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STUDY OF THE PHYSICAL AGING OF AN EPOXY/CYCLOALIPHATIC AMINE RESIN MODIFIED WITH ABS

C. Ramírez, M. J. Abad, L. Barral[*]*, J. Cano, F. J. Díez and J. López*

Departamento de Física, E. U. P. Ferrol, Universidad de A Coruña, Avda. 19 de Febrero s/n 15405 Ferrol, Spain

Abstract

Using differential scanning calorimetry (DSC) we have studied the physical aging of an epoxy resin based on the diglycidyl ether of bisphenol A (DGEBA) modified by two different contents of an acrylonitrile–butadiene–styrene (ABS) and cured with 1,3-bisaminomethylcyclohexane (1,3-BAC). Samples fully cured were annealed at temperature of 125°C for periods of time of 72 and 120 h, to determine the process of physical aging. The apparent activation energy for the enthalpy relaxation, Δh^*, is determined as the sample is heated at 10°C min^{-1} following cooling at various rates through the glass transition region. DSC studies suggested that the presence of thermoplastic inhibits the process of relaxation.

Keywords: acrylonitrile–butadiene–styrene, differential scanning calorimetry, epoxy blends, physical aging

Introduction

The physical properties of polymeric materials in the glassy state are generally affected by the thermal history. A glassy polymer sample quenched from the molten state to below the glass transition temperature, T_g, is not in the equilibrium state. When the sample is annealed at a temperature, T_a, near but below T_g, the physical properties change toward the equilibrium conditions result from the change and relaxation of the chain conformation. This process is called physical aging by Struik [1]. The internal structure of polymeric materials changes and relaxes as a result of a change in the chain conformation by molecular motions. The scale of the motion varies with the segmental length, and the mobility depends on temperature.

In this work, we investigate the process of physical aging of an epoxy system containing diglycidyl ether of bisphenol A (DGEBA) and 1,3-bisaminomethylcyclohexane (1,3-BAC) as curing agent, and its blends with the thermoplastic

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[*] Author for correspondence: E-mail: labpolim@udc.es

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acrylonitrile–butadiene–styrene (ABS) at 5 and 15 phr (where phr represents the number of parts by mass quantity of ABS per hundred parts of DGEBA epoxy resin).

We have previously reported the effect of ABS on the curing of this epoxy system [2] and over the mechanical properties [3]. Studies of physical aging have been performed with differential scanning calorimetry of epoxy–amine systems based on DGEBA [4, 5] but not too much about these systems modified with thermoplastics [6].

Experimental

Material and cure procedure

The studied system is based on a commercial diglycidyl ether of bisphenol A (DGEBA), Araldite GY 260 from Ciba-Geigy, with mass per epoxy equivalent of 205.1 g eq^{-1}. The neat epoxy resin and its blends with acrylonitrile–butadiene–styrene (ABS), QI-300 manufactured by Polidux, were cured with a cycloaliphatic diamine hardener, 1,3-bisaminomethylcyclohexane (1,3-BAC), from Aldrich Chemical, with a molecular mass of 142.25 and manufacturer purity value of >99% according to the supplier. All components were commercial products, and they were used without any further purification.

The epoxy amine system was prepared according to reference [5]. Epoxy resin/ABS mixtures with 5 and 15 phr of ABS were also prepared. ABS was held in an oven at 70°C in order to dry, then it was dissolved in dichloromethane, and the resulting polymer solution was mixed with the epoxy resin at room temperature. Subsequently the diamine was slowly added, with continuous stirring to the DGEBA/ABS. The mixture was submitted to a cured cycle of 2 h at room temperature, followed by 5 h at 40°C and then postcured 8 h at 60°C. This 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 230°C.

Thermal analysis

Differential scanning calorimetry measurements were carried out using a calorimeter Perkin Elmer, DSC 7, equipped with an intracooler and supported by a Perkin Elmer computer for data acquisition/analysis. The thermal response and the temperature were calibrated with the heat of fusion and the melting point of pure indium. A dry nitrogen flow of 40 mL min^{-1} was used as purge gas. Samples of about 10 mg were sealed in aluminium pans.

Two modes of experiments were carried: heating and cooling runs. For heating experiments, the same sample, for each different blend, was heated above T_g for several minutes to eliminate its previous thermal history and then it was quenched to aging temperature, T_a=125°C. After the selected time, the samples were brought to room temperature and immediately reheated through the glass transition region to obtain the first scan. A second scan was made in all experiments to obtain the reference or unannealed scan and the specific heat capacity, ΔC_p, can be determined.

For cooling experiments, each sample was cooled in the calorimeter from T_g+50°C to room temperature at a fixed rate of 0.25, 0.5, 1, 5, 10 or 50°C min^{-1} and the measurements were made as the sample was then heated back to T_g+50°C at 10°C min^{-1}. This testing was performed for the two blends and the neat system. Fictive temperature, T_f, calculations were conducted on the heating scans using the Perkin Elmer analysis software, based on the equal areas method [7].

The heating scans obtained after the various cooling rates allow the determination of T_f as a function of cooling rate and so the evaluation of the apparent activation energy, Δh^*. The use of a simple sample for these experiments is important in reducing experimental error.

Results and discussion

Heating rate experiments

Differential scanning calorimetry is widely used in monitoring the response of glasses to experiments involving heating at constant rate through the glass transition region. This gives rise to the well known endothermic peaks (or overshoot) which are superimposed upon an apparently sigmoidal step like change from glassy to liquid like behavior. The height of such peaks and their location on the temperature scale are both dependent on the experimental conditions. Figure 1 shows DSC scans for the neat system and the blends of 5 and 15 phr of ABS between 100 and 160°C at 72 and 120 h of aging at the temperature of 125°C, and the second scan as reference.

A dominant endothermic peak is seen for all the samples, which shows the effect of physical aging. This phenomenon, the enthalpy relaxation, is due to a change in the segmental conformation of glassy polymers during aging and it is noticed in all the studied systems. Thus, the increase in the area of the endothermic peak of the neat system and blend of 5 phr of ABS, suggest that the amount of segmental relaxation increases with aging [8]. In the blend of 15 phr of ABS, the peak area does not increase on the same form, because the aging temperature is in the range of the glass transition temperature. Besides, the thermoplastic inhibits the process of relaxation, but if the amount of ABS increases (Fig. 2), the blend trends to behave as the neat system, probably due to a process of phase separation.

In these epoxy systems, as in the case of many resins [9], it is not possible to determine the changes in the specific heat capacity in the cooling experiments, then the measurements of ΔC_p were made using a heating rate of 10°C min^{-1} immediately after cooling and averaging several samples.

As the glassy and liquid heat capacity lines are not parallel [10], 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 [11] 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 limiting enthalpy relaxation, Δh_∞, is calculated through the equation [12]

$$\Delta h_\infty = \Delta C_p (T_g - T_a) \tag{1}$$

The Δh_∞ values obtained for the aging temperature of 125°C are listed in Table 1. These values were calculated on the second scans.

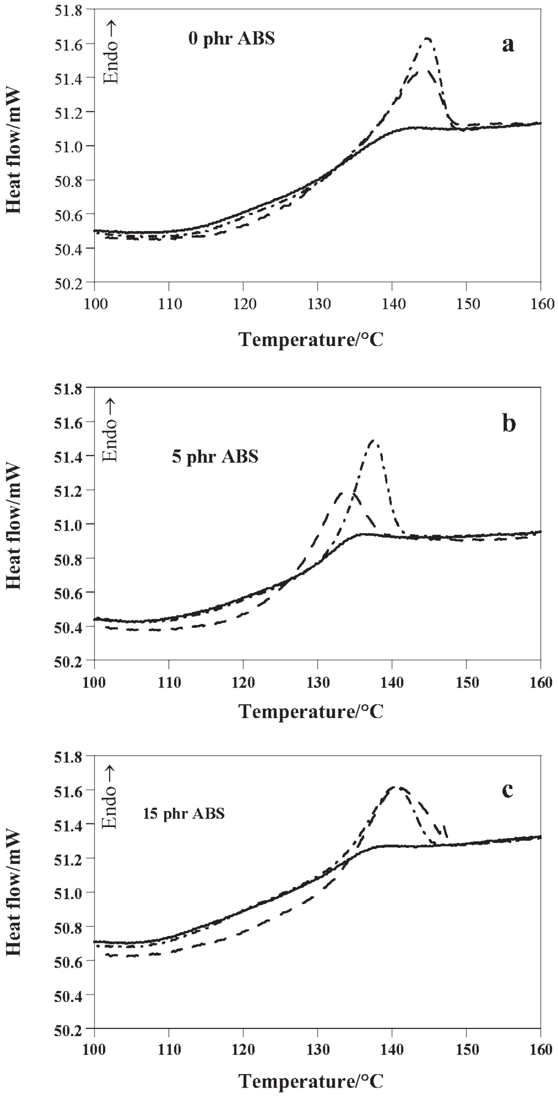

Fig. 1 DSC curves of ABS/epoxy blends at 72 (- - -) and 120 h (-·-·-) of aging and reference scan (—), at the temperature of 125°C

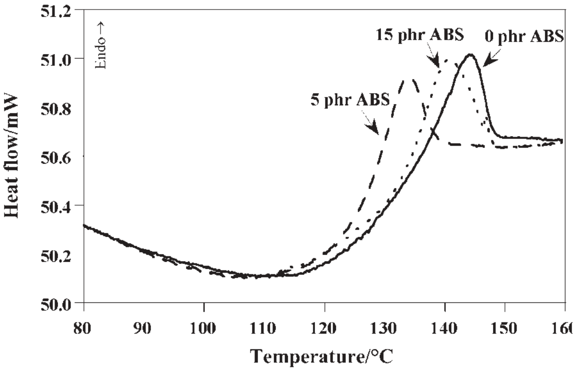

Fig. 2 DSC curves of ABS/epoxy blends aging 72 h at 125°C

Table 1 Limiting enthalpy relaxation for different epoxy blends at the aging temperature of 125°C and values of $\Delta h^*/R$

System	T_g/°C	ΔC_p/J g^{-1}°C^{-1}	Δh_∞/J g^{-1}	$\Delta h^*/R$/kK
Neat	132.1	0.35	2.48	147
5 phr ABS	128.3	0.33	1.09	105
15 phr ABS	125.6	0.25	0.15	90

Cooling rate experiments

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 noticeable when the cooling rate is greater than the heating rate. The upper peak is characterized by its temperature T_u and its height. It is a clear behavior on the heating curves, both the neat system and the blend with low content in ABS, that the peak initially decreases as the cooling rate decreases and then, when the cooling rate decreases below about 1°C min^{-1} it begins to increase again (Fig. 3). This behavior was extensively studied by Hutchinson and Ruddy [13] in order to distinguish clearly between the two types of peak, that occurring for well stabilized glasses (main peak) and for poorly stabilized glasses (upper peak).

DSC curves obtained in the sample cooled at different cooling rates, q_1, allow the determination of the fictive temperature of the epoxy, which is a thermodynamic property characteristic of the glass structure [14]. The dependence of T_f on the cooling rate in this intrinsic cycle leads to the determination of the apparent activation energy Δh^* [7].

$$\frac{\Delta h^*}{R}=-\left[\frac{\partial \ln|q_1|}{\partial(1/T_f)}\right]_{\bar{\delta}_H=O,q_2} \tag{2}$$

where q_2 is the heating rate of the DSC trace which is constant and equal to 10°C min^{-1}. The apparent activation energy is a characteristic parameter of the structural relaxation of

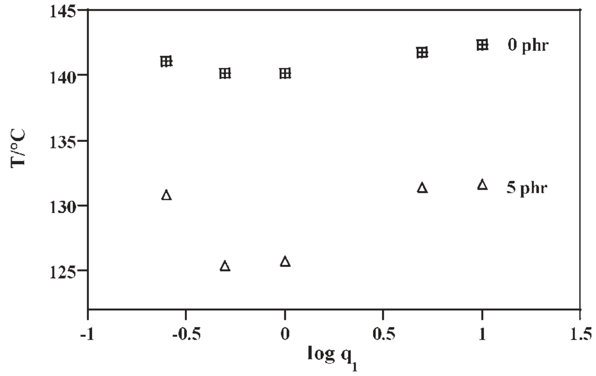

Fig. 3 Dependence of peak temperature on log(cooling rate) for the heating curves. The heating rate is 10°C min^{-1}

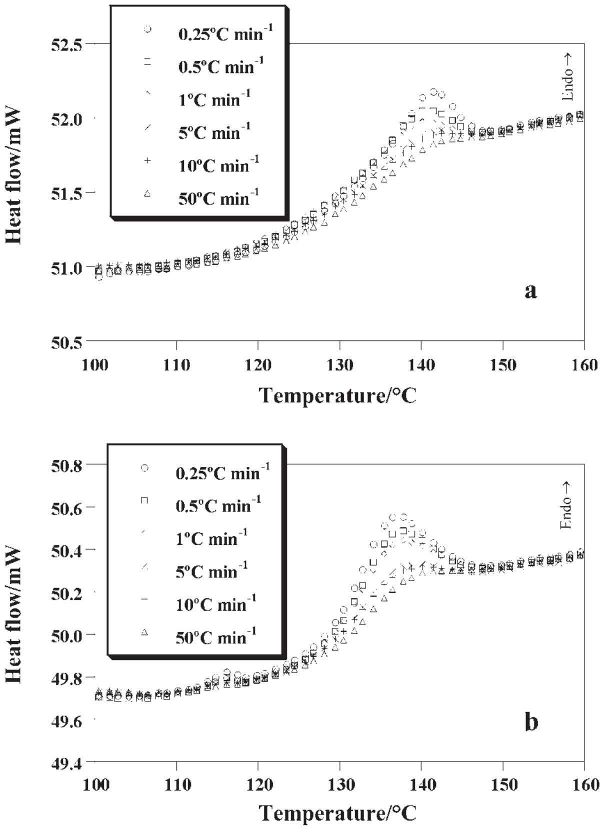

Fig. 4 Heating scans at 10°C min^{-1} for samples cooled at various rates and then immediately reheated in the DSC; a – neat system; b – 15 phr ABS

the epoxies. Figure 4 shows the DSC curves for the neat system and the system with 15 phr of ABS, obtained at a heating rate q_2 immediately after the samples were cooled from 180°C at the different cooling rates, q_1. A novel phenomenon was found when the phr ABS was high. There were dual endothermic peaks appearing when the cooling rate was low. It was also found that the magnitude of both dual endothermic peaks increase with decreasing rate of cooling run. This fact may be due to a phase separation.

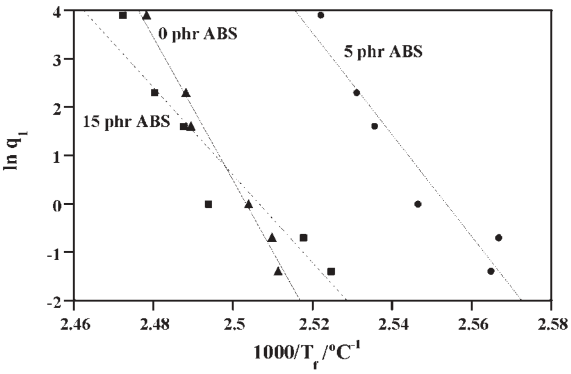

Fig. 5 Plot of the logarithm of the cooling rate as function of the reciprocal fictive temperature for the neat and modified systems

The fictive temperature for a given cooling rate is found by the equal areas method used by the Perkin Elmer analysis software. The apparent activation energy is evaluated from the slope of a plot of logarithm of the cooling rate as a function of the reciprocal fictive temperature (Fig. 5). The values of $\Delta h^*/R$ are given in Table 1. The value of Δh^* for the neat system of 1228 kJ mol^{-1} is much higher than the values of modified systems 875 and 748 kJ mol^{-1}, therefore the ABS inhibit the process of relaxation.

Conclusions

The process of physical aging both the neat and blends of ABS systems was determined. As the epoxy resin is modified with ABS its apparent activation energy, Δh^*, decreases. A decrease in Δh^* means that the internal mobility of the internal chains increases. The presence of thermoplastic inhibits the process of relaxation.

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