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SHORT COMMUNICATION

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Enthalpy relaxation in an epoxy-cycloaliphatic amine resin

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Abstract Enthalpy relaxation in a system containing the diglycidyl ether of bisphenol A (DGEBA) resin and a diamine, 1,3-bisaminomethylcyclohexane (1,3-BAC) as curing agent, has been investigated by differential scanning calorimetry (DSC). Samples fully cured were annealed at temperature T_g–15 °C for periods of time from 1 h to a maximum of 168 h. The enthalpy relaxation is analyzed by the peak shift method, in which the sample is heated at 10 °C/min following cooling at various rates through the glass transition region. The key parameters of structural relaxation determined were the non-linearity parameter $x = 0.47 \pm 0.02$, the apparent activation energy $\Delta h^* = 1264 \pm 48$ kJ/mol or $\Delta h^*/R = 152 \pm 6$ kK and the non-exponentiality parameter $\beta \approx 0.3$. The results, obtained by the same method, were compared with those for other systems based on fully cured DGEBA. The correlations among these parameters with the peak shift model should be considered with caution. However, the results show that a correlation between crosslink lengths and the value of Δh^* can be considered. The relaxation process for DGEBA/1,3-BAC proves to be highly cooperative.

Key words Enthalpy relaxation · Physical aging · Epoxy resin · Differential scanning calorimetry

Introduction

Polymers are known to be not in an equilibrium glassy state, but can gradually approach equilibrium in a temperature range below the glass transition temperature, T_g. The time dependence of changes in this behavior is the subject of physical aging. Physical aging of glassy polymers has been extensively studied since this strongly affects the physical and mechanical performance of the materials [1].

One of the approaches towards a better understanding of the physical aging process in glasses has been to attempt to model the response on heating the glass at a constant rate in the differential scanning calorimeter (DSC). This endothermic response displays a peak in the specific heat capacity, the magnitude and position of which depend upon, among other things, the initial state of the glass before heating in the DSC. By annealing a glass for various lengths of time at a temperature below the glass transition temperature, a family of such heating endotherms is obtained, and can be analyzed in terms of the parameters controlling the kinetics of structural recovery. The kinetics of the structural relaxation or physical aging process are generally recognized to exhibit both non-linear and non-exponential behavior.

It is assumed that the relaxation time, τ, for enthalpy relaxation depends on both the temperature, T, and the structure of the glass, identified by its fictive temperature, T_f, according to the so-called Tool-Narayanaswamy-Moynihan equation [2–4] or TNM equation (Eq. 1):

$$\tau = \tau_0 \exp\left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right] \tag{1}$$

where τ_0 is the value of τ in equilibrium at infinitely high temperature.

This equation introduces the apparent activation energy Δh^*, and the non-linearity parameter x, which is a partitioning parameter ($0 \leq x \leq 1$) defining the relative contributions of structure and temperature to the relaxation times [5]. This x parameter is a material constant, independent of annealing temperature, annealing time and heating rate over substantial ranges of these experimental variables [6]. A value of x close to zero indicates that the contribution is only due to structure whereas a value close to one shows that the contribution is from the temperature.

The non-exponentiality in the relaxation process is a consequence of the existence of a distribution of relaxation times. A widely used expression is the stretched exponential response function (Eq. 2):

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \qquad (2)$$

which is referred to as the Kohlrausch-Williams-Watts (KWW) function [7, 8], where β is the non-exponential parameter ($0 \leq \beta \leq 1$). It is related to the width of the spectrum of these relaxation processes and the average relaxation time.

These equations, together with a constitutive equation expressing the rate of relaxation as being proportional to the excess enthalpy, are sufficient to describe the response of the glass to any thermal history such as is used in conventional DSC [9].

There are various approaches for the analysis of DSC data, in particular the Adam-Gibbs (AG) non-linear formalism [10], that allows an interpretation of structural relaxation in terms of the molecular entities rearranging cooperatively during the relaxation process. The procedure used in this work was the TNM model because, with this formalism, the values of the key parameters of the structural relaxation can be compared for different epoxy systems in an attempt to achieve a better understanding of the process of relaxation for these systems. This model was successful used by other authors for studying the connection between the parameters and structure [11–13].

In this work, the enthalpy relaxation in an epoxy resin based on the diglycidyl ether of bisphenol A (DGEBA) and cured by 1,3-bisaminomethylcyclohexane (1,3-BAC) was investigated by differential scanning calorimetry. Previously, the kinetics of the cure reaction [14], the mechanical properties [15] and the degradation kinetics [16] of this system were studied.

Materials and methods

Materials, cure procedure and technique

The studied system is based in the commercial diglycidyl ether of bisphenol A, from Araldite GY 260 CIBA, with a weight per epoxy equivalent of 205.1 g/eq as determined by hydrochlorination [17]. The curing agent was a cycloaliphatic diamine, 1,3-bisaminomethylcyclohexane (1,3-BAC), from Aldrich Chemical; with a molecular weight of 142.25 and manufacturer purity value of >99%. The formulation used was 100 g DGEBA to 17 g 1,3-BAC. The resin and the hardener were stirred under vacuum at room temperature for 10 min. The mixture was cured for 24 h at room temperature followed by 8 h at 60 °C, and then post-cured for 2 h at 120 °C. These curing conditions ensure that the resin becomes practically fully cured, this means that no residual exothermic reaction is detected in a DSC scan when the cured sample is heated up to 200 °C.

A Perkin Elmer differential scanning calorimeter, model DSC-7, equipped with an intracooler was used. The baseline was checked frequently, and temperature scale calibration was made at regular intervals using the melting transition of pure indium. The purge gas was dry nitrogen at a controlled flow rate.

Cooling experiments

A set of experiments was required in order to determine the apparent activation energy for enthalpy relaxation Δh^*. This can be found from the dependence of the fictive temperature, T_f, on the cooling rate [10].

A single sample was used throughout. The sample was initially heated in the DSC at 10 °C/min to 160 °C in order to erase its thermal history. It was then cooled at 200 °C/min to room temperature and immediately reheated at 10 °C/min to 160 °C, to obtain the reference scan. This procedure was repeated using cooling rates of 50, 25, 10, 5, 2.5, 1, 0.5, 0.25, and 0.1 °C/min, each time reheating from 30 to 160 °C at 10 °C/min and the heating scan was recorded.

The heating scans obtained after the various cooling rates permit the determination of T_f as a function of cooling rate. The use of a single sample for these experiments is important in reducing experimental error because the changes that are being measured are rather small.

Enthalpy relaxation experiments

The samples, weighted on a microbalance and sealed in standard aluminum pans, were subjected to the following thermal treatment. Initially, all samples were heated above the glass transition temperature of the epoxy system in the DSC to 160 °C at 20 °C/min, and left at this temperature for several minutes to eliminate their previous thermal history. They were then cooled at 10 °C/min to the aging temperature T_a.

Following the annealing treatment for the length of time selected (up to 168 h), the samples were brought to room temperature and then immediately reheated at 10 °C/min to 160 °C through the glass transition region to obtain the first (annealed) scan. The same sample was cooled again to 30 °C and then reheated at 10 °C/min to 160 °C to obtain the second (unannealed, or reference) scan. After these two scans the same sample was used again for further annealing times.

Results and discussion

Cooling rate effect on T_g-overshoot

Physical aging in polymers can occur at different rates at any isothermal temperature below T_g. The kinetics of aging have been demonstrated to be dependent on both time and temperature. Alternatively, if the polymers are cooled down from above T_g at finite cooling rates, the extents of aging are expected to be affected by the cooling rate. An endothermic peak, which is the well known recovery of enthalpy (also known as T_g-overshoot), is noted in the thermograms. The magnitudes of the overshoot peak area are greater for the samples that were cooled at slower cooling rates. This suggests that, at an infinitely slow cooling rate, the cooled polymer would gradually approach the equilibrium glassy state with a maximum aging extent [18].

A typical heating endotherm for one such intrinsic cycle is shown in Fig. 1. This illustrates the various features of the curve, which are to be used in the subsequent analysis. T_u is the upper peak temperature while the quantities *a* and *b* are used to define the normalized specific heat at T_u.

Figure 2 shows the DSC thermograms for DGEBA/1,3-BAC obtained at a heating rate $q_2 = 10$ °C/min immediately after the sample was cooled from 160 °C at the different cooling rates, q_1.

The apparent activation energy Δh^*, is evaluated from the dependence of the fictive temperature, T_f, on the cooling rate, in intrinsic cycles [9]. The dependence of the fictive temperature on the cooling rate may be written as

$$\frac{\Delta h^*}{R} = -\left[\frac{\partial \ln|q_1|}{\partial(1/T_f)}\right]_{\bar{\delta}_H=0,q_2} \qquad (3)$$

The fictive temperature for a given cooling rate is found by the equal areas method [4] and a near linear relationship was indeed found when ln $|q_1|$ was plotted against $1/T_f$ (Fig. 3).

The slope of this straight line was found to be $\Delta h^*/R = 152 \pm 6$ kK (correlation coefficient = 0.995) and an apparent activation energy of $\Delta h^* = 1264 \pm 48$ kJ/mol was determined. It is difficult to compare the result with the values reported in the literature because of the great differences found among the different systems based on DGEBA, even if we consider only the fully cured systems. Reported values for $\Delta h^*/R$ are in the range between 97 and 126 kK [13, 19], these values are for DGEBA fully cured by aliphatic or aromatic diamines. Large values of apparent activation energy are associated with fragile behavior [12, 15].

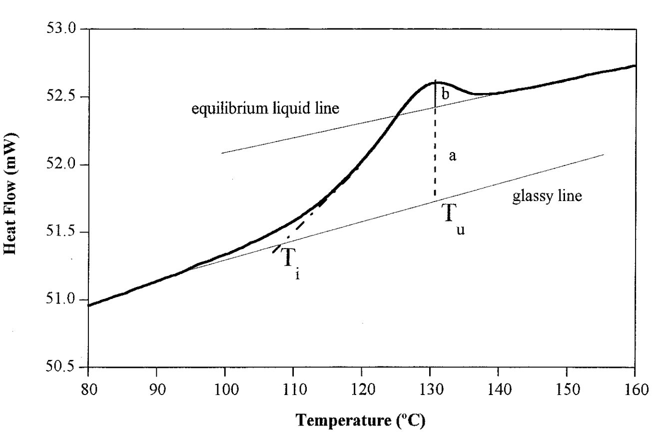

Fig. 1 Variation of DSC power output as function of temperature. The upper peak temperature T_u is indicated in the scan. The heating rate was 10 °C/min after the cooling at 0.5 °C/min

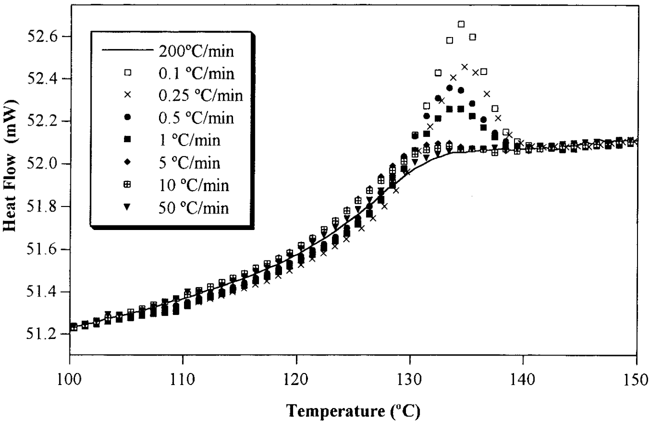

Fig. 2 Heating scans at 10 °C/min for DGEBA/1,3-BAC samples cooled at various tested rates and then immediately reheated in the DSC. Note that only a part of the complete scan from 30 to 160 °C is shown here for clarity

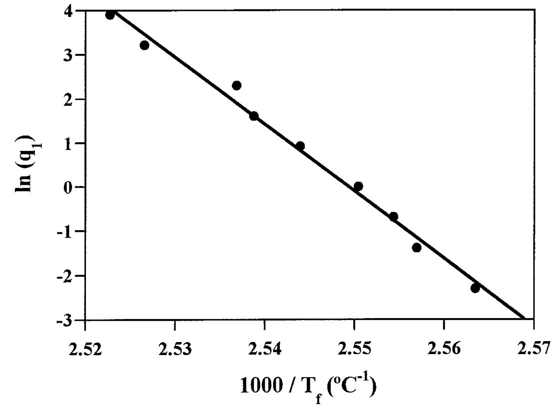

Fig. 3 Plot of the logarithm of the cooling rate as a function of the reciprocal fictive temperature for DGEBA/1,3-BAC

Measurement of ΔC_p

The change in the specific heat capacity, ΔC_p, between its extrapolated glassy, $C_{p,g}$, and liquid-like, $C_{p,l}$, values, in this epoxy system cannot be determined in the cooling experiments as in the case of many resins [20]. ΔC_p was determined from a heating scan at 10 °C/min run immediately after cooling and averaging several samples; however, the values of ΔC_p were consistent for each sample with small differences between the samples.

As the glassy and liquid heat capacity asymptotes are not parallel [21], it is necessary to specify the temperature at which ΔC_p is evaluated. In this paper the measurement of T_g was determined from the reference DSC scan obtained by heating immediately after cooling. The T_g of the sample is expected to be close to its T_g obtained by cooling if the heating follows immediately after cooling [22] from $T_0 > T_g$. The value of T_g was determined as the inflection point of the endothermic shift in the region where the transition takes place. The value of ΔC_p for DGEBA/1,3-BAC was 0.34 ± 0.01 J/g · °C with $T_g = 145$ °C.

Measurement of non-linearity parameter, *x*

Figure 4 shows the family of DSC traces obtained for a wide range of annealing times including that for the unannealed sample.

From these curves, the values of enthalpy loss $\bar{\delta}_H$ and of the peak temperature T_p can be established as a function of annealing time t_a. The values are shown in Fig. 5. The enthalpy loss on aging, is found simply from the area difference under the DSC curves for aged and for the reference scans. From the best-fit straight lines with these data we find slopes of 1.6 J/g and 4.5 °C per decade, respectively.

The x parameter can be calculated from these experimental results by the so-called shift method [23], where the following dimensionless peak shift can be obtained:

$$\hat{s}(\bar{D}) = \Delta C_p \left(\frac{\partial T_p}{\partial \bar{\delta}_H}\right)_{q_1,q_2,T_a} \qquad (4)$$

where $\Delta C_p = C_{p,l} - C_{p,g}$ is the difference between the specific heat capacities of the equilibrium liquid and of the glass.

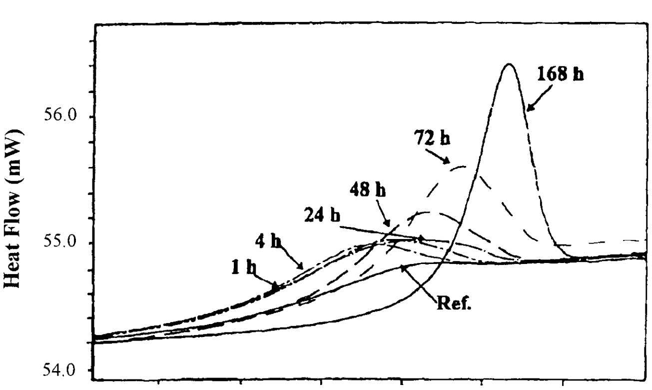

Fig. 4 DSC heating scans at 10 °C/min for DGEBA/1,3-BAC at 130 °C for the times (in hours) indicated against each curve and the reference scan

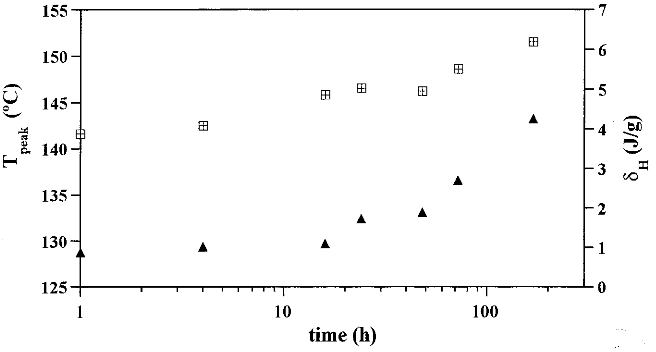

Fig. 5 Dependence of the peak temperature (⊞) and the enthalpy loss (▲) vs. time at aging temperature of 130 °C

The advantage of the peak shift method lies in the observation that the shift $\hat{s}(\bar{D})$ defined by Eq. 4 is a strong function of the non-linearity parameter x but is almost independent of the distribution of relaxation times. The dependence $\hat{s}(\bar{D})$ on x has been determined theoretically for a wide range of distributions and is shown in Fig. 15 of the quoted reference [23].

From the average values of $\partial\bar{\delta}_H/\partial \log t_a$ and $\partial T_p/\partial \log t_a$ per decade found above, a value of $\partial T_p/\partial\bar{\delta} = 2.81$ g/kJ is obtained. When multiplied by $\Delta C_p = 0.34$ J/g · °C, this gives $F(x) = \hat{s}(\bar{D}) = 0.96$, and from the dependence of $F(x)$ upon x, a value of $x = 0.47 \pm 0.02$ is found in the master curve for our epoxy system. The values reported in references [13, 19] are in the range of 0.25 ± 0.04 and 0.47 ± 0.03.

Estimation of non-exponentiality parameter, *β*

The same set of cooling rate experiments may be used to estimate the non-exponentiality parameter β introduced in the Eq. 2.

For each cooling rate, the heating scan made immediately afterwards in the DSC displays a small endothermic peak, called the upper peak. This peak is most noticeable when the cooling rate is greater than the heating rate. The upper peak shows a different dependence on the experimental variables from that found in the main peak obtained in annealing experiments: its magnitude is more sensitive to the non-exponentiality parameter β than to the non-linearity parameter x. The upper peak is characterized by its temperature T_u and its height. It is clear from the heating curves shown in Fig. 2 that the peak temperature initially decreases as the cooling rate decreases and then, when the cooling rate decreases below about 5 °C/min, it begins to increase again (see Fig. 6).

This behavior was anticipated by other authors [6, 9] and represents a change in the nature of the endothermic peak from an upper peak at the faster cooling rates.

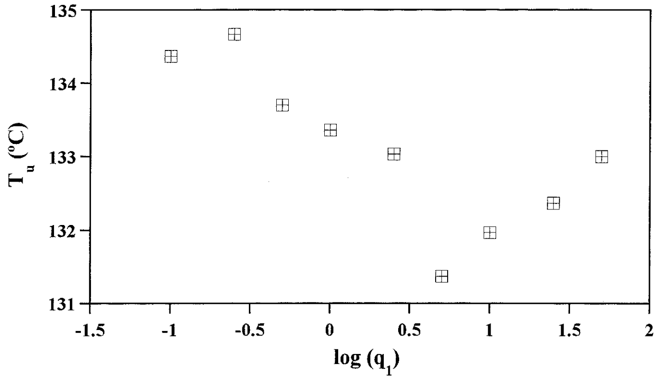

Fig. 6 Dependence of peak temperature on log (cooling rate) for the heating curves shown in Fig. 2

A normalized upper peak height $C^N_{p,u}$ can be defined from the intrinsic cycles:

$$C^N_{p,u} = \frac{C_{\mathrm{p,u}} - C_{\mathrm{p,g}}}{C_{\mathrm{p,l}} - C_{\mathrm{p,g}}} = \frac{a+b}{a} \tag{5}$$

where $C_{\mathrm{p,u}}$ is the magnitude of C_{p} at the upper peak temperature T_{u} that depends on the ratio of cooling rate q_1 to heating rate q_2, on the parameter β and, to a lesser extent, on the non-linearity parameter x. This implies that the normalized response of the sample on heating increases from zero in its initial glassy state to finally unity in the equilibrium liquid-like state. The experimental evaluation of $C^N_{p,u}$ is through the measurement of quantities a and b as illustrated in Fig. 1.

The variation of $\Delta C^N_{p,u}$ with the ratio of cooling rate to heating rate has been evaluated theoretically for various combinations of the material parameters x and β following the same approach as was used in the derivation of the master curve $F(x)$ and a characteristic dependence can be observed [6]. A comparison with experimental data, for which x has previously been determined independently of β by the peak shift method, allows an estimate of β to be made.

A comparison of the experimental and theoretical variations of $C^N_{p,u}$ and the quotient between the cooling and heating rates (q_1/q_2) for DGEBA/1,3-BAC allows an estimate of the value of β if x is already known from the peak-shift method. Introducing our results in the plots developed by Hutchinson and Ruddy [6] an approximate value of $\beta \approx 0.3$ can be estimated.

Conclusions

The peak shift method, the cooling rate experiments, and the normalized upper peak height thus allow the determination of each of the three parameters which characterize the kinetics of enthalpy relaxation, namely the non-linearity parameter x, the apparent activation energy Δh^*, and the non-exponentiality parameter β, respectively.

These parameters are compared with those obtained for different systems based on DGEBA fully cured by other authors following the peak-shift method in Table 1.

From Table 1 it is clearly seen that, even reducing the comparison only to systems based on fully cured DGEBA with different aliphatic, aromatic or cycloaliphatic diamines, it is difficult to establish a correlation of Δh^* with x. The same problem occurs when we try to establish a correlation between x and β. Although a universal correlation between the three parameters should be considered with caution, an effect of crosslink lengths on the enthalpy relaxation of these systems can be shown. This fact, previously reported for DGEBA with FEDA (ethylenediamine), FJ230 and FJ400 (diamines of polyoxypropylene with 2,6- and 5,6-oxypropylene units) can also be assessed when we include the systems DGEBA/aromatic diamine (HY830) and DGEBA/cycloaliphatic diamine (1,3-BAC). The crosslink lengths of the curing amines can be connected through the glass transition temperature (see Table 1). For the aliphatic amines, the chemical structures indicate that the crosslink length increases in the order FEDA < FJ230 < FJ400 [13]. So, more than an establishment of correlation among these parameters, it is interesting to see that when the crosslink lengths decreases the magnitude of Δh^* increases. This fact is consistent with the studies of enthalpy relaxation made with the theories based on the Adam-Gibbs (AG) formalism, that is, the relaxation becomes more cooperative as the crosslink lengths decreases. The short crosslink lengths in DGEBA/1,3-BAC system can explain the relatively high value of Δh^*, and the low value of β is consistent with the idea that this relaxation process is highly cooperative.

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Table 1 Values of glass transition temperature, apparent activation energy, the non-linearity parameter and non-exponentiality parameter for different systems based on fully cured DGEBA

Sample	T_g (°C)	$\Delta h^*/R$ (kK)	x	β	Ref.
DGEBA/1,3-BAC	145	152 ± 6	0.47 ± 0.02	≈0.3	This work
DGEBA/HY830	102	126 ± 17	0.37 ± 0.04	$0.2 < \beta < 0.3$	[19]
DGEBA/FEDA	121	124 ± 20	0.25 ± 0.04	≈0.3	[13]
DGEBA/FJ230	80	112 ± 10	0.36 ± 0.02	$0.3 < \beta < 0.456$	[13]
DGEBA/FJ400	47	97 ± 20	0.47 ± 0.03	$0.3 < \beta < 0.456$	[13]

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