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Relaxation in partially cured samples of an epoxy resin and of the same resin modified with a carboxyl-terminated rubber

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Abstract

This study examines the relaxation process at different temperatures in partially cured samples of an epoxy resin and of the same resin modified with 11.1% carboxyl-terminated butadiene acrylonitrile copolymer (CTBN). A differential scanning calorimeter (DSC) was used, which enabled the relaxation enthalpy, the glass transition temperature (T_g) and the relaxation peak temperature to be found. CTBN modifies the cure reaction and the relaxation process of the epoxy resin. The study of the relaxation process has a practical interest in addition to a theoretical one. It is known that, with these thermosets, a fully cured sample cannot be obtained at the first step. The introduction of an elastomeric modifier is a normal way of increasing the toughness of these materials. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Physical aging; Thermosets; Rubber modifiers

1. Introduction

When an epoxy resin is isothermally cured, its molecular weight and its glass transition temperature (T_g) increase as a result of an increase in the crosslink density of the material. When the resin's T_g reaches the curing temperature, it vitrifies. This process involves a physical transformation from a liquid or rubbery state to a glassy state. As this is not a state of equilibrium, structural relaxation (physical aging) occurs. This is characterized by the decrease in some properties (volume, enthalpy [1], toughness [2]) with time. Densification (volume reduction) is a consequence of slow diffusion of segments within the polymer network [3].

If a vitrified sample of the resin is quenched in a DSC (differential scanning calorimeter) and heated at a certain rate, it reaches an endothermic peak superimposed on the glass transition, associated with the structural relaxation process in the sample. Fig. 1 shows the heating process of the sample (curve CXD): the maximum is point X, whose temperature is represented as T_P. When the endothermic peak has passed (point D), the process is stopped. The sample is then quenched another time and heated at the same rate as before. This time, the endothermic peak does not appear and we only see the glass transition (dashed line of Fig. 1); the temperature of the middle point (F) of this transition is the T_g of the sample [1]. Subtracting both curves we obtain the enthalpy relaxation (on the left the area is negative and on the right it is positive).

Fig. 2 shows sample enthalpy versus temperature, on integration of the heat flow of both curves over time. The curve CXD corresponds to the first scan and the curve EFD to the second one (in the opposite direction EFD represents the sample quenching made after the first scan). The difference between the enthalpies of points E and C is the relaxation enthalpy (in the first scan the sample absorbs energy and then the enthalpy of E is greater than that of C). The slope of the second scan changes at point F, whose temperature is T_g. The inflection point of the first scan (X) is the maximum shown in Fig. 1. If the curve DF (corresponding to the rubbery or liquid state of the sample) is extended to the left, the temperature at the intersection with the curve CD (corresponding to the glassy state of the sample) is the fictive temperature (T_f) of the sample [4]. This T_f is a hypothetical temperature at which the structure of the glassy state is in equilibrium with the structure of the liquid or rubbery state [5,6].

The enthalpies of the glassy state (H_g) and the liquid or rubbery state (H_l) are the same at T_f:

$$H_{gf} = H_{lf} \tag{1}$$

At constant pressure the difference between the enthalpies

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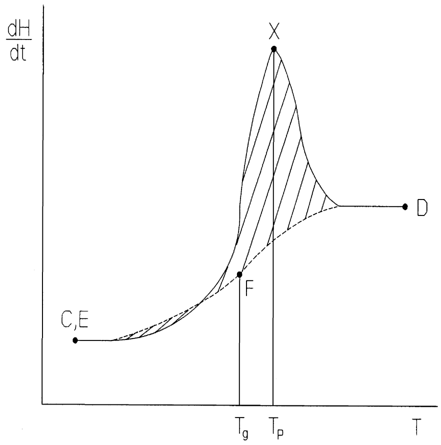

Fig. 1. Endothermic heat flow versus temperature for the first and second DSC scans of a sample with a structural relaxation.

of the glassy state at the temperatures T_f and T_1 (T_1 is smaller than T_f) can be expressed as:

$$H_{gf} - H_{g1} = \int_{T_1}^{T_f} C_{Pg}\,\mathrm{d}T \tag{2}$$

where C_P is the heat capacity at constant pressure.

Likewise, the difference between the enthalpies of the liquid or rubbery state at the temperatures T_2 and T_f (T_2 is greater than T_f) can be expressed as:

$$H_{l2} - H_{lf} = \int_{T_f}^{T_2} C_{Pl}\,\mathrm{d}T \tag{3}$$

Adding Eqs. (2) and (3) and applying Eq. (1):

$$H_{l2} - H_{g1} = \int_{T_1}^{T_f} C_{Pg}\,\mathrm{d}T + \int_{T_f}^{T_2} C_{Pl}\,\mathrm{d}T \tag{4}$$

If the heat capacity at a constant pressure ($C_P = \mathrm{d}H/\mathrm{d}T$) is multiplied and divided by dt, and as the heating rate in the DSC scans is $\phi = \mathrm{d}T/\mathrm{d}t$:

$$C_P = \frac{\mathrm{d}H}{\mathrm{d}T}\cdot\frac{\mathrm{d}t}{\mathrm{d}t} = \frac{\mathrm{d}H}{\mathrm{d}t}\cdot\frac{1}{\phi} \tag{5}$$

Replacing this expression in Eq. (4):

$$H_{l2} - H_{g1} = \int_{T_1}^{T_f} \frac{\mathrm{d}H_g}{\mathrm{d}t}\cdot\frac{1}{\phi}\,\mathrm{d}T + \int_{T_f}^{T_2} \frac{\mathrm{d}H_l}{\mathrm{d}t}\cdot\frac{1}{\phi}\,\mathrm{d}T \tag{6}$$

As ϕ is constant, rearranging this equation:

$$\phi\cdot(H_{l2} - H_{g1}) = \int_{T_1}^{T_f} \frac{\mathrm{d}H_g}{\mathrm{d}t}\,\mathrm{d}T + \int_{T_f}^{T_2} \frac{\mathrm{d}H_l}{\mathrm{d}t}\,\mathrm{d}T \tag{7}$$

The integral of the first DSC scan in Fig. 1 between the temperatures T_1 and T_2, as $\phi = \mathrm{d}T/\mathrm{d}t$, can be expressed as:

$$\int_{T_1}^{T_2} \frac{\mathrm{d}H}{\mathrm{d}t}\,\mathrm{d}T = \int_{T_1}^{T_2} \mathrm{d}H\cdot\phi = \phi\cdot(H_{l2} - H_{g1}) \tag{8}$$

Comparing Eqs. (7) and (8):

$$\int_{T_1}^{T_2} \frac{\mathrm{d}H}{\mathrm{d}t}\,\mathrm{d}T = \int_{T_1}^{T_f} \frac{\mathrm{d}H_g}{\mathrm{d}t}\,\mathrm{d}T + \int_{T_f}^{T_2} \frac{\mathrm{d}H_l}{\mathrm{d}t}\,\mathrm{d}T \tag{9}$$

Using this expression, we can find T_f.

In partially cured samples with physical aging, the conversion degree, the fictive temperature, the glass transition temperature (T_g) and the endothermic peak temperature (T_P) increase with curing time. The endothermic peak temperature is the highest one and the difference between T_f and T_g increases with curing time. Fig. 11 shows these characteristics, with the isothermal cure at 50°C of the epoxy resin studied. The conversion degree (α) increases, although the system has vitrified (see Fig. 12) because the densification (volume reduction) of the structure may facilitate further chemical reactions between the remaining unreacted components [3].

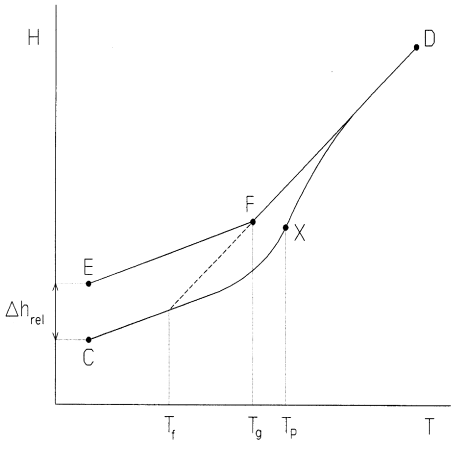

Fig. 2. Enthalpy–temperature diagram of the scans shown in Fig. 1 [2].

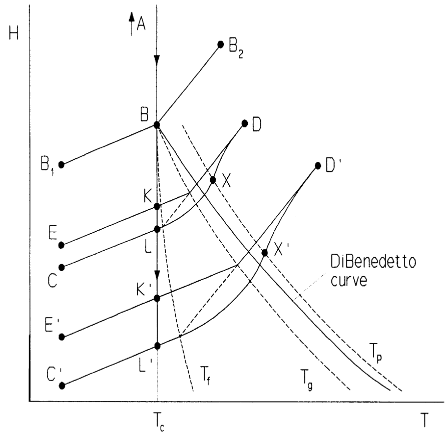

Fig. 3. Enthalpy-temperature diagram showing the increase of enthalpy relaxation with time.

Relaxation enthalpy also increases with curing time. This can be seen in Fig. 3, which shows the enthalpy of the system versus the temperature. After the different components of the epoxy resin are mixed (point A), they begin to react, losing heat and so decreasing in energy; if the reaction takes place at a constant temperature (T_c), the system follows the trajectory AB. In B, T_g is equal to T_c and the system vitrifies (if T_c is lower than the maximum glass transition temperature, $T_{g\infty}$). If the sample is then cooled, it will follow the curve BB_1; if the sample is heated as soon as it arrives at B_1, it will then follow the curve B_1B_2 and at B the heat capacity of the system ($C_P = dH/dT$) will change, which signifies glass transition.

If, on arrival at B, the system is maintained at the same temperature, the reaction between the different components of the resin continues (chemical aging) and relaxation or physical aging occurs. This phenomenon causes a heat loss, which is additional to the loss in the chemical reaction. If, after a certain curing time, the system arrives at L and the sample is cooled until C and the same process shown in Fig. 1 is followed, the difference between the enthalpies of points K and L will be the relaxation enthalpy in the system (see Fig. 2); in the first scan the system absorbs heat (endothermic process) and then its energy increases, for which reason the enthalpy at point K is greater than at L. To represent this process, we have taken into account the relative positions of T_g, T_f, T_P and the DiBenedetto curve found with the experimental results shown in Fig. 13.

The DiBenedetto curve relates the T_g and the conversion degree (α) of a thermoset when it is not vitrified. DiBenedetto [7], as cited by Nielsen [8], characterized the influence of crosslinks on the T_g by:

$$\frac{T_g - T_{go}}{T_{go}} = \frac{\left(\frac{\varepsilon_x}{\varepsilon_m} - \frac{F_x}{F_m}\right)\cdot\alpha}{1 - \left(1 - \frac{F_x}{F_m}\right)\cdot\alpha} \qquad (10)$$

where T_{go} is the glass transition temperature of the uncrosslinked polymer as reference, $\varepsilon_x/\varepsilon_m$ is the ratio of the lattice energies of crosslinked and uncrosslinked monomer units and F_x/F_m is their mobility ratio at T_g.

If the system had been longer at the same temperature T_c and, on reaching L′, had been cooled until C′ and then the same process as before had taken place, there would have been a greater difference between the enthalpies at points K′ and L′ than at K and L. The relaxation enthalpy increases with time, which is due to the increase of the difference between T_g and T_f with time [2].

The relaxation enthalpy depends on the curing temperature. When the aging time (the time elapsed after the system has vitrified) is small, the higher temperatures (always lower than $T_{g\infty}$) have a greater relaxation enthalpy. But, as the curing time increases, the values of the relaxation enthalpy at higher temperatures tend to be stable; while at lower temperatures the values continue rising and surpass the higher ones. If the times are sufficiently high, the relaxation enthalpy increases when the curing temperature decreases [1].

This is described in Fig. 4, in which the system enthalpy versus temperature is shown. If the system is cured at T_c, when it arrives at B (where it finds the DiBenedetto curve), it vitrifies and physical aging begins. If the curing time is sufficiently long, the system is fully cured and reaches equilibrium (the equilibrium states are represented by the dashed line of Fig. 4). Then, the relaxation enthalpy is the difference in enthalpy between R and S (R is above the heating and cooling curve of the completely cured sample). If the cure is made at a temperature T_c' greater than T_c, then the system vitrifies at B′. If the time is sufficiently long and the system reaches equilibrium, then the relaxation enthalpy is the difference in enthalpy between R′ and S′. This difference is smaller than that found when the cure temperature was T_c.

The objective of this paper is to study the relaxation process at different temperatures in partially cured samples of an epoxy resin and of the same resin modified with 11.1% carboxyl-terminated butadiene acrylonitrile copolymer (CTBN). Apart from the theoretical interest of this phenomenon, there is a practical purpose in understanding changes in the properties of these materials when they are not completely cured [1,2]. An elastomeric modifier is introduced into an epoxy resin to increase the toughness of these materials [9–11].

2. Experimental procedures

2.1. Materials

For this study, we used the following commercial products: DGEBA (Ciba-Geigy GY250), an aromatic aminic hardener (Ciba-Geigy HY830) and a carboxyl-terminated butadiene acrylonitrile copolymer (BF Goodrich HYCAR CTBN1300X31).

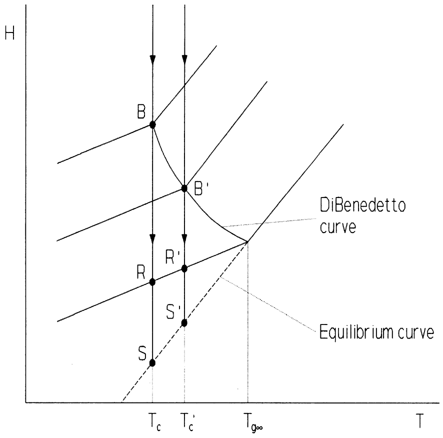

Fig. 4. Enthalpy–temperature diagram that shows the effect of temperature on the relaxation enthalpy.

2.2. Techniques

A Mettler TA4000 DSC (differential scanning calorimeter) was used.

2.3. Experimental process

Stoichiometric proportions of DGEBA and the hardener were mixed to make the neat epoxy resin; the mixture was then stirred vigorously by hand at room temperature for 2 min. We then put 10 mg of the sample in sealed aluminium pans and cured them at a specific temperature for different curing times. Then the sample was quenched to −120°C and was immediately scanned at a heating rate of 10°C/min to 300°C. If a relaxation peak appeared, the experiment was stopped again at −120°C and the dynamic scan was repeated.

The same operation was used to prepare samples of epoxy resin with 11.1% CTBN, with the difference that this elastomer was added when DGEBA and the hardener had already been mixed.

3. Results and discussion

We studied the effect of temperature on the relaxation of partially cured samples of the epoxy resin and of the same resin modified with 11.1% CTBN.

3.1. Epoxy resin

Fig. 5 shows the dynamic scans after the epoxy resin was cured isothermally at 50°C for the times indicated. If the curing time is 8.33 h or less, only the glass transition, whose temperature increases with curing time, occurs; it can also be seen that the change in the heat capacity at the glass transition decreases when the curing time increases. For curing times equal to or greater than 12.5 h, an endothermic relaxation peak superimposed over the glass transition appears. The temperature and the size of this peak increase with curing time.

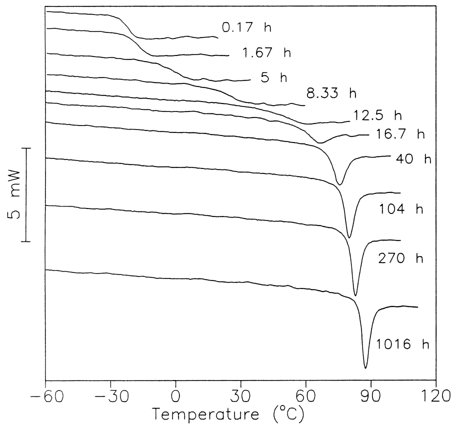

Fig. 5. Dynamic scans at 10°C/min of the epoxy resin after it was cured isothermally at 50°C for the times indicated.

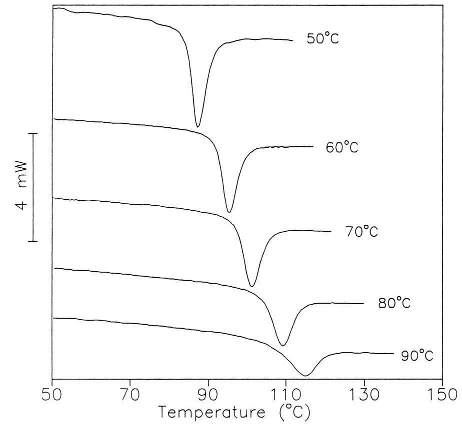

Fig. 6. Dynamic scans at 10°C/min after the epoxy resin was cured for 1016 h at the temperatures indicated.

Fig. 6 shows dynamic scans at 10°C/min of epoxy resin cured for 1016 h at different temperatures. The peak size decreases when the curing temperature rises, while the peak temperature increases with the curing temperature.

Fig. 7 shows the inter-dependence of relaxation enthalpy and the curing time. At 90°C the system vitrifies quicker than at other temperatures (see Fig. 10). At 90°C the system reaches equilibrium in less time and at the longest curing times has a lower relaxation enthalpy than at other temperatures. As was commented in the introduction, the relaxation enthalpy decreases when the curing temperature increases if the curing time is long.

Fig. 8 shows relaxation enthalpy versus aging time. Aging time is the time that the system is relaxed, equivalent to the difference between the curing and the vitrification times. When aging time is low, relaxation enthalpy increases with curing temperature, because the rate of the relaxation process is greater at high temperatures. But as at higher temperatures the system tends to reach equilibrium

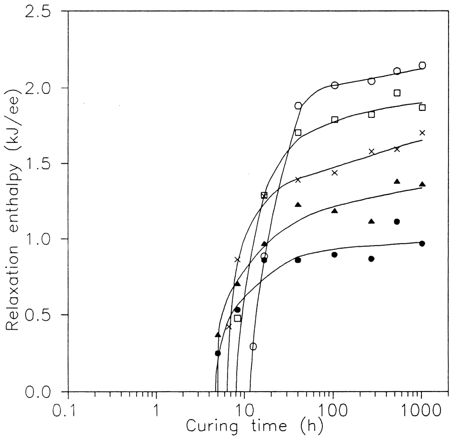

Fig. 7. Relaxation enthalpy versus curing time for the epoxy resin at different temperatures: 50°C (○), 60°C (□), 70°C (×), 80°C (▲) and 90°C (●).

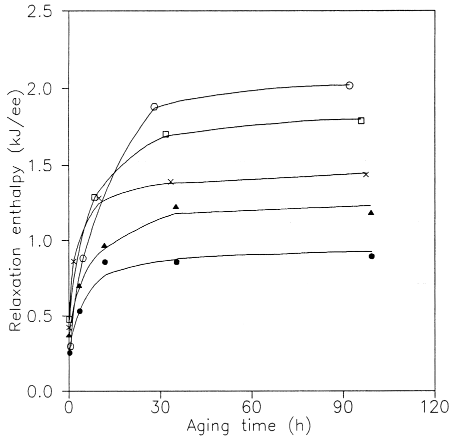

Fig. 8. Relaxation enthalpy versus aging time for the epoxy resin at different temperatures: 50°C (○), 60°C (□), 70°C (×), 80°C (▲) and 90°C (●).

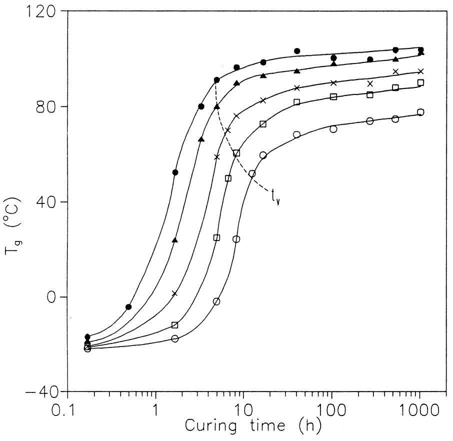

Fig. 10. Glass transition temperature (T_g) versus curing time for the epoxy resin at different temperatures: 50°C (○), 60°C (□), 70°C (×), 80°C (▲) and 90°C (●).

quickly, the relationship changes (Fig. 8 shows the aging time only up to 120 h, so that the relaxation process can be better appreciated).

Fig. 9 shows the relaxation peak temperature versus the curing time at different temperatures. The peak temperature increases with curing time and temperature. At low curing temperatures, the variation in peak temperature is bigger than at high temperatures when the aging time is short. If it is long the variation in the peak temperature with the logarithm of time is practically linear and does not differ very much between the different temperatures.

Fig. 10 shows the dependence between T_g (obtained in the second dynamic scan if a relaxation peak appeared in the first one) and the curing time at different temperatures. The dashed curve represents the vitrification time (t_v). T_g values increase with time and temperature. After vitrification the variation of T_g with time is smaller (the reaction proceeds more slowly).

Now, we are going to compare the values of T_P, T_g and T_f for epoxy resin isothermally cured at 50°C. The fictive temperature was found with Eq. (9). When the system is not vitrified, then T_f is equal to T_g [2].

Fig. 11 plots the three temperatures mentioned against the curing time. Before the system relaxes the fictive temperature is equal to T_g and so only the cross symbol representing T_g is shown. When the system has vitrified and relaxation appears, its temperature (T_P) is greater than T_f and T_g. T_f is the lowest and increases with time very slowly. The difference between T_g and T_f increases with time.

Fig. 12 plots the three temperatures mentioned before versus the conversion degree (α). This is defined by:

$$\alpha = \frac{\Delta h_t}{\Delta h_T} \qquad (11)$$

where Δh_t is the heat lost from the beginning of the reaction until a determined time and Δh_T is the total heat reaction, which comes from a dynamic scan of a sample recently prepared. Δh_t is the difference between Δh_T and the residual heat Δh_{res} [2,12] which is obtained in the dynamic scan made after the isothermal cure (in the second one, if in

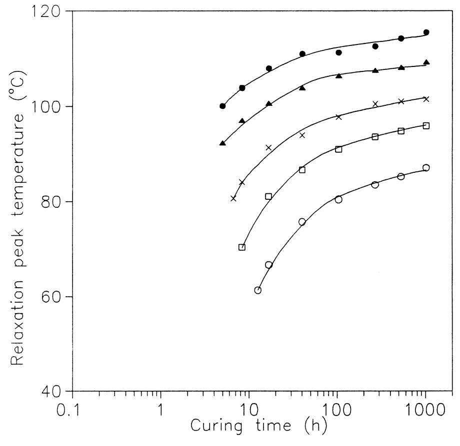

Fig. 9. Relaxation peak temperature versus curing time for the epoxy resin at different temperatures: 50°C (○), 60°C (□), 70°C (×), 80°C (▲) and 90°C (●).

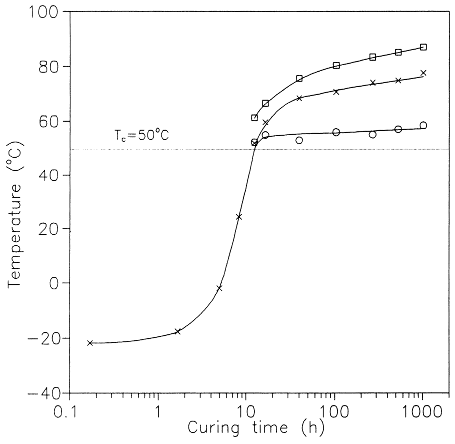

Fig. 11. Fictive (○), glass transition (×) and relaxation peak (□) temperatures versus curing time for the epoxy resin at 50°C.

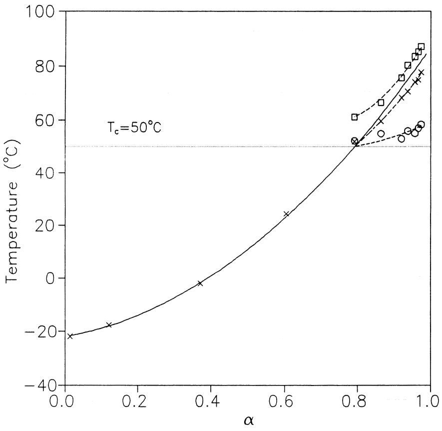

Fig. 12. Glass transition (×), fictive (○) and relaxation peak (□) temperatures versus the conversion degree (α) for the epoxy resin at 50°C.

the first a relaxation peak appeared). From Eq. (11):

$$\alpha=\frac{\Delta h_T-\Delta h_{\mathrm{res}}}{\Delta h_T}=1-\frac{\Delta h_{\mathrm{res}}}{\Delta h_T} \tag{12}$$

The continuous curve is derived from the DiBenedetto equation (Eq. (10)). The values of $\varepsilon_x/\varepsilon_m$ and F_x/F_m were found in an earlier study [13] and are 0.64 and 0.43, respectively. The three temperatures increase with conversion degree. When the system is not vitrified the values of T_g coincide with the continuous curve, but if the resin is relaxing the values of T_g are below this curve (the DiBenedetto equation is only valid when the system is not vitrified). The relaxation peak temperature is above the continuous curve. T_f is smaller than T_g and the difference between these temperatures increases with conversion degree.

Δh_t corresponds to the difference between the initial enthalpy of the system (H_o) and what it contains at this later stage (as the system loses energy, H_o becomes bigger than H). From Eq. (11):

$$\alpha=\frac{\Delta h_t}{\Delta h_T}=\frac{H_o-H}{\Delta h_T} \tag{13}$$

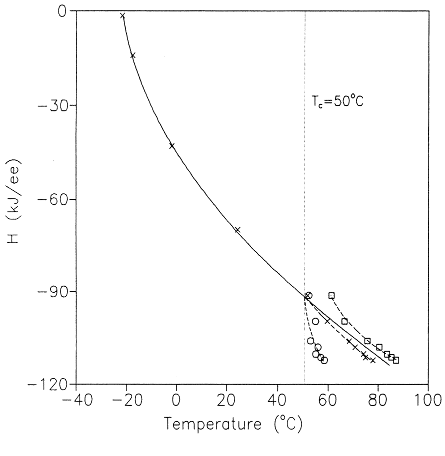

Fig. 13. Enthalpy versus glass transition (×), fictive (○) and relaxation peak (□) temperatures for the epoxy resin at 50°C.

From this equation, the value of the system enthalpy is:

$$H=H_o-\alpha\cdot\Delta h_T \tag{14}$$

Fig. 13 shows this enthalpy versus the temperature. We have taken a reference value of 0 for H_o, and then for $\alpha=1$ (the resin completely cured), $H=-\Delta h_T$. The continuous curve is derived from the DiBenedetto equation (Eq. (10)). As in Fig. 12, T_g is coincident with the DiBenedetto curve before the system vitrifies; when the system vitrifies, the values of T_g are below this curve, the values of T_P are above it, the T_f values are lower than T_g and the difference between these last two temperatures increases as the system enthalpy decreases. The Fig. 13 diagrams were the basis for the positions of the curves in Fig. 3.

3.2. Epoxy resin with 11.1% CTBN

Now, we will study the influence of CTBN on the relaxation process of epoxy resin. This modifier accelerates the reaction of epoxy resin because it has carboxylic groups that facilitate the opening of the epoxy group of the resin, and so decrease the vitrification time [13,14]. During the curing reaction CTBN forms a phase which is different from neat epoxy resin, and increases its toughness [9–11]. CTBN dissolves a part of the plasticizer (di(butyl)phthalate) that contains the hardener of the epoxy resin. This causes the T_g of the epoxy phase to increase. The $T_{g\infty}$ (the maximum T_g) of the neat epoxy resin is 102.0°C and that of the epoxy phase when the resin is modified with 11.1% CTBN is 118.4°C [15].

Fig. 14 shows the relationship between relaxation enthalpy and curing time. This enthalpy increases with time. The vitrification time decreases as the cure temperature rises (vitrification times are lower than in epoxy resin, due to the accelerating effect of CTBN, as explained above) and so the higher temperatures show relaxation at shorter curing times. The higher temperatures reach equilibrium more quickly. If the curing time is long (about 1000 h),

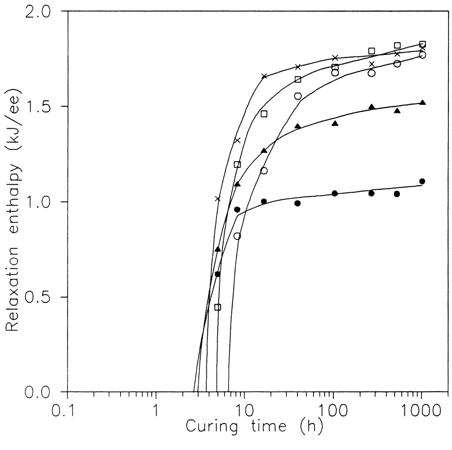

Fig. 14. Relaxation enthalpy versus curing time for the epoxy resin modified with 11.1% CTBN at different temperatures: 50°C (○), 60°C (□), 70°C (×), 80°C (▲) and 90°C (●).

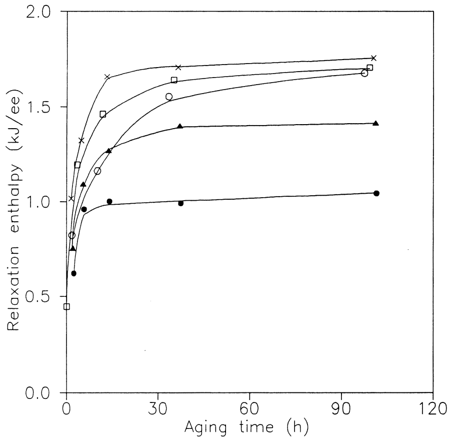

Fig. 15. Relaxation enthalpy versus aging time for the epoxy resin modified with 11.1% CTBN at different temperatures: 50°C (○), 60°C (□), 70°C (×), 80°C (▲) and 90°C (●).

the relaxation enthalpy decreases when the curing temperature increases, but in this system the enthalpies at 60°C and 70°C are greater than at 50°C. More time is required for this temperature to reach a relaxation enthalpy point higher than 60°C and 70°C. In the epoxy resin, at the same time, there were bigger differences between the relaxation enthalpies at these temperatures and the lower temperatures had greater enthalpies. This is surely due to the fact that the $T_{g\infty}$ of the epoxy resin is lower than that of the epoxy resin modified with CTBN. The time taken to reach equilibrium decreases when the difference between $T_{g\infty}$ and the cure temperature does.

Fig. 15 plots relaxation enthalpy against aging time. When aging time is short, the enthalpy increases with curing temperature, as happened with the neat epoxy resin. Here aging time is only shown up to a value of 120 h, but at 165 h, the 60°C and 70°C isotherms intersect. The 50°C isotherm is always below the 60°C and 70°C isotherms, as in Fig. 14.

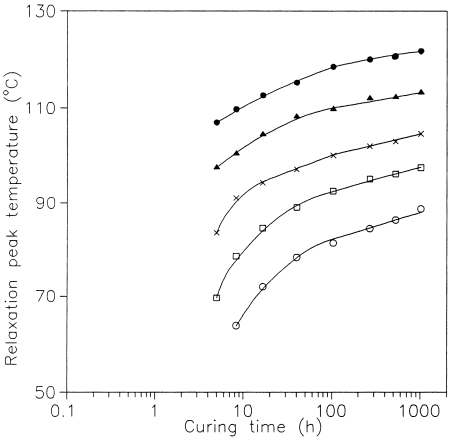

Fig. 16. Relaxation peak temperature versus curing time for the epoxy resin modified with 11.1% CTBN at different temperatures: 50°C (○), 60°C (□), 70°C (×), 80°C (▲) and 90°C (●).

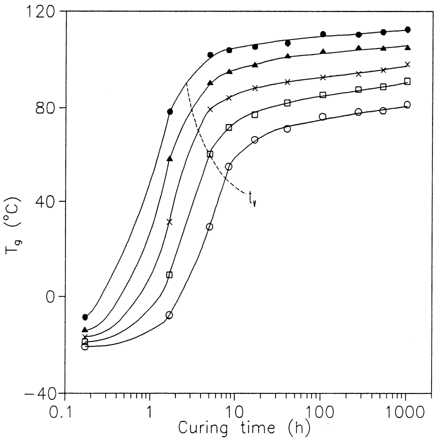

Fig. 17. Epoxy phase T_g versus curing time for the epoxy resin modified with 11.1% CTBN at different temperatures: 50°C (○), 60°C (□), 70°C (×), 80°C (▲) and 90°C (●).

Fig. 16 shows the relationship between the relaxation peak temperature and the curing time for different temperatures. As occurred with the neat epoxy resin, this peak temperature increases with curing time and temperature.

Fig. 17 plots the relationship between the T_g of the epoxy phase and the curing time. This T_g increases with curing time and temperature. The dashed curve represents the vitrification times (t_v). After vitrification, the reaction rate decreases and the values of T_g change more slowly.

4. Conclusions

This study of the physical aging of partially cured samples of an epoxy resin and of the same resin modified with an elastomer has shown the important changes in these materials over time, due to the effects of the residual cure and of the formation of an elastomeric second phase (in the resin which contains the elastomeric modifier) in structural relaxation.

DSC has enabled, from experimental results, the glass transition temperature (T_g), the fictive temperature (T_f), the relaxation peak temperature (T_P) and the relaxation enthalpy to be found. Knowing the values of these properties means that the magnitudes of the structural relaxation in these materials can be quantified and compared.

In the samples studied, the relaxation peak temperature and enthalpy increase with curing time. At longer curing times, the relaxation enthalpy of the two systems studied decreases as the curing temperature rises, although for the resin modified with 11.1% CTBN a longer curing time is needed for this phenomenon to occur, because CTBN increases the $T_{g\infty}$ and consequently, the difference between this temperature and the curing temperature. CTBN also modifies T_g and the relaxation peak temperature of the epoxy resin.

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References

[1] Montserrat S. J Appl Polym Sci 1992;44:545.

[2] Plazek DJ, Frund ZN Jr. J Polym Sci: Part B: Polym Phys 1990;28:431.

[3] Wasserman S, Johari GP. J Appl Polym Sci 1993;48:905.

[4] Pascault JP, Williams RJJ. J Polym Sci: Part B: Polym Phys 1990;28:85.

[5] Tool AQ. J Res Natl Bur Stds 1930;5:627.

[6] O'Reilly JM, Tribone JJ, Greener J. Polymer preprints, 30, 1985.

[7] DiBenedetto AT. J Polym Sci: Part B: Polym Phys 1987;25:1949.

[8] Nielsen L. J Macromol Sci, Rev Macromol Chem 1969;C3:69.

[9] Kinloch AJ, Shaw SJ, Tod DA, Hunston DL. Polymer 1983;24:1341.

[10] Maazouz A, Sautereau H, Gérard JF. Polym Network Blends 1992;2 (2):65.

[11] Romano AM, Garbassi F, Braglia R. J Appl Polym Sci 1994;52:1775.

[12] Salla JM, Martín JL. Thermochim Acta 1988;126:339.

[13] Salla JM, Morancho JM. In: Vázquez M, Hernando A, editors. Nanostructured and non-crystalline materials. Singapore: World Scientific, 1995:298.

[14] Morancho JM, Salla JM. J Non-Crystal Sol 1994;172-174:656.

[15] Salla JM, Morancho JM, Marroyo LM, Cadenato A, Ramis X. In: Ribas J, López MA, editors. Non-crystalline and nanoscale materials. Singapore: World Scientific, 1998:136.