

# Vitrification and Further Structural Relaxation in the Isothermal Curing of an Epoxy Resin

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## SYNOPSIS

Isothermal curing of an epoxy resin based on diglycidyl ether of bisphenol A, using a hardener derived from phthalic anhydride, has been performed at curing temperatures between 30 and 130°C. Samples were cured isothermally at various intervals of time and analyzed by differential scanning calorimetry (DSC), the glass transition temperature  $T_g$ , and the conversion degree being determined by the residual enthalpy technique. The vitrification phenomenon and a further structural relaxation process, occurring at curing temperatures ( $T_c$ ) lower than the maximum  $T_g$  (109°C), at which  $T_g$  equalizes  $T_c$ , have been studied at curing temperatures between 30 and 100°C. The structural relaxation process is analyzed by the endothermic peak that appears superposed on  $T_g$  in dynamic DSC scans. The area of this peak ( $Q$ ) is a measure of the recovery enthalpy, and thus of the extent of the relaxation process. This process begins at higher curing times ( $t_c$ ) when  $T_c$  decreases because the vitrification of the system starts later. Both the enthalpy recovery ( $Q$ ) and the temperature of the endothermic peak ( $T_m$ ) increase with the annealing time ( $t_a$ ), calculated as the difference between  $t_c$  and the time in which vitrification occurs, and tend to have a limiting value due to the fact that the system loses mobility when the free volume decreases during its asymptotic approach toward the metastable equilibrium state. Furthermore, the dependence of  $Q$  and  $T_m$  on  $t_a$  at different  $T_c$  shows that the relaxation process in partially cured resins depends on the conversion degree of the system and consequently on the crosslinking density of the network.

## INTRODUCTION

Epoxy resins are widely used as polymeric materials, as polymer matrices for composite materials, and as adhesives. The conversion of linear epoxy resins to three-dimensional crosslinked and thermosetting materials is performed by curing reaction. Epoxy resins are commonly cured by amines and anhydrides, with or without the use of catalysts and accelerators. Curing epoxy resins with cyclic anhydrides is an important process in the manufacture of high-grade electrical insulation materials whose exothermic reaction and polymerization mechanisms have been recently analyzed in various kinds of epoxy resins.<sup>1-4</sup>

Curing kinetics of epoxy resins has been studied with different techniques, such as infrared spectroscopy (IR), Fourier transform IR, thermal analysis as differential scanning calorimetry (DSC), direct current conductivity, etc. Recently, Prime<sup>5</sup> and Barton<sup>6</sup> have published excellent reviews of applications of DSC to the study of curing kinetics.

However, the isothermal curing reaction of an epoxy resin is usually complicated as a consequence of the interaction of the chemical kinetics of curing with other physical processes, causing important changes in the macroscopic physical properties of the reacting system.<sup>7,8</sup> These processes are phase separation, gelation, vitrification, and devitrification.

According to Flory,<sup>9</sup> gelation is the incipient formation of an infinite network in the first stages of curing. At this point the system changes its macroscopic properties. Its occurrence depends on the

functionality of the resin and stoichiometry of the components but not on experimental conditions such as curing temperature.

Vitrification involves a physical transformation from a liquid or rubbery state to a glassy state as a result of an increase in the crosslinking density of the material. It is well known that this phenomenon occurs when the glass transition temperature,  $T_g$ , becomes equal to the curing temperature  $T_c$ . The system is in the glassy state when  $T_c$  becomes higher than  $T_g$ . Vitrification dramatically affects the progress of curing reaction since the degree of conversion becomes practically quenched.<sup>7,8,10</sup>

In addition, when the system is annealed at a temperature lower than  $T_g$ , the structural relaxation process or physical aging appears<sup>11</sup> due to the fact that the glassy state is not an equilibrium thermodynamic state, and its properties, such as volume, entropy, and enthalpy, decrease with time.<sup>12,13</sup>

Finally, devitrification of the material occurs when  $T_g$  decreases through the isothermal temperature as a consequence of the thermal degradation.<sup>7,14</sup>

This paper studies the conditions of temperature and time of curing of an epoxy resin at which the vitrification process appears and, also, the effect of the extent of the curing reaction on the structural relaxation process. The differential scanning calorimetry technique is used to monitor the curing reaction and to evaluate the thermal properties of the resin during the curing.

## EXPERIMENTAL

### Materials

The epoxy resin used in this study was a diglycidyl ether of bisphenol A (DGEBA) modified type (Ciba-Geigy Araldite CY 225) with an epoxy content between 5.0 and 5.3 mol/kg. A hardener derived from phthalic anhydride with an accelerator (Ciba-Geigy Hardener HY 225) was used to cure the resin.<sup>15</sup>

### Curing Procedure

Resin and hardener with an accelerator were used as received and mixed at a weight ratio of 10 : 8. The mixture was stirred at room temperature for 20 min, and then was degassed in a vacuum chamber for 15 min. Samples were enclosed in aluminium DSC pans, introduced in Pyrex tubes under a nitrogen atmosphere, and placed in thermostatic baths at curing temperatures  $T_c$  between 30 and 130°C for

various periods of curing time  $t_c$ . For short curing times (less than 2 h), the samples were cured inside the DSC module.

### Differential Scanning Calorimetry

A Mettler Thermoanalyzer TA3000 with a differential scanning calorimetry DSC 30 module, previously calibrated with indium, lead, and zinc standards, was used to measure the heat flow as a function of temperature. The thermal history to which samples were subjected was as follows: After the isothermal curing, the resin samples were cooled freely to room temperature, introduced in the DSC module, cooled to  $-80^\circ\text{C}$ , and then scanned at a heating rate of 10 K/min to  $280^\circ\text{C}$ , under nitrogen atmosphere.

The glass transition temperature  $T_g$  and the residual enthalpy of curing  $\Delta H_R$  were determined in each dynamic DSC curve.  $T_g$  was measured as the half-way point of  $\Delta C_p$ , when the polymer passes from the glassy state to the rubbery state. An apparent degree of conversion of the curing reaction is calculated from the residual enthalpy  $\Delta H_R$  of the partially cured resin and from the total enthalpy of reaction  $\Delta H_T$  (297.2 J/g) corresponding to one "as-mixed" sample without curing treatment:

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

After the first scan, the sample was cooled freely in the DSC module and a second scan was carried out from 20 to  $130^\circ\text{C}$  at the same heating rate. This second scan only gives the glass transition temperature of the resin almost fully cured, without any noticeable residual enthalpy of curing.

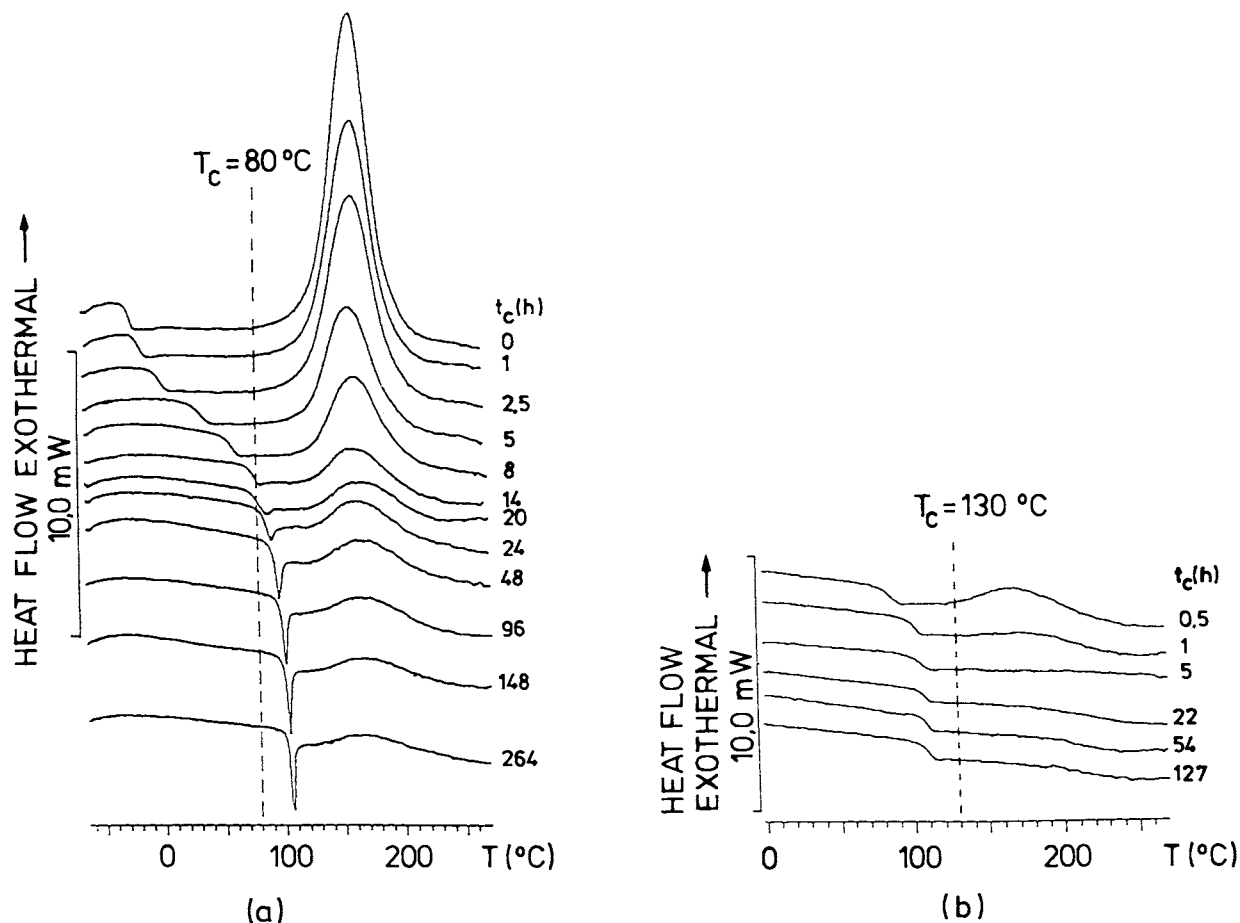
### Thermogravimetric Analysis

Loss of weight was measured using a thermogravimetric analyzer (TG-50 module) coupled to a Mettler Thermoanalyzer TA3000. Temperature scans (50 to  $600^\circ\text{C}$ ) were performed by heating uncured mixtures of resin and hardener at a heating rate of 10 K/min in a nitrogen gas flow (200 mL/min).

## RESULTS AND DISCUSSION

### DSC Thermograms

For a given curing temperature, the temperature of glass transition increases and the residual heat of curing decreases with the curing time as a conse-



**Figure 1** DSC thermograms of samples cured at temperatures of (a) 80°C and (b) 130°C for different curing times.

quence of the increase in the crosslinking density in the network of the material. Both effects can be observed in the DSC thermograms in Figure 1 at curing temperatures of 80 and 130°C.

The vitrification process is observed in DSC thermograms for a curing temperature of 80°C [Fig. 1(a)], which is lower than the maximum glass transition  $T_{g\infty}$  of the resin, whose value is about 109°C.<sup>16</sup> When  $T_g$  equalizes  $T_c$ , the system vitrifies and a peak superposed on  $T_g$  appears as a consequence of the structural relaxation process. Under these conditions residual curing starts just beyond the endothermic relaxation peak. The maximum of curing exotherm rises slightly from 163 to 165°C (for  $T_g < T_c$ ) to 168–172°C (for  $T_g \geq T_c$ ). These effects have also been observed in amine-cured DGEBA.<sup>17</sup>

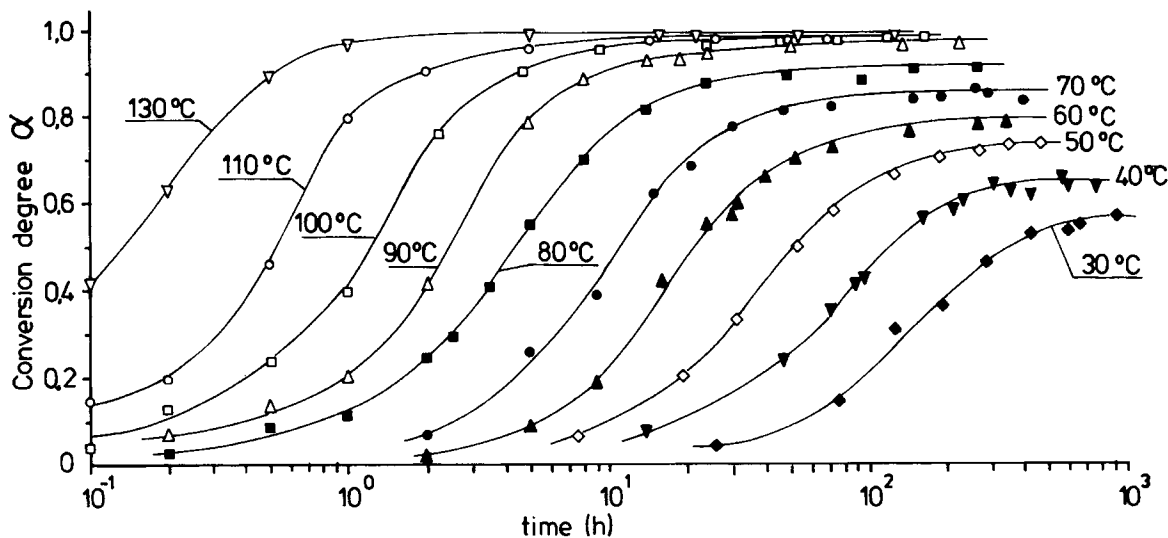
When the curing temperature is higher than  $T_{g\infty}$ , the curing reaction occurs in the rubbery state. Under these conditions, as the DSC thermograms show in Figure 1(b) obtained at  $T_c = 130^\circ\text{C}$  for different

curing times, vitrification, and further structural relaxation no longer appears.

#### Dependence of the Conversion Degree with the Curing Conditions

For a given curing temperature, the conversion degree increases with a sigmoidal shape and tends to have a limiting conversion degree, the value of which depends on the temperature of curing (Fig. 2).

When  $T_c < T_{g\infty}$ , isothermal curing progresses through two different curing stages. The first one is controlled by the chemical reactivity of groups, the curing reaction develops in liquid state and the  $T_g$  of the system is lower than the  $T_c$ . The reaction progresses at a rate depending on  $T_c$  until the  $T_g$  equals  $T_c$ . On reaching this point, the second stage of curing starts: the system vitrifies and the reaction rate decreases considerably until the reaction becomes practically quenched due to the fact that the



**Figure 2** Dependence of the degree of conversion on curing time for different curing temperatures.

mobility of the reacting groups becomes very restricted. The reaction time required to reach  $T_g = T_c$  is named vitrification time  $t_v$ . Its values at different  $T_c$ , obtained from  $T_g$  data versus time, are shown in Figure 4. When the system reaches the glassy state, the chemical reaction becomes controlled by diffusion.<sup>8,10,17-19</sup> The slow segmental motions caused by the structural relaxation process are the only ones permitted, and the conversion degree tends to have a practically constant limiting value  $\alpha_\infty$ , thus preventing the full conversion of the chemical reaction to be reached.

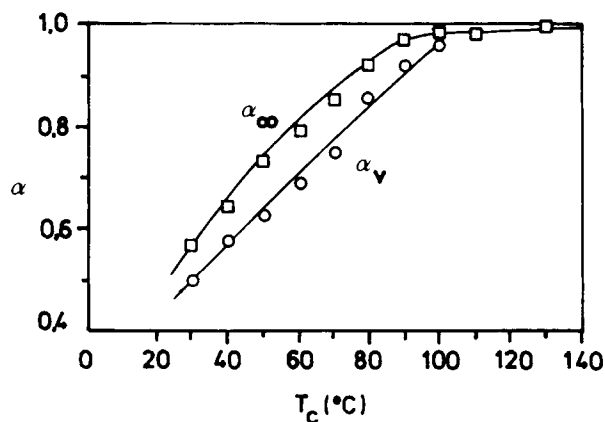
Figure 3 shows these two stages in a diagram of conversion degree versus the curing temperature. The conversion degree at vitrification time,  $\alpha_v$ , determines the progress of curing controlled by chemical reaction. The difference between  $\alpha_\infty$  and  $\alpha_v$  shows the progress of the crosslinking reaction in the glassy state controlled by diffusion. When  $T_c > T_{g\infty}$ , the curing reaction is only controlled by chemical reactivity, the rate being faster as the isothermal curves of 110 and 130°C show in Figure 2.

#### Dependence of the Glass Transition Temperature on the Curing Conditions

As stated earlier, during the isothermal curing at  $T_c$ , the  $T_g$  of the system has been noticed to continue increasing with the curing time  $t_c$  as a consequence of the increase in the crosslinking density of the network. For samples cured at  $T_c < T_{g\infty}$ , deceleration has been observed to occur near to  $T_g = T_c$  as a consequence of the system vitrification (Fig. 4). Be-

yond the vitrification time,  $T_g$  becomes higher than the curing temperature, and as a result the system is annealed at a lower temperature than  $T_g$  and a structural relaxation process or physical aging begins.<sup>11-13</sup> Then  $T_g$  increases slowly with the annealing time at a temperature of  $T_c < T_g$  and approaches asymptotically to a limiting value depending on  $T_c$ . At  $T_c = 100^\circ\text{C}$ , the limiting  $T_g$  is reached at about  $109^\circ\text{C}$ , but at  $T_c = 70^\circ\text{C}$  this limiting value can rise to  $92^\circ\text{C}$ . At low  $T_c$  (30 or  $40^\circ\text{C}$ ), the limiting  $T_g$  was not reached in the times tried in this study.

If the  $T_g$ - $t_c$  curves are shifted along the logarithmic time scale by an amount of  $\log a_T$  to superpose at a given reference temperature  $T_0$ , a common



**Figure 3** Dependence of limiting conversion degree  $\alpha_\infty$  ( $\square$ ) and conversion degree at vitrification time  $\alpha_v$  ( $\circ$ ) on the curing temperature.

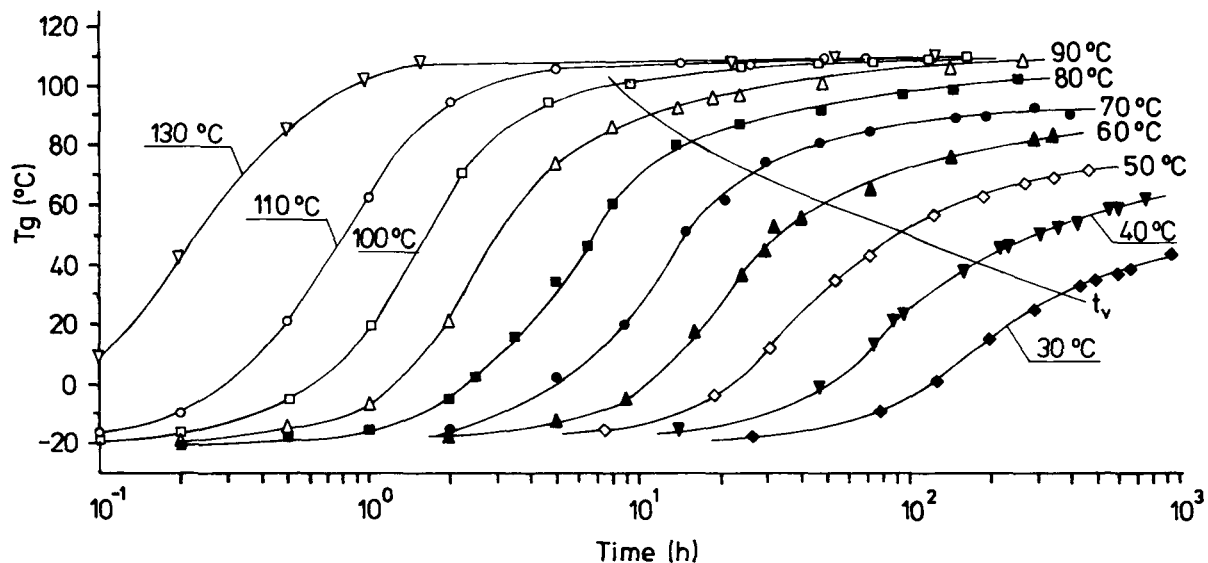


Figure 4 Variation of  $T_g$  with the curing time at different curing temperatures.

master curve can be obtained at the lower  $T_g$  temperature end. The resulting curve with  $T_0 = 80^\circ\text{C}$  is shown in Figure 5. An acceptable good superposition is obtained for curing times lower than  $t_v$  and  $T_g$  values lower than about  $T_c - 20^\circ\text{C}$ , where the curing reaction is controlled by chemical kinetics. Deviations to the master curve occur near the vitrification of the system, and obviously at  $T_g > T_c$  when the reaction is controlled by diffusion. A sim-

ilar behavior has been observed by Gillham and co-workers<sup>19,20</sup> in amine-cured DGEBA. Recently, Choy and Plazek<sup>21</sup> obtained a master curve of fictive temperatures vs.  $\log t_c$ , applying a scaling factor to fictive temperature and a shift factor to time.

The shift factors  $a_T$  listed in Table I follow an Arrhenius relationship:

$$\log a_T = 10.92 - 3.84 \times 10^3/T$$

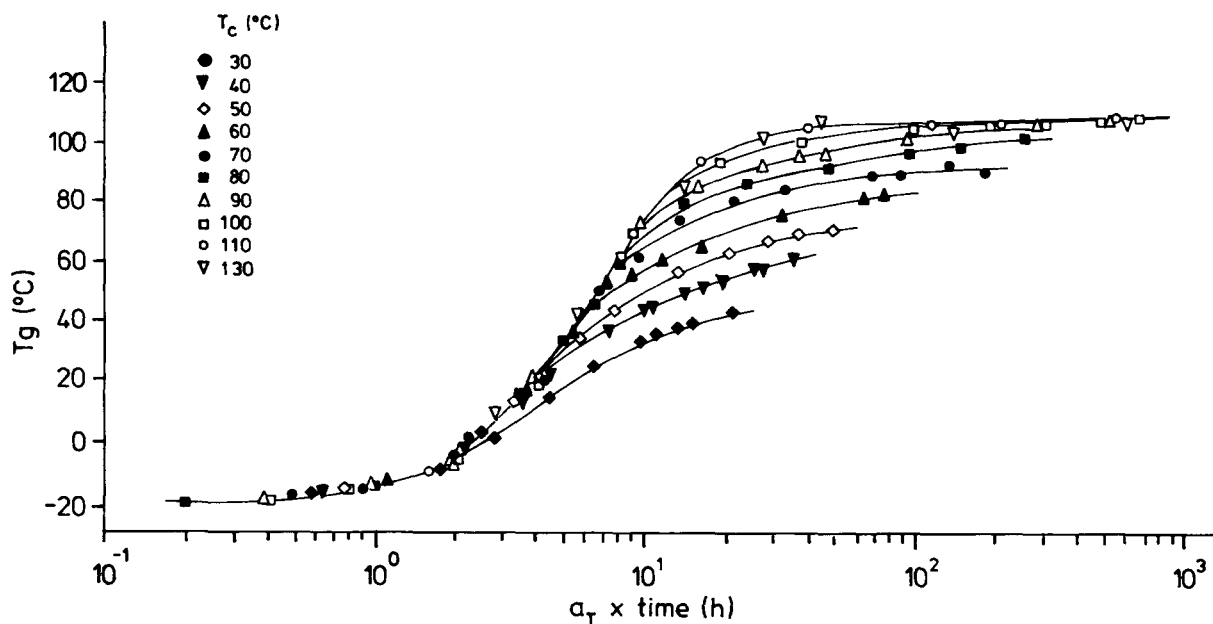


Figure 5 Time-temperature superposition:  $T_g$  versus  $\log$  (shifted) time at different curing temperatures for a reference temperature of  $T_0 = 80^\circ\text{C}$ .

**Table I** Shift Factors at Different  $T_c$  Referred to  $T_0 = 80^\circ\text{C}$ 

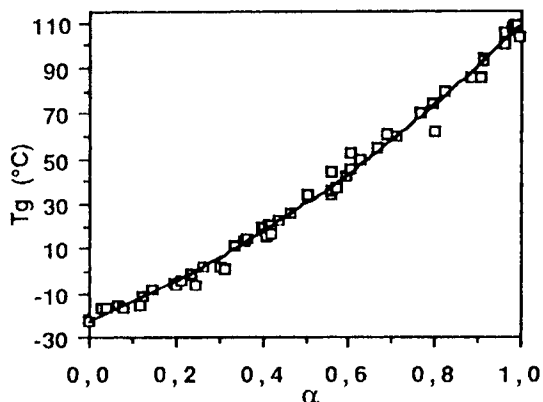
$T_c$ ( $^\circ\text{C}$ )	$a_T$	$a_\alpha$
130	29.9	—
110	8.3	7.6
100	4.1	3.4
90	2	1.75
80	1	1
70	0.46	0.39
60	0.23	0.22
50	0.107	0.09
40	0.047	0.043
30	0.021	—

with a determination coefficient of  $r^2 = 0.998$ . The slope yields an apparent activation energy of 17.5 kcal/mol (73.3 kJ/mol). Similarly, the same procedure can be applied to the conversion degree–time curves in Figure 2. Shift factors  $a_\alpha$  obtained are shown in Table I. The Arrhenius relationship is

$$\log a_\alpha = 10.79 - 3.82 \times 10^3 / T$$

with a determination coefficient of  $r^2 = 0.997$ . The slope yields an apparent activation energy of 17.4 kcal/mol (72.7 kJ/mol), which corresponds to the overall curing reaction.

The fact that these two activation energy values are identical shows the existence of a good correspondence between the values of  $T_g$  and the degree of conversion. On the other hand, the dependence of  $T_g$  values (obtained without physical aging effects at  $t_c < t_v$ ) on the conversion degree (Fig. 6) shows that  $T_g$  is an index of the reaction extent,<sup>19,20,22,23</sup>

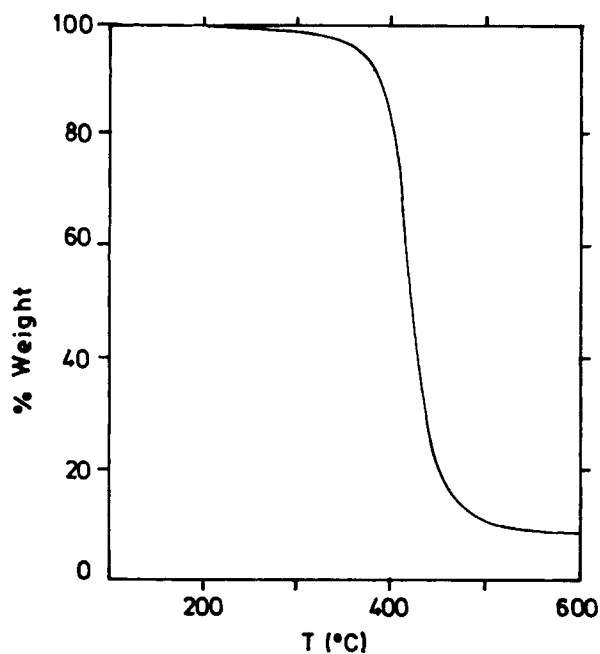
**Figure 6** Dependence of  $T_g$  on degree of conversion from various curing temperatures. The  $T_g$  values represented are without physical aging effects, corresponding to  $T_g < T_c$ .

regardless of the curing temperature. The existence of this relation between  $T_g$  and  $\alpha$  clearly shows that the same reaction mechanism is followed in the range of tested curing temperatures between 30 and  $130^\circ\text{C}$ .

The  $T_g$  values of the second scan, after the first heating up to  $280^\circ\text{C}$ , are slightly lower than  $T_{g\infty}$ . Their average values range between  $100^\circ\text{C}$  (for  $T_c < 100^\circ\text{C}$ ) and  $105^\circ\text{C}$  (for  $T_c \geq 100^\circ\text{C}$ ). The higher  $T_g$  value obtained on the second scan is lower than  $109^\circ\text{C}$ , the maximum glass transition temperature,  $T_{g\infty}$ , as indicated earlier. This decrease is possibly due to the beginning of the thermal degradation that the resin may undergo when heating up to  $280^\circ\text{C}$  in the first scan. Figure 7 shows the thermogravimetric (TG) temperature scan of the uncured resin–hardener mixture; here it is clearly seen that the weight loss begins at  $250$ – $300^\circ\text{C}$ , when the resin is almost fully cured, and concludes at  $550^\circ\text{C}$  with a substantial weight loss (90%). The initial thermal degradation between  $250$  and  $300^\circ\text{C}$  may lead to a slight decrease in the crosslinking density, and therefore of the  $T_g$  of the cured resin.

#### Analysis of the Structural Relaxation Process

It is well known that the glassy state is not a thermodynamic equilibrium state, and so the system

**Figure 7** TG temperature scan for uncured resin–hardener system: weight percent versus temperature with a heating rate of 10 K/min. Initial weight = 8.67 mg.

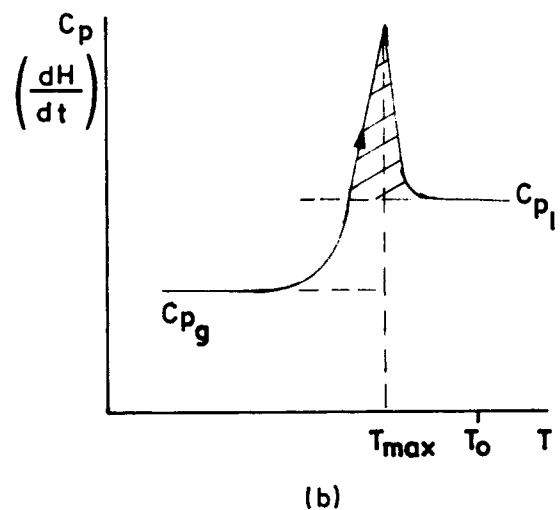
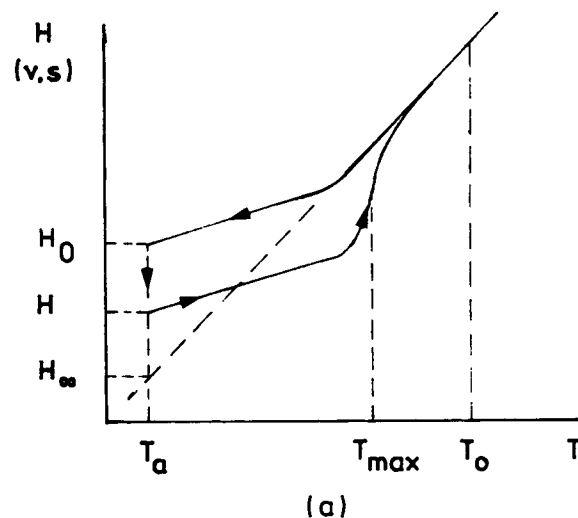
tends to evolve to an equilibrium (metastable) state, its properties such as volume, enthalpy, and entropy decreasing with time [see the schematic diagram in Fig. 8(a)]. The free volume of the system is reduced and consequently the molecular mobility of the chain segments decreases.

When the material annealed at  $T_a$  during an annealing time  $t_a$  is submitted to heating up to a temperature above the glass transition zone, the molecular mobility increases and the system recovers its equilibrium properties at an established temperature, as shown in Figure 8(a). Additionally, an endothermic peak superposed on  $T_g$  appears in the derivative curve. In the diagram of Figure 8(b) the endothermic peak, which appears in DSC thermograms (heat capacity or heat flow versus temperature), is represented schematically. In thermoplastic polymers,<sup>11-13,24-27</sup> fully cured resins,<sup>28-31</sup> and partially cured resins,<sup>32</sup> the intensity, position, and area of the endothermic peak depend on the annealing time at  $T_a < T_g$ .

The area of the relaxation peak ( $Q$ ) in the heat flow versus temperature scan, taking as the baseline that of the extrapolated liquid or rubbery line, is a measure of the recovery of enthalpy<sup>24,25</sup> and thus of the extent of the relaxation process taking place at the isothermal temperature of curing ( $T_c < T_g$ ) in a given time. In a partially cured resin, the occurrence of the structural relaxation process depends on  $T_c$ , as it starts when the system vitrifies at the vitrification time  $t_v$ . For high values of  $T_c$  the process begins at low values of  $t_v$ , and vice versa as shown in Figure 4.

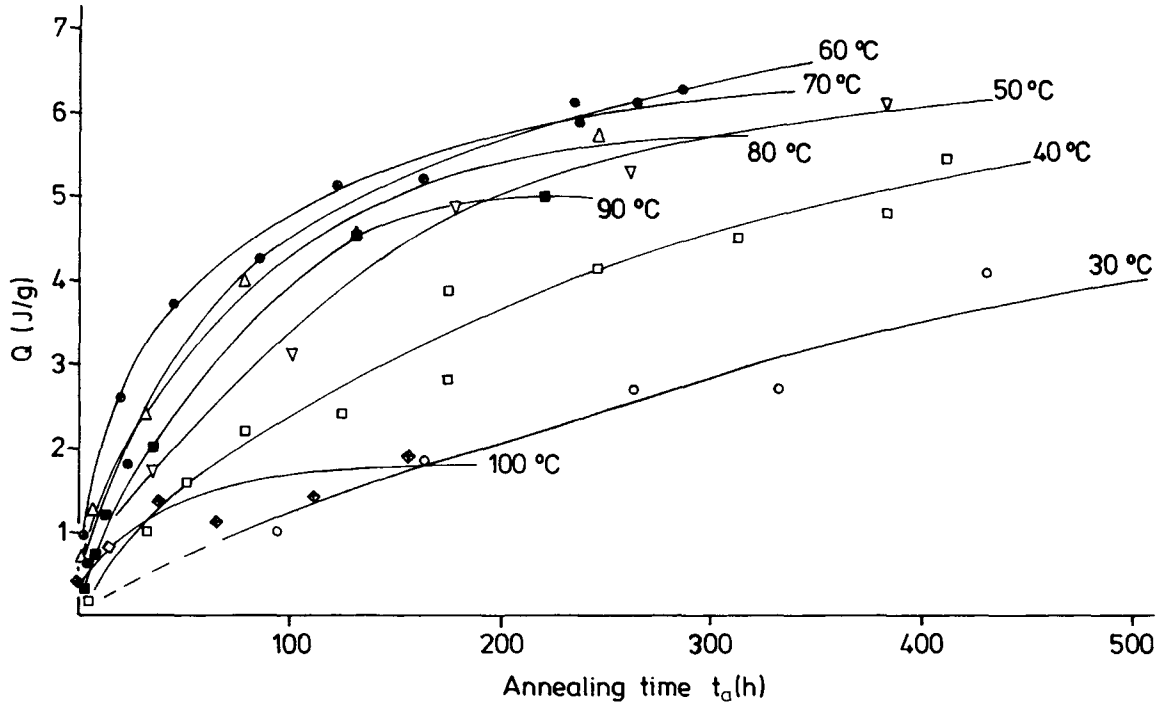
The dependence of recovery enthalpy ( $Q$ ) on the annealing time ( $t_a$ ), calculated as the difference between the curing time and the vitrification time ( $t_a = t_c - t_v$ ), is shown in Figure 9. Its values depend on both the annealing or curing temperature and the annealing time. For a curing temperature,  $Q$  increases with annealing time as in thermoplastic and thermosetting polymers. The rate of the relaxation process of the system ( $dQ/dt_a$ ) tends to decrease with the annealing time according the annealing temperature, because the system loses mobility as free volume decreases during its asymptotic approach toward the metastable equilibrium state.

For curing temperatures equal to or higher than 70°C,  $Q$  increases with  $t_a$  and tends to have a maximum value,  $Q_m$ , which depends on  $T_c$ , as shown in Figure 9. For  $T_c = 60^\circ\text{C}$  we estimated a  $Q_m$  of about 7 J/g, but for  $T_c$  values lower than 60°C we have no results of  $Q_m$  since the total curing times ( $t_c = t_v + t_a$ ) required are very high. In Figure 9 we can see that for  $T_c \geq 70^\circ\text{C}$ ,  $Q_m$  decreases with the curing



**Figure 8** Schematic diagrams of (a) enthalpy-temperature and (b)  $C_p$  (or  $dH/dt$ )-temperature illustrating structural relaxation effects.

time. The kinetics of the structural relaxation slows down as  $T_c$  increases. This means that the maximum value of the extent of the relaxation process decreases with  $T_c$  because the segmental mobility of the system becomes more restricted as a consequence of the increase in the limiting conversion degree and therefore of the increase in the crosslinking density of the network. This effect is plotted in Figure 10:  $Q_m$  decreases with the limiting degree of conversion. However, a great decrease in  $Q_m$  is observed when  $T_c$  passes from 90 to 100°C, which may be due to the proximity of the glass transition interval [at  $T_c = 100^\circ\text{C}$ ,  $T_{g(\text{onset})}$  is about 95°C and  $T_{g(\text{end})}$  about 122°C].

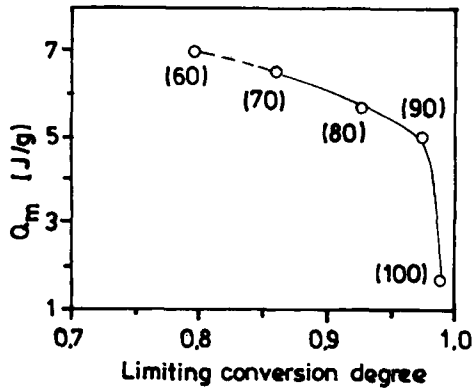


**Figure 9** Dependence of enthalpy recovery  $Q$  on the annealing time  $t_a$  ( $t_a = t_c - t_v$ ) for different curing temperatures: 30 (○), 40 (□), 50 (▽), 60 (●), 70 (⊕), 80 (△), 90 (■), and 100°C (⊕).

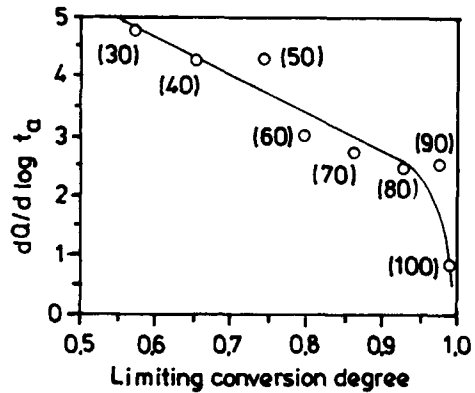
In thermoplastics<sup>24-27</sup> and thermosets,<sup>28-31</sup> a linear relationship is observed in the dependence of the enthalpy recovery versus the logarithm of the annealing time when a wide range of  $t_a$  is applied. The slope ( $dQ/d \log t_a$ ) represents the overall change in the enthalpy recovery when the annealing time increases by one decade; in fact this could be a characteristic parameter of the relaxation process at a given annealing temperature. Similar param-

eters have been applied in physical aging studies by creep,<sup>11</sup> volume relaxation,<sup>33</sup> and enthalpy relaxation.<sup>34</sup> In the epoxy system studied, this parameter tends to decrease with the annealing temperature and also with the limiting conversion degree, as Figure 11 shows, while in thermoplastic polymers, a step increase is first observed, later passing through a maximum and finally decreasing near  $T_g$ .<sup>11,33,34</sup>

Similarly, the position of the relaxation peak  $T_m$

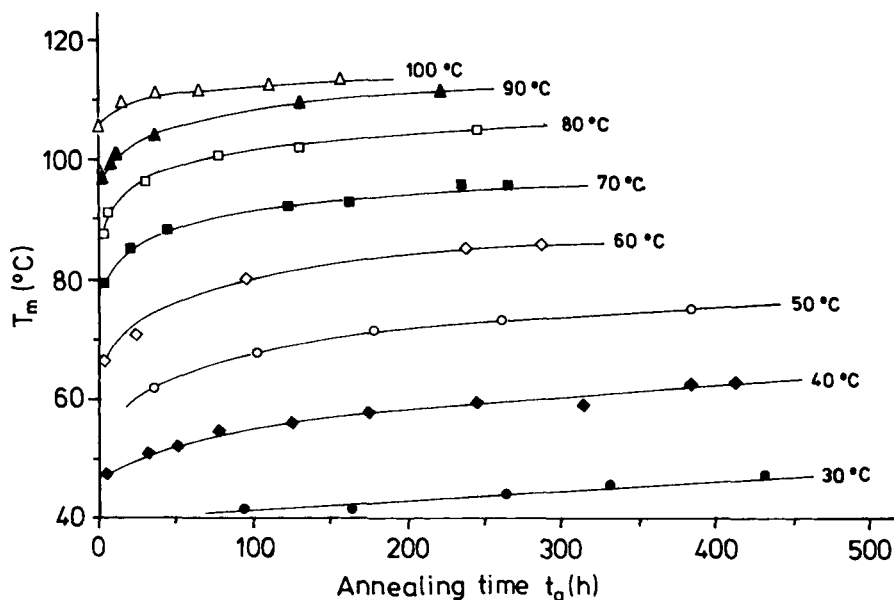


**Figure 10** Dependence of  $Q$  maximum ( $Q_m$ ) on the limiting conversion degree. Curing temperature values are indicated in brackets. The  $Q_m$  value for  $T_c = 60^\circ\text{C}$  is approximate.



**Figure 11** Representation of  $dQ/d \log t_a$  with limiting conversion degree. Curing temperature values are indicated in brackets.





**Figure 12** Dependence of the peak temperature ( $T_m$ ) on the annealing time  $t_a$  ( $t_a = t_c - t_v$ ) at the stated curing temperatures.

increases with the annealing time as a consequence of the progress of the relaxation process, as has been shown in other polymers<sup>24-32</sup> and tends to have a limiting value depending on  $T_c$  (Fig. 12). Alternatively,  $T_m$  values corresponding to equal values of annealing time increase with  $T_c$  due to the increase in the conversion degree or the crosslinking density of the system, which causes a shift of the glass transition interval to higher temperatures.

## CONCLUSIONS

Isothermal curing at temperatures lower than the maximum  $T_g$  of the resin shows two curing stages: the first one is controlled by chemical reactivity and proceeds until  $T_g$  equalizes  $T_c$ . On reaching this point, the system becomes vitrified while the second curing stage begins; here, the system is in the glassy state and the reaction becomes mostly quenched, which makes the curing reaction become controlled by diffusion. Due to phenomenon of vitrification, the conversion degree tends to have a limiting value, which depends on  $T_c$ . At the same time,  $T_g$  increases, although slowly, as a result of the structural relaxation process of the system and approaches asymptotically closer to a limiting value depending on  $T_c$ .

This relaxation process is analyzed by the endothermic peak superposed on  $T_g$  in dynamic DSC scans. The area of this peak ( $Q$ ) is a measure of the recovery enthalpy, and thus of the extent of the re-

laxation process. This process begins at a higher  $t_c$  when  $T_c$  decreases because the vitrification of the system starts later. The rate of structural relaxation of the system depends on both the annealing time and the annealing temperature. The system loses mobility as the free volume decreases during its asymptotic approach toward a metastable equilibrium state, and as a result the rate of relaxation decreases with the annealing time and  $Q$  tends to have a maximum value.

For curing temperatures equal to or higher than 70°C, the maximum value of the enthalpy recovery ( $Q_m$ ) decreases with  $T_c$  because the limiting conversion degree of the system increases; the crosslinking density of the network also increases, and consequently the segmental mobility becomes more restricted.

Finally, the dependence of  $Q$  on the logarithm of  $t_a$  is a linear relationship whose slope always decreases with the annealing temperature, unlike the behavior of thermoplastic polymers for which this slope shows a steep increase passes through a maximum, and decreases near to  $T_g$ . This different behavior in the structural relaxation with the annealing temperature is a consequence of the gradual changes in the reticulation degree and also of the network crosslinking density in the partially cured resin.

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## REFERENCES

1. K. Kretzschmar and K. W. Hoffmann, *Thermochim. Acta*, **94**, 105 (1985).
2. B. Steinmann, *J. Appl. Polym. Sci.*, **37**, 1753 (1989).
3. B. Steinmann, *J. Appl. Polym. Sci.*, **39**, 2005 (1990).
4. J. Vogt, Communication in *Symposium on Chemical Thermodynamics, Calorimetry and Thermal Analysis*, Basel (1989).
5. R. B. Prime, in *Thermal Characterization of Polymeric Materials*, E. A. Turi Ed., Academic Press, New York, 1981, Chap. 5, pp. 435-569.
6. J. M. Barton, in *Epoxy Resins and Composites I*, K. Dusek Ed., *Advances in Polymer Science*, Vol. 72, Springer-Verlag, Berlin, 1985, pp. 112-154.
7. J. B. Enns and J. K. Gillham, *J. Appl. Polym. Sci.*, **28**, 2567 (1983).
8. J. K. Gillham, *Polym. Eng. Sci.*, **26**, 1429 (1986).
9. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1967, Chap IX.
10. E. F. Oleinik, *Epoxy Resins and Composites IV*, K. Dusek, Ed., *Advances in Polymer Science*, Vol. 80, Springer-Verlag, Berlin, 1986, pp. 49-99.
11. L. C. E. Struik, *Physical Aging in Amorphous Polymers and other Materials*, Elsevier, Amsterdam, 1978.
12. A. J. Kovacs, *Adv. Poly Sci.*, **3**, 394 (1963).
13. G. W. Scherer, *Relaxation in Glass and Composites*, Wiley, New York, 1986.
14. S. Gan and J. K. Gillham, *J. Appl. Polym. Sci.*, **37**, 803 (1989).
15. Ciba-Geigy, publication num. 24504/f, Switzerland (1979).
16. S. Montserrat, Poster Presentation in *Reunión Nacional de Materiales Polímeros*, Valencia (1989).
17. H. E. Bair, *Polym. Preprints*, **26**, 10 (1985).
18. I. Havlicek and K. Dusek, in *Crosslinked Epoxies*, B. Sedlacek and J. Kahovec Eds., Walter de Gruyter, Berlin, 1987, pp. 417-424.
19. G. Wisanrakkit and J. K. Gillham, *J. Coating Tech.*, **62**, 35 (1990).
20. K. P. Pang and J. K. Gillham, *J. Appl. Polym. Sci.*, **37**, 1969 (1989).
21. I. C. Choy and D. J. Plazek, *J. Polym. Sci., Polym. Phys.*, **24**, 1303 (1986).
22. K. P. Pang and J. K. Gillham, *Am. Chem. Soc., Proc. Div. Polym. Mater., Sci. Eng.*, **55**, 64 (1986).
23. J. P. Pascault and R. J. J. Williams, *J. Polym. Sci., Polym. Phys.*, **28**, 85 (1990).
24. S. E. B. Petrie, *J. Macromol. Sci., Phys.*, **B12**, 225 (1975).
25. S. Montserrat and P. Cortés, *Makromol. Chem., Macromol. Symposia*, **20/21**, 389 (1988).
26. K. H. Illers, *Makromol. Chem.*, **127**, 1 (1969).
27. C. R. Foltz and P. V. McKinney, *J. Appl. Polym. Sci.*, **13**, 2235 (1969).
28. Z. H. Ophir, J. A. Emerson, and G. L. Wilkes, *J. Appl. Phys.*, **49**, 5032 (1978).
29. E. S. W. Kong, in *Epoxy Resin Chemistry II*, Am. Chem. Soc. Symposium Series, Vol. 221, American Chemical Society, Washington, DC, 1983, pp. 171-191.
30. E. S. W. Kong, in *Epoxy Resins and Composites IV*, K. Dusek, Ed., *Advances in Polymer Science*, Vol. 80, Springer-Verlag, Berlin, 1986, pp. 126-171.
31. J. Mijovic and K. F. Liu, *J. Appl. Polym. Sci.*, **32**, 3211 (1986).
32. D. J. Plazek and Z. N. Frund, *J. Polym. Sci., Polym. Phys.*, **28**, 431 (1990).
33. R. Greiner and F. R. Schwarzl, *Rheol. Acta*, **23**, 378 (1984).
34. S. Montserrat, *Anales Física, B*, **83**, 87 (1987).

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