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THE USE OF DSC TO CHARACTERIZE STRUCTURAL RELAXATION IN THERMOSETTING POLYMERS

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Abstract

Structural relaxation in different epoxy-anhydride and epoxy-diamine resins has been investigated by differential scanning calorimetry using annealing and cooling rate experiments. The annealing experiments lead to the determination of enthalpy loss, ΔH, at an equivalent annealing temperature $T_a=T_g-20$, and for periods of annealing time, t_a, between 1 h and 4 months. The variation of ΔH with $\log t_a$, defines a relaxation rate per decade, *rrpd*, which is very sensitive to changes of the epoxy network. The cooling rate experiments allow the determination of the apparent activation energy, Δh^*. The effect of the degree of crosslinking, the addition of a reactive diluent, which acts as flexibilizer, and the length of cross-link on *rrpd* and Δh^* was studied.

Keywords: cross-linking degree, DSC, enthalpy relaxation, epoxy resins, physical aging, reactive diluent

Introduction

When an amorphous polymer is cooled through the glass transition region, it undergoes a process of structural relaxation. This process is characterized by the slow change of bulk properties such as specific volume, enthalpy, and mechanical and dielectric response which attempt to establish equilibrium. In the free volume framework, the free volume of the system, and consequently also the mobility of the chain segments, decreases slowly and continuously. The resulting effect is to cause continuous changes in any property of the polymer which is dependent upon segmental mobility [1].

In particular, structural relaxation during isothermal treatment at a temperature below the glass transition temperature T_g, which has been called physical aging [2, 3], is an area of considerable interest in view of its practical consequences for the durability of thermosetting polymers. However, structural relaxation also takes place during the cooling or the heating of the polymer in the glassy state. In the last

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thirty years, differential scanning calorimetry (DSC) has been widely used to study this process by enthalpy relaxation, as shown recently by Hodge in a review [4].

The objective of this paper is to study the behavior of two epoxy systems (epoxy-anhydride and epoxy-amine systems) in the glassy state by calorimetric experiments of annealing and cooling rate. The relaxation rate may be evaluated from the experiments of annealing and the effect of network changes can be studied. The cooling rate experiments allow us to calculate the activation energy, Δh^*, which is a characteristic parameter of the structural relaxation. Within an epoxy series, Δh^* is correlated with the relaxation rate per decade.

The epoxy resins studied are derived from diglycidyl ether of bisphenol A (DGEBA) cured both by a cyclic carboxylic anhydride with accelerator [5, 6], and by a diamine. The network is modified by intramolecular effects, through changes in the chemical structure of the backbone chains by the introduction of an aliphatic diepoxide, or by intermolecular effects, either by modifying the cross-link degree of the network or by changing the length of cross-links.

Experimental

Epoxy-anhydride systems

The epoxy-anhydride system was a commercial epoxy resin based on DGEBA (Ciba-Geigy Araldite CY 225), with an epoxy equivalent of 200 g/equiv., cured by a carboxylic anhydride derived from methyltetrahydrophthalic anhydride (MTHPA) with accelerator (Ciba-Geigy HY 225), with a ratio resin:hardener of 10:8 by weight, at 130°C for 8 h giving a fully cured epoxy as shown in a previous work [7]. This epoxy will be called CY100, and its T_g was 100°C. The glass transition temperature has been measured in all the epoxy systems as the mid-point of ΔC_p in a DSC scan obtained by heating at 10 K min^{-1} immediately after the cooling from a temperature $T_0=T_g+20$°C at 20 K min^{-1}. This cycle is called an intrinsic cycle. The same epoxy-anhydride system was obtained partially cured, with a conversion degree of 70% (CY070, $T_g=50$°C), after curing at 80°C for 6 h [7].

An epoxy-anhydride system with a reactive diluent was obtained by curing a DGEBA (Ciba-Geigy Araldite F), with an epoxy equivalent of 188.3 g/equiv., cured by a carboxylic anhydride derived from MTHPA (Ciba-Geigy HY905) with accelerator (Ciba-Geigy DY061) and a reactive diluent (RD) which was a low viscosity aliphatic diglycidyl ether (Ciba-Geigy Araldite DY026), with an epoxy equivalent of 113.8 g/equiv. The epoxy resins were mixed at a weight ratio of 100:50 (DGEBA:RD) as described in Ref. [8] and cured at 100°C for 13 h. The T_g of this system (FRD50) was 73°C.

Epoxy-diamine systems

The epoxy based on DGEBA (Araldite F) was cured with ethylenediamine in a stoichiometric ratio at 70°C for 3 h, and postcured at 150°C for 12 h. The T_g of this epoxy (named FEDA) was 121°C. Diamines of polyoxypropylene (Jeffamine D-230 with $x=2.6$ oxypropylene units and Jeffamine D-400 with $x=5.6$) were used in order to obtain different lengths of cross-link. The curing with Jeffamine D-230 in a stoichiometric ratio at 70°C for 2 h, and postcuring at 120°C for 8 h gave a resin (named FJ230) with a T_g of 80°C. The resin obtained with Jeffamine D-400 (2 h at 80°C and 4 h at 125°C) led to a resin (FJ400) with a T_g of 47°C.

Thermal analysis

The calorimetric measurements were performed using a Mettler TA 4000 DSC 30 in the laboratory of the Universitat Politècnica de Catalunya (UPC), and a Perkin Elmer DSC 4 in Aberdeen University (AU).

The calorimetric experiments were performed in two different ways.

a) Annealing experiments were made at T_g 20°C in order to measure the enthalpy loss, ΔH, by using the conventional thermal treatment [5]: samples were heated to $T_0=T_g+20$ for 5 min, then cooled at a controlled rate of 20 K min^{-1} to the annealing temperature $T_a=T_g-20$ where they were held for a period of time t_a, cooled at 20 K min^{-1} to the initial temperature of the scan, and immediately reheated at 10 K min^{-1} to T_0 (DSC scan of the aged sample). The cycle was repeated without the annealing period to obtain a DSC scan of the non-aged sample. As shown in other references [1–5, 9], the enthalpy loss is determined from the difference between the DSC scans of the aged sample and the non-aged sample, while the peak temperature T_p is found from the maximum of the endotherm for the aged sample.

b) Intrinsic cycles were obtained at different cooling rates (from –40 to –0.5 K min^{-1}), in all cases immediately reheating at a constant rate of 10 K min^{-1}. These intrinsic cycles allow the determination of the apparent activation energy Δh^*.

Results and discussion

Annealing experiments

Figure 1 shows the values of enthalpy loss on annealing, ΔH, over a wide range of annealing times for the epoxy-anhydride systems. From these data the values of the slope, $\partial(\Delta H)/\partial \log t_a$, in J g^{-1} per decade were determined: 0.80 (average value between 0.84 and 0.77 from UPC and AU, respectively) for the fully cured epoxy CY100, 1.24 for the partially cured (70%) epoxy CY070, and 0.89 for the epoxy with 50 pbw of reactive diluent FRD50. This slope gives a measure of the 'relaxation rate per decade' (*rrpd*) which is characteristic of each epoxy when they are annealed at equivalent temperatures, 20°C below their T_g. The decrease of the cross-linking degree from CY100 to CY070 increases the *rrpd*. In addition, the comparison of CY100 and FRD50 shows that the introduction of aliphatic diepoxide segments between the DGEBA units increases the *rrpd* of the system.

A similar tendency can be observed in the slope $\partial T_p/\partial \log t_a$, calculated from the plot of peak temperature, T_p, *vs.* log annealing time (Fig. 2). The values of these slopes in K per decade are the following: 2.70 (averaged between 2.43 and 2.98

from UPC and AU, respectively) for CY100, 3.45 for CY070 (averaged between 3.51 and 3.40 from UPC and AU respectively), and 3.24 for FRD50.

Figure 3 summarizes the values of *rrpd* indicated by the slope $\partial(\Delta H)/\partial \log t_a$, as a function of the glass transition temperature of the epoxy; a decrease of the *rrpd* is related with an increase of the T_g of the resin. Decreasing the length of cross-links also gives a decrease of *rrpd*, but the change from the system FJ400 to FJ230 is very small. These results show that the change of the length of cross-links (when

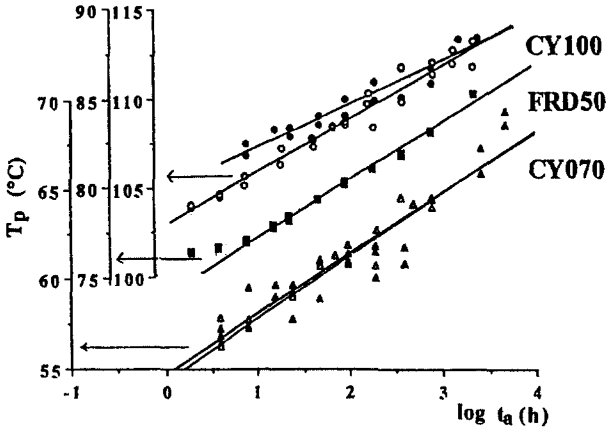

Fig. 1 Dependence of enthalpy loss during annealing at T_g 20°C on log annealing time for the epoxy-anhydride systems: CY100 (T_a=80°C) (•, o), CY070 (T_a=30°C) (▲, △), and FRD50 (T_a=53°C) (■). Filled symbols are values obtained by a Mettler TA 400 instrument and open symbols by a Perkin Elmer DSC 4. Solid lines are linear fits to experimental data for times greater than 4 h

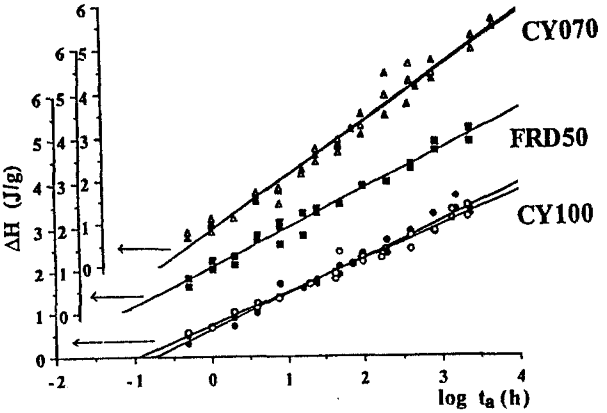

Fig. 2 Dependence of peak temperature during annealing at T_g 20°C on log annealing time for the epoxy-anhydride systems: CY100 (•, o), CY070 (▲, △), and FRD50 (■). Filled symbols are values obtained by a Mettler TA 400 instrument and open symbols by a Perkin Elmer DSC 4. Solid lines are linear fits to experimental data for times greater than 4 h

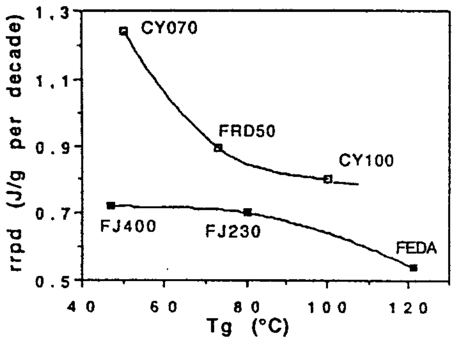

Fig. 3 Dependence of the 'relaxation rate per decade' (*rrpd*) on T_g for the indicated epoxy resins. *rrpd* values correspond to the slopes of the plot of ΔH *vs.* log annealing time (Fig. 1)

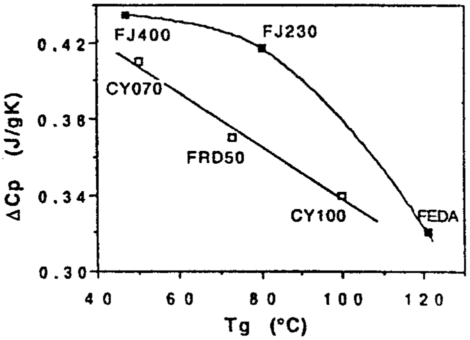

Fig. 4 Dependence of ΔC_p on T_g for the indicated epoxy resins

FJ230 is compared with FEDA), has a lower effect on *rrpd* than the change of the number of cross-links (comparing CY100 with CY070).

For a given epoxy system, a decrease of *rrpd* is also correlated with a decrease of ΔC_p, ΔC_p being the change of heat capacity at T_g, measured for the non-aged sample: $\Delta C_p = C_{p_l} - C_{p_g}$, where C_{p_l} and C_{p_g} are the values of the heat capacity in the liquid and the glassy state, respectively. This observation can be obtained by comparing Figs 3 and 4.

Cooling rate experiments

The DSC curves obtained in samples cooled at different cooling rates q_1 allow the determination of the fictive temperature T_f of the epoxy, which is a thermodynamic property characteristic of the glass structure [10]. The dependence of T_f on the cooling rate in this intrinsic cycle leads to the determination of the apparent activation energy Δh^* [11]:

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

where q_2 is the heating rate of the DSC trace which is constant and equal to 10 K min^{-1}. According to Moynihan *et al.* [11], the activation energy, Δh^*, expresses the temperature dependence of the logarithm of the relaxation times in a range near the equilibrium, and is a characteristic parameter of the structural relaxation of the epoxy.

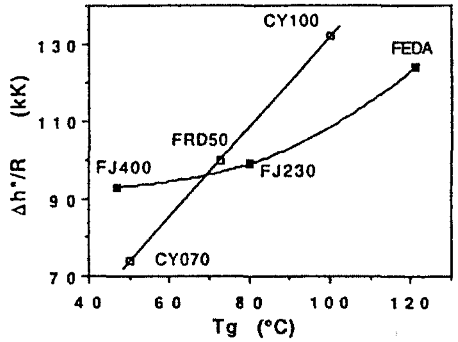

Fig. 5 Dependence of the reduced activation energy $\Delta h^*/R$ on T_g for the indicated epoxy resins

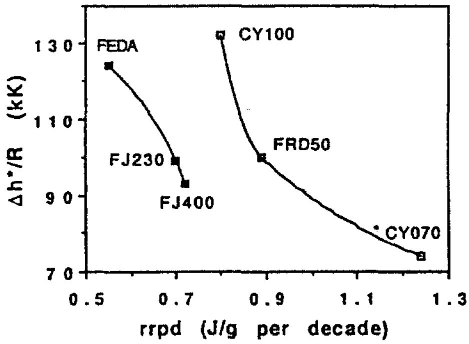

Fig. 6 Dependence of the reduced activation energy $\Delta h^*/R$ on the relaxation rate per decade for the indicated epoxy resins

The calculated values of the reduced activation energy, $\Delta h^*/R$, against T_g in Fig. 5, reveal a continuous increase of $\Delta h^*/R$ with increasing T_g, although the change observed between the epoxy-diamines FJ230 and FJ400 is very small. Relating these results with those obtained for the values of *rrpd* from the annealing experiments, within an epoxy series there is further observed a correlation between an increase of the *rrpd* and a decrease in the activation energy (Fig. 6).

Conclusions

The effects of the degree of crosslinking, the addition of a reactive diluent, which acts as flexibilizer, and the length of cross-link on the structural relaxation of different epoxy-anhydride and epoxy-diamine resins has been studied. The structural (enthalpy) relaxation has been investigated by DSC using annealing and cooling rate experiments.

The annealing experiments lead to the determination of the enthalpy loss whose variation with log annealing time, t_a, defines a relaxation rate per decade, *rrpd*. The experiments performed at different cooling rates and reheating at a constant rate allow the calculation of the fictive temperature T_f. The dependence of $1/T_f$ on $\ln|\text{cooling}|$ ratel leads to the calculation of the activation energy, Δh^*.

Results show that within an epoxy series there is a correlation between *rrpd* and Δh^*, whereby *rrpd* increases as Δh^* decreases. A decrease of the degree of crosslinking, and the addition of a reactive diluent, which acts as flexibilizer, gives an increase of *rrpd*, and consequently a decrease of Δh^*. Increasing the length of cross-links increases slightly the *rrpd* (and decreases Δh^*), though the changes are less significant when the length is increased from 2.6 to 5.6 oxypropylene units compared with the change from ethylene diamine to the diamine with 2.6 oxypropylene units.

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