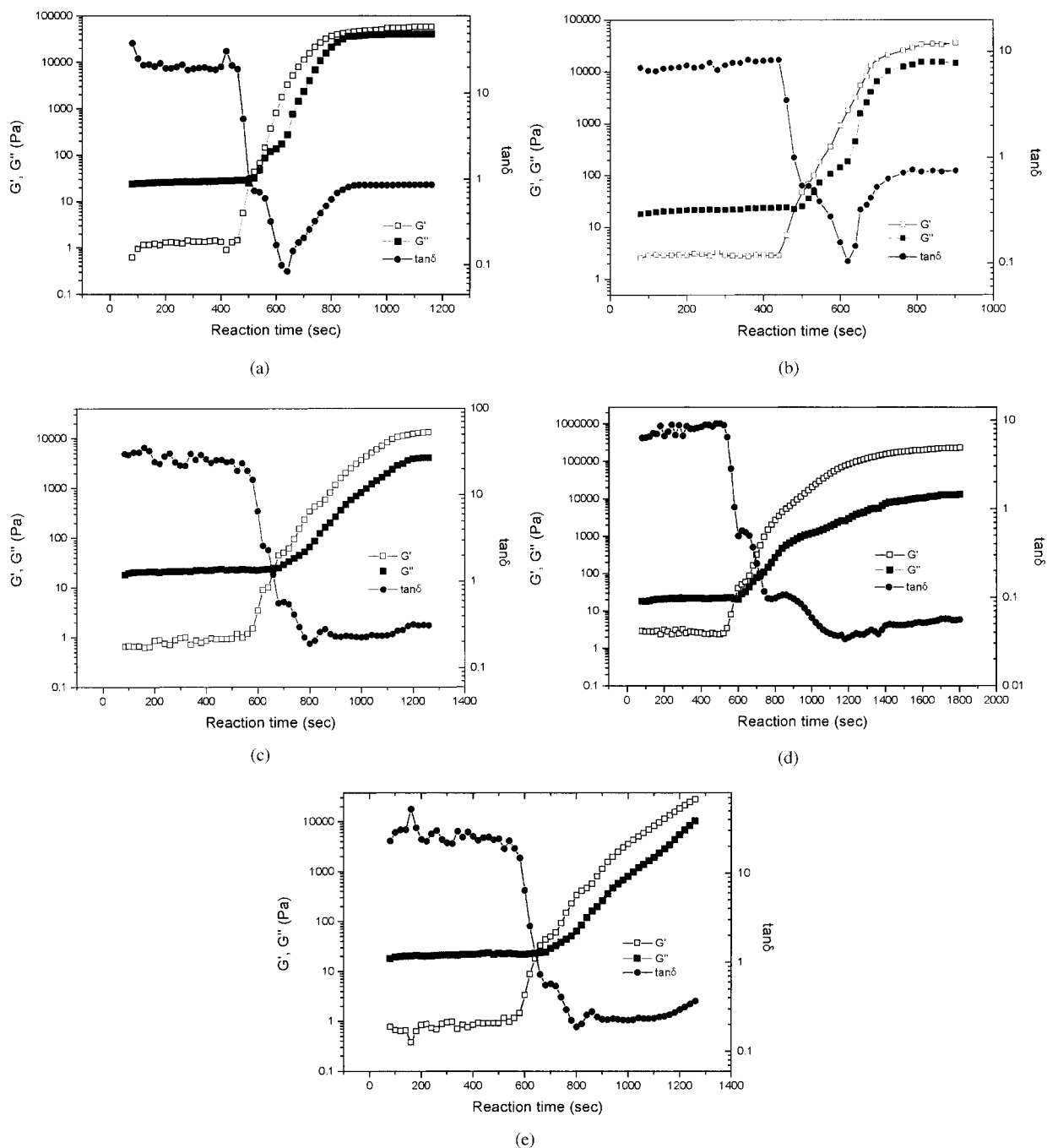
The response of the system yields the storage modulus, which indicates the elastic character of the materials, and the loss modulus, which is related to the viscous response of the material. The gel point is defined clearly as the instant at which the weight-average molecular weight diverges to infinity. At this point the sol–gel transition occurs and the molecular weight distribution is infinitely broad.<sup>18</sup>

At the gel point ( $p = p_c$ ) the  $\omega^*$  tends to zero and the following power law is predicted in all the frequency ranges below  $\omega_0$ :

$$G' \sim G'' \sim \omega^\Delta \quad (4)$$

where  $\Delta = (2\delta/\pi)$ .

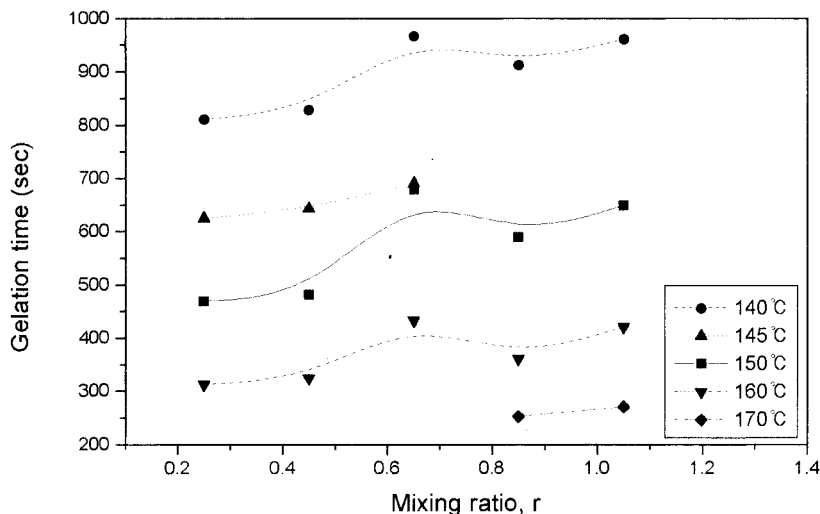
The storage and viscous modulus do not coincide at the gel point and the loss tangent becomes independent of the frequency. Rheological meth-



**Figure 4** Plots of  $G'$ ,  $G''$ , and  $\tan \delta$  as a function of the reaction time measured at  $150^\circ\text{C}$  with mixing ratios of (a) 0.25, (b) 0.45, (c) 0.65, (d) 0.85, and (e) 1.05.

ods to determine the gel point have become quite popular. Obtaining the gel time by measurements of the viscosity or the equilibrium modulus involves a certain amount of extrapolation.<sup>12</sup> The criterion that the gel point is associated with the crossover point of  $G'$  and  $G''$  (i.e.,  $\tan \delta = 1$ ) was originally introduced by Tung and Dynes.<sup>19</sup>

Figure 4 shows the storage modulus, loss modulus, and loss tangent as a function of the reaction time near the gel point for this system with different mixing ratios at  $150^\circ\text{C}$ . As the reaction went on the  $G'$  dramatically increased but the  $\tan \delta$  showed a reverse trend near the gel point. In this so-called critical gelation domain, the moduli



**Figure 5** The gelation time obtained from the relation between  $G'$  and  $G''$  as a function of the mixing ratio at different reaction temperatures.

and loss angles are both independent of the reaction extent. As shown in Figure 4, the limiting behavior of the  $G'$  indicated that the system behaved like a Newtonian liquid before the gel point and tended toward the behavior of a classical network after the gel point.<sup>16,17</sup> A crosslinking polymer, such as epoxy at its gel point, is in a transition state between a liquid and a solid.<sup>18</sup> From a technological standpoint, it is necessary to know when the sol–gel transition occurs because the polymer can be easily processed only before the gel point while it can still flow and the stresses applied can relax to zero.<sup>18</sup> Alternatively, the gel point is associated with a change in the slope of the developing modulus ( $G'$ ) versus the time curve or with the crossover point of  $G'$  and  $G''$ .<sup>19</sup> The gel point was delayed when increasing the anhydride content as shown in Figure 4(a–c) and the maximum value is shown in Figure 4(c) ( $r = 0.65$ ). However, the changes in the slope were not directly observed in all systems studied and the crossover points as shown in Figure 4 were coincident with gelation in this crosslinking epoxy system.<sup>18</sup> Otherwise, the fully cured network  $G''$  was followed by power law behavior. The  $G''$  was greater than the  $G'$  before the gel point. When the curing was completed, the ultimate moduli showed behavior independent of the reaction time in which the values of  $G'$  were significantly larger than those of  $G''$  (i.e., characteristic of crosslinked systems). Fully cured network behavior is shown in Figure 4(a–d); but an increase of  $G'$  and  $G''$  is observed after the gel point in Figure 4(e), result-

ing in a lack of a fully 3-dimensional network in a given time scale.

Figure 5 shows the gelation time obtained from the relation between  $G'$  and  $G''$  from Figure 4 as a function of the mixing ratio at different reaction temperatures. The time increased with increasing anhydride content and showed a maximum value at a mixing ratio of 0.65. These results showed good agreement with the viscosity profiles. It was revealed that the 0.65 mixing ratio provided more frequent interaction between activated hydroxyl groups and epoxies than the 0.45, 0.85, and 1.05 mixing ratios.

The system became brittle with a rapid gelation time. When the composition ratio exceeded 0.65, the system could not form a toughened network structure because of bleeding or the effects of unreactive NMA.<sup>20</sup>

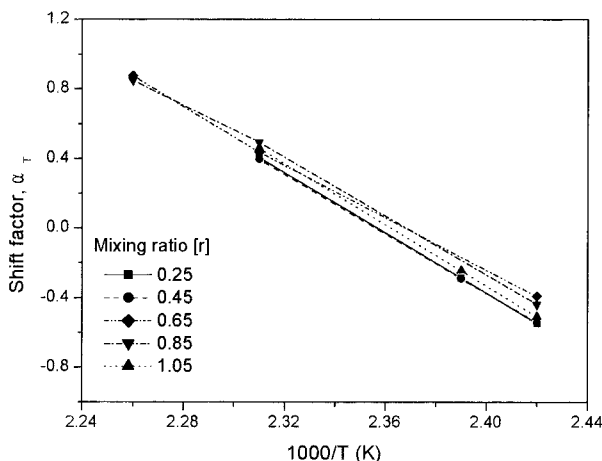
### Crosslinking Activation Energy

The apparent activation energy for the crosslinking reaction can be calculated from knowledge of the gel time at different temperatures.<sup>21</sup> The increase in conversion in the region where the crosslinking is kinetically controlled can be expressed by a constitutive equation in the following manner<sup>22</sup>:

$$\frac{dx}{dt} = Af(x)\exp\left(\frac{-E_c}{RT}\right) \quad (5)$$

Integrating eq. (5) at constant temperature and taking natural logarithms,





**Figure 6** Plots of the shift factor versus the curing temperature for this system.

$$\ln t_{\text{gel}} = \ln \int_0^{x_{\text{gel}}} \frac{dx}{f(x)} - \ln A + \frac{E_c}{RT} \quad (6)$$

where  $E_c$  is the crosslinking activation energy,  $t_{\text{gel}}$  is the gelation time,  $R$  is the gas constant, and  $T$  is the cure temperature.

Because the network structure is a unique function of conversion, the conversion at the gel point can be considered as a constant and independent of the temperature. Therefore, eq. (6) can be rewritten as

$$\ln t_{\text{gel}} = \frac{E_c}{RT} \quad (7)$$

Equation (7) can be written for an arbitrary reference temperature,  $T_r = 150^\circ\text{C}$ , as

$$\ln t_{\text{gel},r} = \frac{E_c}{RT_r} + \text{const} \quad (8)$$

By subtracting eq. (7) from eq. (8), a shift factor ( $\alpha_T$ ) may be defined as

$$\alpha_T = \ln t_{\text{gel},r}(T_r) - \ln t_{\text{gel}}(T) = \frac{E_c}{RT_r} - \frac{E_c}{RT} \quad (9)$$

The  $E_c$  can be calculated from the slope of a plot of the shift factors against  $(1/T)$ , as shown in Figure 6. As an experimental result, the  $\alpha_T$  values calculated from different cure temperatures and crosslinking activation energies are shown in Table II. Observe in the table that the  $E_c$  increased on increasing the anhydride content and showed

a maximum value at a mixing ratio of 0.65. The values for this system were found to be from 65 to 73 kJ/mol and correlated with typical values reported for the crosslinking of DGEBA-based epoxy resins.<sup>23</sup> Therefore, it can be expected that the same catalytic mechanism (i.e., catalysis by hydroxyls) is operative in DGEBA-based epoxies and anhydride-cured epoxies.

## CONCLUSION

The thermal latency, viscosity profiles, and viscoelastic properties for an epoxy resin cured with anhydride hardener and catalyzed by BPH were studied near the gel point in the temperature range between 140 and 170°C.

The BPH acted as a good thermal latent catalyst during the cure. The reactivity and conversion rate decreased when the anhydride content was increased because of its poor reactivity in nature. Because of the composition dependence of the initiation reaction, the growing behavior of the viscosity and the structural changes, such as linear growth and gelation, depended on the anhydride concentration and cure temperature.

The crosslinking activation energies were determined from the Arrhenius plot based on the shift factor and cure temperature. As a result, the maximum gelation time and crosslinking activation energy was observed at the mixing ratio of

**Table II** Shift Factor ( $\alpha_T$ ) and Crosslinking Activation Energy ( $E_c$ ) of This System

Mixing Ratio	Reaction Temp. (°C)	$\alpha_T$	$E_c$ (kJ/mol)
0.25	140	-0.39	65
	145	0.43	
	160	0.87	
0.45	140	-0.44	67
	145	0.49	
	160	0.85	
0.65	140	-0.51	73
	145	-0.25	
	160	0.46	
0.85	140	-0.55	70
	160	-0.29	
	170	0.39	
1.05	140	-0.55	72
	160	-0.29	
	170	0.41	

0.65. This revealed that the optimum condition to make a compact crosslinking structure without a side reaction was a mixing ratio of 0.65 in this system.

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