

Addition of a Reactive Diluent to a Catalyzed Epoxy–Anhydride System. II. Effect on Enthalpy Relaxation

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SYNOPSIS

Enthalpy relaxation in an epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) with a reactive diluent cured with methyl-tetrahydrophthalic anhydride (MTHPA) with an accelerator was investigated by differential scanning calorimetry. The reactive diluent (RD) added was an aliphatic diglycidyl ether which was mixed in a proportion of 50 parts by weight (pbw) per 100 parts of DGEBA, with the stoichiometric quantity of MTHPA. The key parameters of the enthalpy relaxation investigated were the nonlinearity parameter, x , the apparent activation energy, Δh^* , and the nonexponentiality parameter, β . The results were compared with other data obtained previously in similar epoxy–anhydride systems without an RD but with different degrees of conversion in order to analyze the effects of (a) the introduction of aliphatic chains of the RD in the epoxy structure and (b) a reduction in the crosslink density of the resin. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Thermosetting resins derived from DGEBA cured by cyclic carboxylic anhydrides have been used extensively in the manufacture of high-grade electrical insulation materials or in electronic components. One method of application of these resins is by impregnation of the components under a vacuum or at atmospheric pressure. The addition of a low-viscosity reactive diluent (RD) is frequently used to improve the impregnation of the different types of components. As was shown in the first part of this work,¹ the addition of RD results in only a slight increase of the heat of curing and only small changes in the cure kinetics. On the other hand, the properties of the network were greatly affected by the RD content. In particular, the glass transition decreases with the RD content as a consequence of a greater flexibility of the chain segments in the network structure.¹ The lowering of the glass transition region can lead to a modification of the kinetics of

structural relaxation of the system, and it is important to know how this change can affect the durability and the range of application of the epoxy resin.

Structural (enthalpy) relaxation in a series of epoxy resins based on diglycidyl ether of bisphenol A (DGEBA) was investigated by differential scanning calorimetry (DSC) over the last 4 years in the laboratories of the Universitat Politècnica de Catalunya (UPC) and of Aberdeen University (AU).^{2–5} The so-called Tool–Narayanaswamy–Moynihan equation was used to characterize the dependence of the relaxation time on temperature and structure, the latter represented typically by the fictive temperature T_f (Refs. 6–8):

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

This equation introduces both the nonlinearity parameter x and the activation energy Δh^* . The distribution of relaxation times was introduced by means of the Kohlrausch–Williams–Watts response function $\phi(t)$ with the nonexponentiality parameter β (Ref. 9):

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Table I Composition in Parts by Weight (pbw) and Glass Transition Temperatures for the Different Epoxy–Anhydride Systems Studied

Name	Epoxy Resin Araldite		Hardener		RD ^c	α^d	T_g (°C)	Ref.
	F	CY225	HY905	HY225				
FRD50 ^a	100		160		50	100	73	This work
CY100 ^b		100		80	—	100	100	4
CY070 ^b		100		80	—	70	50	5

^a FRD50 contains 1 pbw of accelerator.

^b CY100 and CY070 contain the accelerator incorporated in the resin CY225.

^c RD is the reactive diluent.

^d α is the degree of conversion determined by DSC using the residual heat of curing method.

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

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.¹⁰

The objective of the present work was to determine the key parameters (Δh^* , x , and β) for the epoxy resin with an RD and to analyze the effect on the kinetics of enthalpy relaxation caused by the introduction of aliphatic chains in the epoxy structure. The results are compared with those obtained earlier on the epoxy without the RD but with different degrees of crosslinking.^{3–5}

EXPERIMENTAL

Materials

The epoxy resin studied was a commercial epoxy resin based on DGEBA, namely, *Araldite F* (CIBA-GEIGY), with an epoxy equivalent weight of 188.3 g equiv⁻¹, and an RD which was a low-viscosity aliphatic diglycidyl ether (CIBA-GEIGY *Araldite DY 026*) with an epoxy equivalent weight of 113.8 g equiv⁻¹. The epoxy resins were mixed at a weight ratio of 100 : 50 (DGEBA : RD) and cured with a cyclic carboxylic anhydride derived from methyltetrahydrophthalic anhydride (MTHPA) (CIBA-GEIGY, hardener *HY 905*) with an accelerator of tertiary amine type (CIBA-GEIGY, accelerator *DY 061*). The quantity of the hardener was in the stoichiometric ratio and that of the accelerator was 1 part by weight (pbw). The epoxy resins and the hardener were vigorously stirred at room temperature

for about 20 min before the addition of the accelerator. The mixture was again stirred for 20 min and, finally, was degassed under vacuum for about 15 min. The epoxy was cured isothermally at 100°C for 13 h. As shown in Ref. 1, after this cure procedure, no residual heat of curing was detected by DSC. This fully cured epoxy with the RD will be referred to as epoxy FRD50.

The results for the enthalpy loss obtained for FRD50 are compared with those obtained earlier for an epoxy resin based on DGEBA with an accelerator (CIBA-GEIGY *Araldite CY 255*) cured by a carboxylic anhydride derived from MTHPA (CIBA-GEIGY, hardener *HY 225*) according to the formulation recently described.^{2,3} Two such epoxy resins were studied: one fully cured⁴ and another one partially (approximately 70%) cured,⁵ which will be referred to as epoxies CY100 and CY070, respectively. The compositions of these systems are summarized in Table I, where their glass transition temperatures T_g are also given.

Calorimetry and Thermal Treatments

The calorimetric measurements were performed using a Mettler TA4000, DSC 30. For the annealing experiments, the samples were first heated to a temperature (T_2) above the glass transition and then cooled at $q_1 = -20$ K min⁻¹ to the annealing temperature (T_a) of 53°C in FRD50. After the annealing period of duration t_a , the samples were cooled to a temperature T_1 well into the glassy region and immediately reheated in the DSC at $q_2 = 10$ K min⁻¹ to T_2 . To measure the enthalpy loss during the annealing period, a second DSC scan on the same sample was obtained for the same thermal history but without the annealing period. The glass tran-

Table II Characteristic Temperatures for Annealing Experiments for the Different Epoxy-Anhydride Systems Studied

System	T_a (°C)	t_a (h)	T_1 (°C)	T_2 (°C)	Ref.
FRD50	53	0.5 to > 2000	0	110	This work
CY100	80	0.5 to > 2000	20	130	4
CY070	30	0.5 to > 4500	-20	75	5

sition temperature ("midpoint T_g ") of the resin FRD50 measured in this latter cycle ($t_a = 0$) was 73°C. Thus, the aging temperature was $T_a = T_g - 20$ K as for the other resins investigated earlier (CY100 and CY070).^{4,5} It is from the dependence of the enthalpy loss, $\bar{\delta}_H$, and the peak temperature, T_p , on annealing time that the nonlinearity parameter is evaluated. Table II summarizes the characteristic temperatures of the thermal treatment used in the epoxy FRD50, as well as for the other two systems without the RD investigated earlier.^{4,5}

Intrinsic cycles for the estimation of β and for the evaluation of the activation energy were made by cooling the FRD50 samples at different rates, from -0.5 to -40 K min⁻¹, and immediately reheating ($\bar{\delta}_H = 0$) in the DSC at 10 K min⁻¹. The change in the specific heat capacity ΔC_p at the glass transition temperature was determined from the intrinsic cycles, cooling at -20 K min⁻¹ and heating at 10 K min⁻¹, using standard procedures and software.

RESULTS

Measurement of the Apparent Activation Energy Δh^*

Figure 1 shows the cooling rate experiments that permit the determination of T_f for each cooling rate. The apparent activation energy Δh^* is evaluated from the dependence of T_f on the cooling rate q_1 in intrinsic cycles⁶:

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

This dependence is shown in Figure 2, where it can be seen that the data fit well to a straight line. The value of Δh^* calculated from the slope of this plot is 831 kJ mol⁻¹. The values reported for the

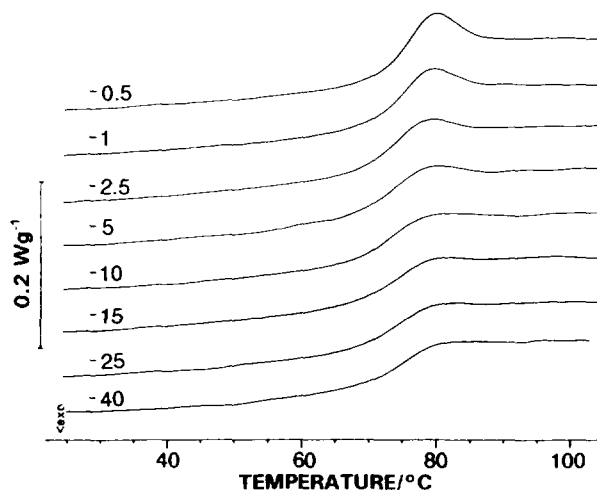


Figure 1 DSC curves for epoxy FRD50 obtained on heating at 10 K min⁻¹ immediately after cooling at rates indicated in K min⁻¹.

other epoxy systems without the RD are 1100 kJ mol⁻¹ for CY100 (Ref. 4) and 615 kJ mol⁻¹ for CY070 (Ref. 5).

Measurement of ΔC_p

The value of ΔC_p determined as an average of nine results from three different samples of the epoxy FRD50 is 0.37 ± 0.01 J g⁻¹ K⁻¹. The values found

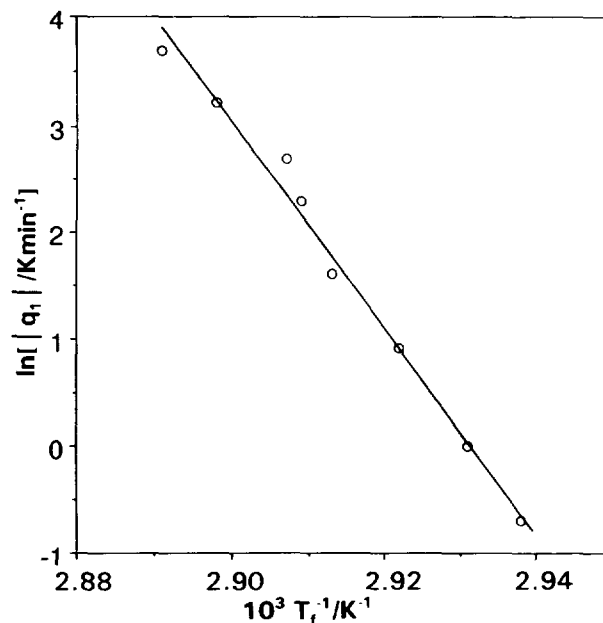


Figure 2 Plot of logarithm of cooling rate as a function of reciprocal fictive temperature for the epoxy FRD50.

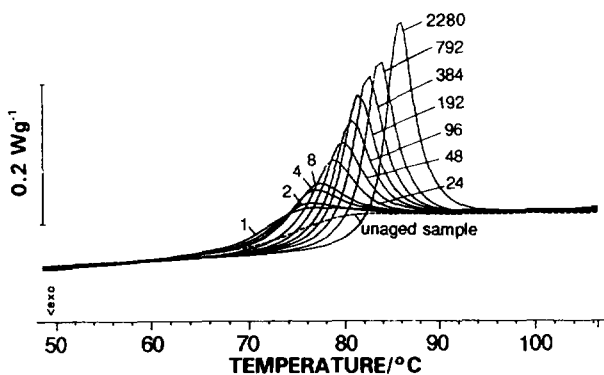


Figure 3 DSC curves for epoxy FRD50 obtained on heating at 10 K min^{-1} after the indicated annealing times (in hours) at 53°C .

for the other epoxy systems without the RD are $0.34 \text{ J g}^{-1} \text{ K}^{-1}$ for CY100 (Ref. 4) and $0.41 \text{ J g}^{-1} \text{ K}^{-1}$ for CY070 (Ref. 5).

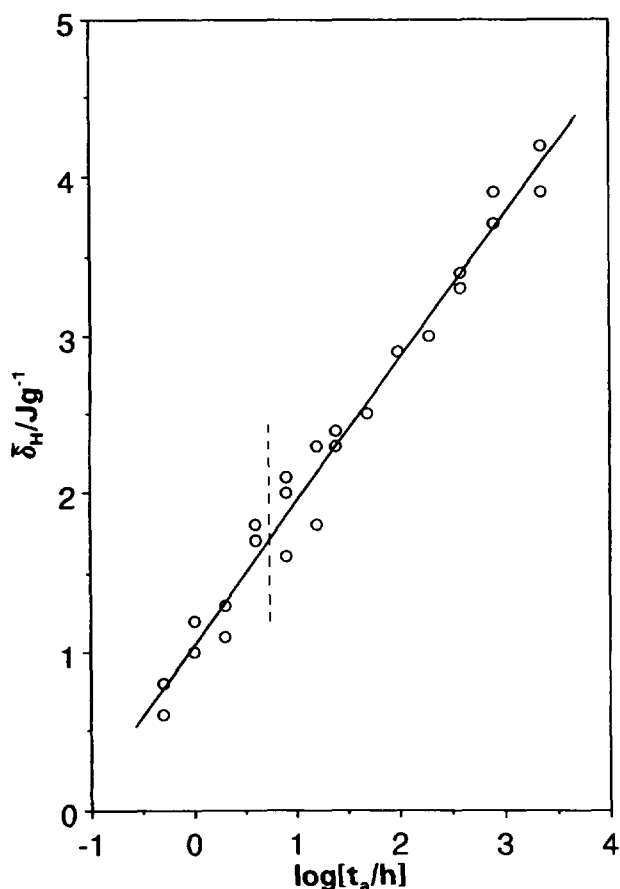


Figure 4 Dependence of enthalpy loss during annealing at 53°C on log annealing time for the epoxy FRD50. Solid line is a linear fit to experimental data for times greater than 4 h.

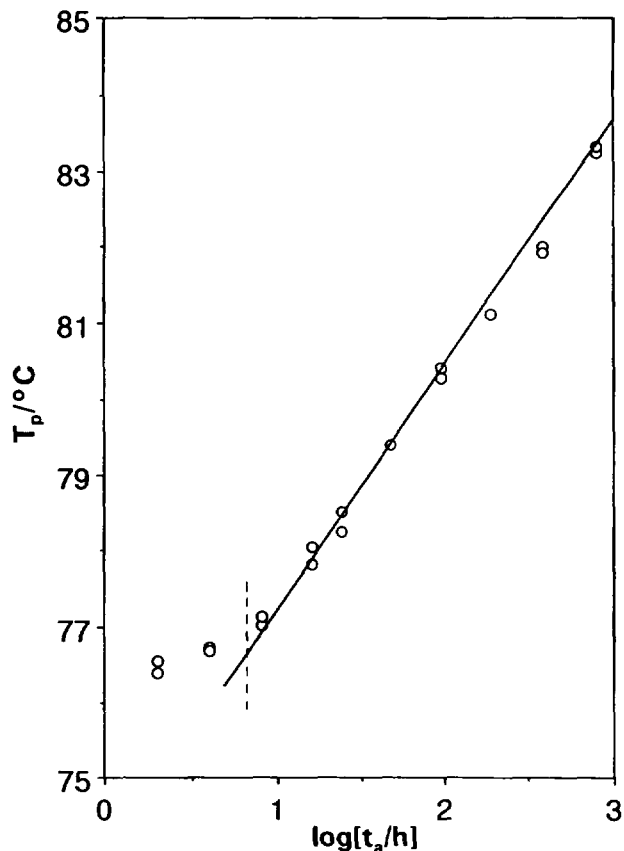


Figure 5 Dependence of peak temperature on log annealing time for the epoxy FRD50 annealed at 53°C . Solid line is a linear fit to experimental data for times greater than 4 h.

Measurement of x

Figure 3 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 results are shown in Figures 4 and 5, respectively. The straight lines represent the best fits utilizing only those data points corresponding to annealing times greater than or equal to 8 h, as indicated by the vertical dashed lines. The reason for this restriction on the range of annealing times can be seen by reference to Figure 5, where a clear departure from a linear dependence can be seen. Such behavior is known to occur at short annealing times,¹⁰⁻¹³ where the endothermic peak takes on a different significance (see following section). Furthermore, for annealing times less than 2 h, this peak was so broad and shallow that a peak temper-

$$\Delta C_{p,u} = \frac{M}{C_{p,l} - C_{p,g}}$$

(6)

rotation of amphoteric chains between the dispersion.

A units of DGEBA causes an easier rotation of

backbone atoms around their bonds than in the epoxy based only on DGEBA.

In thermoplastic polymers, a correlation between Δh^* , x , and β has often been observed.^{19,20} According to this correlation, the value of Δh^* usually increases as the parameter x decreases, and this trend is illustrated by the open circles in Figure 7 for several amorphous thermoplastics, for which the data have been taken from the literature,^{13,14,21-27} with the reference numbers located within the open circle data points. The trend is reasonable, although there are clearly quite large uncertainties in some cases (e.g., Refs. 21, 22, and 25).

In rather surprising contrast, the fully cured epoxy resin CY100 was found earlier to be significantly displaced from this trend for the glassy thermoplastics.⁴ The crosslinked structure had been anticipated to provide a "strengthening" effect, in the Angell sense,²⁸ with a resulting low apparent activation energy and a correspondingly relatively high value of x , similar to the observations in network-forming inorganic glasses. Equally surprising was the result found for the partially (70%) crosslinked epoxy resin system,⁵ for which the apparent activation energy decreased relative to the fully cured resin, while the value of x remained essentially constant. These results are indicated in Figure 7 by the filled symbols, circles and squares, respectively.

A possible rationalization of this result was suggested by Hodge.²⁹ Starting from the Adam-Gibbs equation,³⁰ one can derive an expression, analogous to eq. (1), for the dependence of the relaxation time on temperature and fictive temperature²⁰:

$$\tau(T, T_f) = A \exp \left[\frac{Q}{T \left(1 - \frac{T_2}{T_f} \right)} \right] \quad (7)$$

where A is a preexponential constant, T_2 is the Kauzmann temperature, at which the configura-

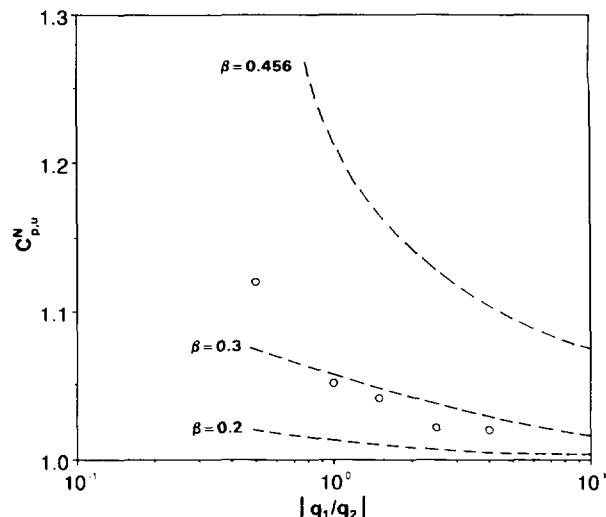


Figure 6 Variation of normalized upper peak height with the logarithm of the ratio of cooling rate to heating rate for intrinsic cycles ($\bar{\delta}_H = 0$) with heating rate 10 K min^{-1} for FRD50 (\circ). The dashed lines correspond to theoretical variations for combinations of $\beta = 0.456$, $\beta = 0.3$, and $\beta = 0.2$, all with $x = 0.4$.

tional entropy reduces to zero, and Q may be written in the form²⁰

$$Q = \frac{N_A s_c^* \Delta \mu}{k_B C} \quad (8)$$

Here, N_A is Avogadro's number; s_c^* , the configurational entropy of the smallest number of particles capable of rearranging; $\Delta \mu$, the "primary" activation energy; k_B , Boltzmann's constant; and C , the value of ΔC_p at T_2 .

Comparison of eqs. (1) and (7) allows approximate relationships between the parameters to be derived; in particular, one can find²⁰

$$\frac{\Delta h^*}{R} \approx \frac{Q}{x^2} \quad (9)$$

Table III Annealing Results and Calculation of Nonlinearity Parameter for the Different Epoxy-Anhydride Systems Studied

System	ΔC_p (J g^{-1} K $^{-1}$)	$\partial \bar{\delta}_H / \partial \log t_a$ (J g^{-1})	$\partial T_p / \partial \log t_a$ (K)	x	Ref.
FRD50	0.37	0.89	3.24	0.37 ± 0.02	This work
CY100	0.34	0.80 ^a	2.70	0.42 ± 0.03	4
CY070	0.41	1.24 ^a	3.45	0.41 ± 0.03	5

^a These values for the slopes are averages of two slightly different slopes obtained in UPC and AU; the individual slopes may be found in the original articles.

from which $Q \approx x^2 \Delta h^*/R$. Thus, the observed constancy of x and decrease of Δh^* as the degree of crosslinking decreases in our epoxy resin systems^{4,5} would imply a decrease in Q as the degree of crosslinking decreases. From eq. (8), this may result from changes in any of s_c^* , $\Delta\mu$, or C . It seems reasonable to assume that the minimum entropy s_c^* and the primary activation energy $\Delta\mu$ might be independent of the degree of crosslinking, provided that the crosslinks are sufficiently far apart. The observed decrease in apparent activation energy Δh^* may therefore arise simply from the well-documented increase in ΔC_p as the degree of crosslinking decreases.³¹

Considering now the effect of the addition of an RD to the epoxy resin (see Fig. 7, filled triangles), relative to the fully cured system, the activation energy decreases significantly while the value of x decreases only slightly. Thus, the increased molecular mobility associated with a reduction in crosslinking degree or addition of an RD draws these crosslinked systems closer to the overall trend observed for linear thermoplastic polymer glasses.

In polymeric and inorganic glasses, a correlation between x and β is also often observed,^{19,20,32} whereby β increases as x increases. Comparison of the results obtained for FRD50 and CY070 with those for CY100 show a significant reduction in β for both of the former, more flexible, crosslinked systems, indicative of a broader distribution of relaxation times, which seems intuitively reasonable. However, correlation of β with x is more difficult because of the rather small changes in x relative to the uncertainty in its value; nevertheless, the reduction in both β and x from CY100 to FRD50 is at least consistent with the usual observations.

It is interesting to note, in this context, that the appearance of sub- T_g peaks has often been associated in the past with a broad distribution of re-

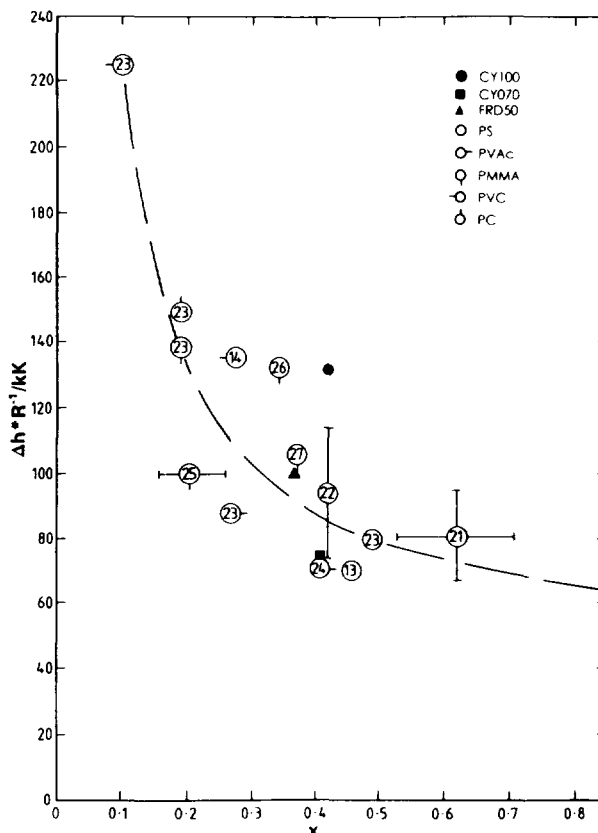


Figure 7 Reduced activation energy, $\Delta h^*/R$, as a function of nonlinearity parameter x for various amorphous thermoplastics, represented by the open circles. Data are extracted from the literature, with references given inside the open circles. Filled symbols represent data for epoxy resin systems: (●) CY100; (■) CY070; (▲) FRD50.

laxation times (small value of β). The classic example of this is PVC, for which a value for β of 0.23, the lowest found for any polymer glass, has been reported.²⁰ Pronounced sub- T_g peaks have also been noted^{33,34} for fully cured epoxies, although for which

Table IV Reduced Apparent Activation Energy $\Delta h^*/R$ and Estimated Nonexponentiality Parameter β for the Different Epoxy-Anhydride Systems Studied

System	Δh^* (kJ mol ⁻¹)	$\Delta h^*/R$ (kK)	β	Ref.
FRD50	831	100	≈ 0.3	This work
CY100	1100	132	0.3–0.456 ^a	4
CY070	615	74	≈ 0.3 ^a	5

^a These values for β correspond to results obtained using the Mettler TA 4000 DSC 30. Slightly different values were obtained for the same resins using a Perkin-Elmer DSC 4. Further details may be found in the original articles.

we do not find a particularly small value of β .⁴ However, as discussed previously in respect to annealing in inorganic glasses,³⁵ a small value of β is neither a prerequisite for nor is it particularly conducive to the appearance of sub- T_g peaks, and the existence or otherwise of such peaks should not be used as an indicator of the magnitude of β .

From the point of view of the applications of these epoxy resins cured by a carboxylic anhydride, the addition of a reactive diluent reduces the viscosity of the initial mixture and improves the processability of the resin. On the other hand, however, the cross-linked resin with the RD exhibits an increased effect of structural relaxation, which could reduce the range of applications when used as coatings and casting products. The formulation of these systems should therefore achieve a compromise between the initial viscosity and the thermal properties of the thermoset.

CONCLUSIONS

The effect of an RD on enthalpy relaxation in an epoxy resin based on DGEBA cured by a cyclic carboxylic anhydride with an accelerator was studied. The addition of this compound modifies the chemical structure of the epoxy by the introduction of aliphatic segments between the bisphenol A units of the DGEBA.

The results show that the addition of an RD to the DGEBA epoxy resin decreases the values of the activation energy, Δh^* , and of the nonlinearity parameter, x , and produces a small reduction of the nonexponentiality parameter β . Contrary to correlations between x and Δh^* observed for other polymers, both x and Δh^* for the epoxy with the RD, FRD50, decrease with respect to the corresponding values for the fully cured epoxy without the RD, CY100. The values of ΔC_p , Δh^* , and the rate of relaxation, expressed as the slopes of both δ_H and T_p as a function of $\log t_a$, for the resin with the RD are intermediate between those for the fully cured and for the partially cured resins.

This work shows also that DSC is a sensitive and reliable technique for studying the structural relaxation process exhibited by thermosets when they are maintained at a service temperature which is lower than the T_g . It is also interesting to note that the formalism used here, based upon three parameters (x , Δh^* , and β), gives a simple and characteristic description of the behavior of the resin in the glassy

state. However, more systematic studies in other thermosetting polymers are needed to interpret the correlation between these structural parameters, in both thermosetting and thermoplastic polymer glasses.

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