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Analysis of the activation energy spectrum for the enthalpy relaxation of a glassy liquid crystalline polymer

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The phenomenology of the physical ageing of glassy materials can be described by using the activation energy spectrum model. This model was originally developed for relaxations in metallic and oxide glasses and this paper applies it to a liquid crystalline polymer, poly(diethylene glycol *p*, *p*′-bibenzoate) (PDEB), in the glassy state.

PDEB samples were quenched from above T_g and isothermally annealed in a differential scanning calorimetry (DSC) equipment, and a description of the enthalpy relaxation of PDEB was achieved by means of the Kohlrausch–Williams–Watts (KWW) equation. The results show that the relaxation time decreases when the annealing temperature increases and can be explained in terms of an Arrhenius-type equation. The predicted value for the apparent activation enthalpy (0.98 eV) is lower than those reported for other polymers. This approach assumes that a unique elemental process with a relaxation time $\tau_0 = 1.3 \times 10^{-13}$ min controls the evolution of the system.

Energy spectra demonstrate that the activation energy values for the mechanisms controlling the relaxation are lower than 1.1 eV and the spectra present a maximum for an activation energy close to 0.98 eV. The total number of available relaxation processes (measured by the area below the curves) decreases if the sub-T_g annealing temperature increases. Moreover, the results show that the distributions widen if the shape parameter of the KWW equation decreases.

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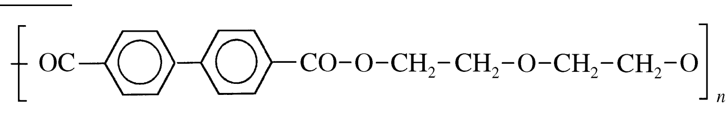
1. Introduction

The study of glass-forming materials is a research area of interest because of its theoretical and technological consequences. On the one hand, some questions about the physics of the glass transition and the nature of the glassy state are open. On the other hand, glassy materials performance and reliability must be predicted during the design process. Consequently, a rather extensive body of literature that includes books [1, 2], reviews [3–5] and proceedings [6–9] concerning this subject has been developed.

If a glass-forming material is cooled from the liquid state through the glass transition, its structure begins to depart from the equilibrium one as a result of the decreasing molecular mobility. The non-equilibrium state tends to relax below the glass transition temperature approaching the corresponding stable state. This time-dependent structural change towards equilibrium, that is known as physical ageing, is accompanied by measurable property changes. The properties' evolution during ageing displays a very rich phenomenology including asymmetry of isothermal recovery and memory or cross-over effects [10]. The Kovacs, Aklonis, Hutchinson and Ramos (KAHR) model describes these and other features of the glassy state but does not provide an explanation for the effective relaxation time paradox [10]. The assumption that the relaxation in complex systems proceeds according to the coupling model leads to a resolution of the mentioned paradox [11].

The phenomenology of the physical ageing of glassy materials can be also described by using the activation energy spectrum (AES) model [12]. Whereas the KAHR model and coupling ones are based on considerations on relaxation time spectrum, this third approach considers a unique relaxation time and an activation energy spectrum. This model was developed for relaxations in metallic and oxide glasses but it can be applicable to any amorphous material.

Poly(diethylene glycol *p,p*′-bibenzoate) (PDEB) is a polyester which exhibits a liquid crystalline character [13] and has the following structural formula



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The presence of the central ether group in the spacer inhibits the transformation of the mesophase into a three-dimensional crystal, found for similar polybibenzoates with all-methylene spacers [14–17]. Some aspects of the ageing of PDEB, analysed by microhardness and differential scanning calorimetry (DSC) measurements, have been previously reported [18]. As usual in mesophase-forming polymers, the liquid crystalline phase cannot be avoided with regular quenching conditions and PDEB displays a glass transition which actually corresponds to a transition from the liquid crystalline glass.

The aim of this paper is, then, to analyse the physical ageing of PDEB and to check if the AES model [12] can describe the sub-T_g annealing of this liquid crystalline glass.

2. Materials and experimental procedure

PDEB was synthesized by melt transesterification of the diethyl ester of *p,p′*-bibenzoic acid (4,4′-biphenyldicarboxylic acid) and diethylene glycol, using isopropyl titanate as catalyst. The obtained polyester was purified by dissolving in chloroform and precipitating in methanol. Its intrinsic viscosity, measured at 25 °C in chloroform [13], was 102 ml g^{-1}.

A Perkin Elmer DSC7 calorimeter was used for the study of the annealing process of PDEB. The glass transition was taken as the temperature where the specific heat change is one half of its total increment at the transition. The magnitude of the ageing process has been estimated from the enthalpy of the endothermic peak appearing at the top of the glass transition (see Fig. 1), considering the baseline resulting from the prolongation of the specific heat curve above the glass transition temperature (T_g).

In order to obtain comparative results, the thermal history imposed to the sample was always the following: starting from a temperature of 75 °C, well above the T_g, the sample was quenched to a specified annealing temperature and after the desired ageing time the DSC heating curve was registered, at a rate of 10 °C min^{-1}.

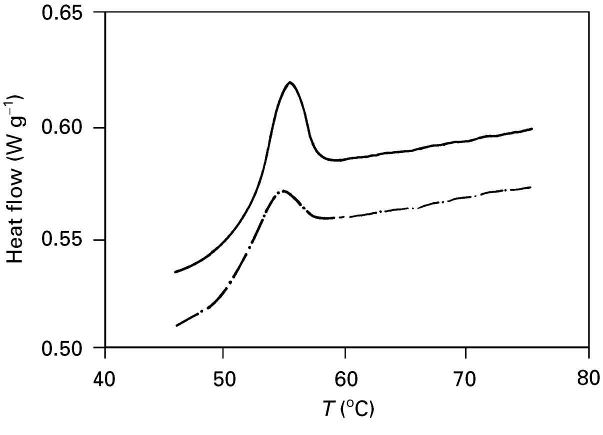

Figure 1 DSC traces (heating rate 10 °C min^{-1}) of PDEB aged at 40 °C for 60 min (upper) and 20 min (lower).

3. The activation energy spectrum

The property changes that occur in glassy polymers upon isothermal annealing below the glass transition temperature, T_g, can be represented in terms of the expression

$$\Delta P(t_A, T_A) = \Delta P(\infty, T_A)(1 - \phi) \tag{1}$$

where $\Delta P(t_A, T_A)$ is the measured property change after the polymer has been annealed for a time t_A at a temperature T_A, $\Delta P(\infty, T_A)$ is the asymptotic value of $\Delta P(t_A, T_A)$ and ϕ is the relaxation function. Those property changes are related to the approach of the system to its corresponding equilibrium state at T_A and are controlled by microscopic processes whose activation energies, E, are distributed over a continuous spectrum according to the AES model [12]. This model predicts that $\Delta P(t_A, T_A)$ can be approached by the integral

$$\Delta P(t_A, T_A) = \int_0^{kT_A \ln(\nu_0 t_A)} P_0(E)\,\mathrm{d}E \tag{2}$$

where $P_0(E)$ is proportional to the number of elemental processes with activation energy E which have contributed to the relaxation after time t_A, k is Boltzmann's constant and ν_0 a pre-exponential factor that is related to the frequency of the elemental relaxation processes. Further manipulations of Equation 2 leads to [19, 20]

$$P_0(E) = \frac{\Delta P(\infty, T_A)}{kT_A} \frac{\mathrm{d}\phi}{\mathrm{d}\ln t_A}\bigg|_{t_A = \frac{1}{\nu_0}\exp\frac{E}{kT_A}} \tag{3}$$

that yields information about the activation energy spectrum of the processes determining the relaxation, if $\Delta P(\infty, T_A)$, ϕ and ν_0 are known. (These kinds of manipulations are well known by rheologists: the calculations parallel those involved in the obtention of the Alfrey's rule that relates the relaxation time spectrum to the modulus [21].

The total available property change, $\Delta P(\infty, T_A)$, depends on the annealing temperature and on the nature of the measured quantity, i.e. on the cooling rate and on the experimental technique. It has been suggested [22] that a linear relationship exists between the asymptotic value of heat absorption in an enthalpy relaxation experiment, $\Delta Q(\infty, T_A)$, and the difference $(T_g - T_A)$, that reads

$$\Delta Q(\infty, T_A) = \Delta c_p(T_g - T_A) \tag{4}$$

Δc_p being the specific heat increment between the liquid and the glassy states at T_g. The values that were obtained for the calorimetric T_g and Δc_p of PDEB are 325 K and 0.222 J g^{-1} K^{-1}, respectively. By substituting these values into Equation 4 and by combining Equations 1 and 4, the relaxation functions can be determined after measuring the heat evolution in enthalpy relaxation experiments.

4. Results and discussion

A phenomenological description of the enthalpy relaxation during isothermal annealing of glassy materials

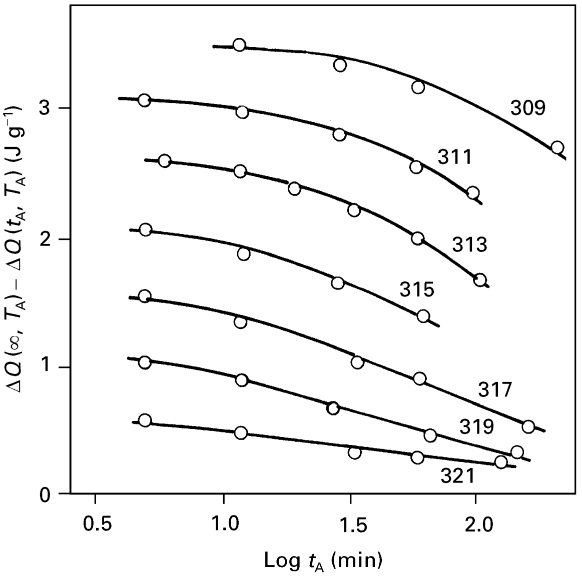

Figure 2 Available enthalpy change, $\Delta P(\infty, T_A) - \Delta P(t_A, T_A)$, as a function of the annealing time, t_A, and temperature, T_A.

can be achieved by means of stretched exponential function [23]

$$\phi = \exp[-(t/\tau)^{\beta}] \qquad (5)$$

where the effective relaxation (or correlation) time, τ, and the shape parameter, β, are related to the kinetics and the width of the relaxation and depend on the temperature. Equation 6 is also known as the Kohlrausch–Williams–Watts (KWW) equation [24].

Fig. 2 shows that our experimental results on PDEB fit KWW equations well. In fact, $\ln(-\ln\phi)$ is a linearly increasing function of t_A for each isothermal set of data with correlation coefficients that are greater than 0.99. It is interesting to point out that this kinetics is different from those described for enthalpy relaxation of other polymers (atactic polystyrene [22] and poly(ethylene terephthalate) [25]): a linear dependence has been observed when $\Delta Q(\infty, T_A) - \Delta Q(t_A, T_A)$ is plotted versus $\ln t_A$. In terms of the AES model [12], this behaviour corresponds to a constant value of $P_0(E)$ for $E > kT_A \ln(\nu_0 t_A)$ whereas the stretched exponential kinetics corresponds to a non-constant activation energy spectrum. Anyway, it must be remarked that these experiments only sample a small fraction of the total energy spectrum and, consequently, the assumption of a constant $P_0(E)$ is not severe.

Fig. 3 displays the variation of the KWW equation parameters, β and τ, with T_A. The upper part of this figure shows that τ decreases when T_A increases and that the results can be explained in terms of an Arrhenius-type equation. At this point, it is important to remark that $P_0(E)$ remains almost unaffected [12] by the choice of ν_0, thus, the frequency factor is not going to be calculated, but estimated by means of the expression

$$\tau = \tau_0 \exp(E_{app}/kT) \qquad (6)$$

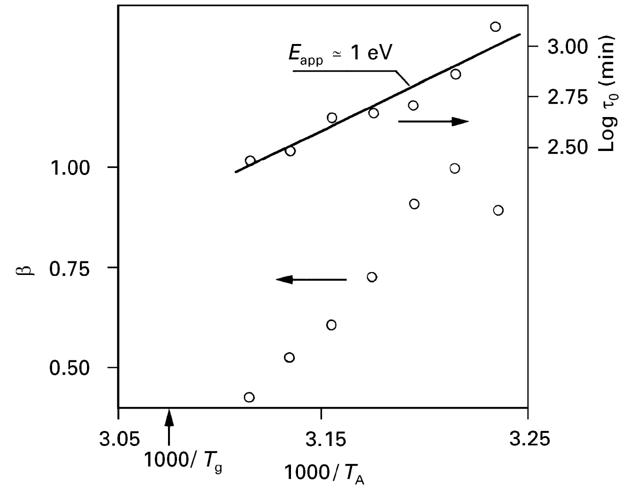

Figure 3 Annealing temperature, T_A, dependence of the parameters β and τ of the relaxation function, Equation 5, for PDEB.

E_{app} being the apparent activation enthalpy. In our calculations the reciprocal of the pre-exponential factor τ_0 is assumed to equal ν_0. This approach assumes that a unique elemental process with a relaxation time $\tau_0 = 1.3 \times 10^{-13}$ min and an $E_{app} = 0.98$ eV controls the evolution of the system and allows the AES obtained from the same experiment for different temperatures to be superimposed [26].

It can be argued that the calculated activation enthalpy is too low for the enthalpy relaxation of amorphous polymers because higher values have been reported (close to 10 eV) [22, 24, 25]. Even more, it has been pointed out that calculations analogous to ours, i.e. those that ignore the non-equilibrium nature of the glassy state, yields too small E_{app} values (about 2 eV for PS) [22]. So, in order to check the validity of our estimations, E_{app} has also been evaluated by using the KAHR model with a single-order parameter. An acceptable agreement with the experimental data has been observed and a confidence interval of 1.1 ± 0.2 eV (confidence level 95%) was obtained for E_{app}. Even more, mechanical relaxation of PDEB by means of microhardness measurements has been studied and KAHR analysis yields an E_{app} value of 1.30 ± 0.15 eV [27]. According to these, it can be considered that 0.98 eV is a sound value of the activation energy for the enthalpy relaxation of PDEB. This low value for E_{app} can be probably related to the liquid crystalline nature of the glassy PDEB.

Fig. 4 shows the energy spectra for the enthalpy relaxation of PDEB at different annealing temperatures. These spectra have been calculated according to Equation 3, with $\nu_0 = 1/\tau_0 = 7.7 \times 10^{12}$ min^{-1}, and the parameters of the KWW equation are those that have been collected in Fig. 3. It can be seen that the activation energy values for the elemental processes controlling the relaxation in these experiments are lower than 1.1 eV and present a maximum for an activation energy close to the apparent activation enthalpy that is obtained when a unique relaxation process is considered. As it can be expected, the total number of available relaxation processes (measured by the area below the curves)

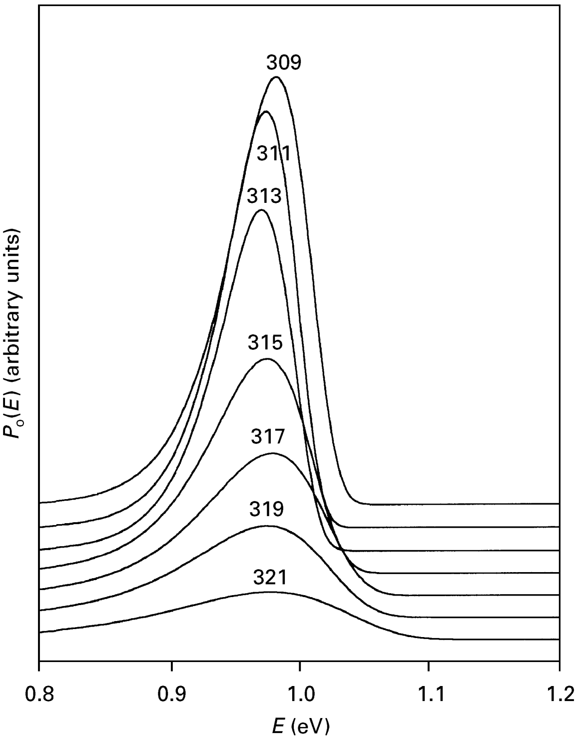

Figure 4 Activation energy, E, spectra for the enthalpy relaxation of PDEB samples aged at the indicated temperatures in K.

decreases if the sub-T_g annealing temperature increases.

The effect of temperature on the width of the spectra will be considered now. It can be seen in Fig. 4 that the curves tend to sharpen when T_A decreases. This behaviour can be explained by taking into account that the shape parameter is closely related to the width of the relaxation spectra: it has been pointed out that the greater β is, the sharper is the relaxation time distribution [28] and it has been found [29] that the conductivity relaxation data of some ionic compounds show that the width of the electric modulus spectra is a linearly increasing function of $1 - \beta$. Then, it can be expected that the activation energy spectra reflect the β dependence on T. As usual, the sharpness of the peaks can be measured by their half-widths, HW, that are plotted versus β^{-1} in Fig. 5, showing that the distributions widen linearly (correlation coefficient 0.991) if the reciprocal of β increases.

5. Summary

In summary, it has been shown that the enthalpy relaxation of PDEB can be described in terms of the KWW equation and an alternative route to analyse experimental results has been proposed. Some of the features of the activation energy spectrum, that provides information about the elemental processes controlling the macroscopic relaxation, can be related to the apparent activation energy and to the shape parameter of the KWW function. It should be interesting to extend this analysis to other polymers and to investigate the ability of the AES model to predict quantitatively the results of cross-over experiments on these types of materials.

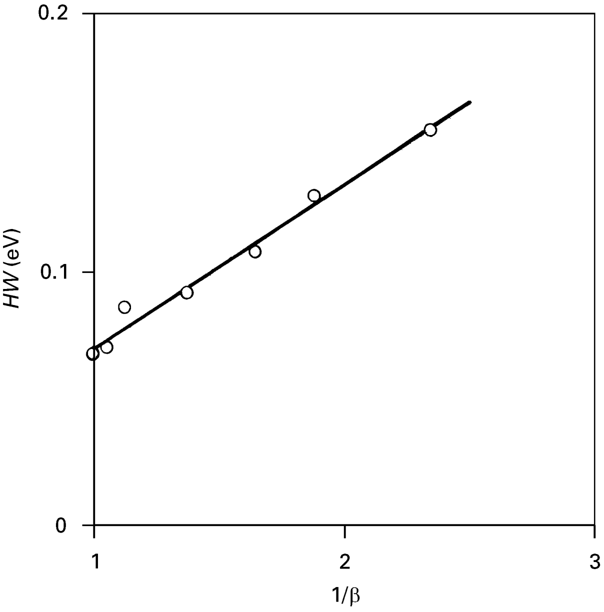

Figure 5 Relationship between the shape parameter, β, of the relaxation functions and the half-width, HW, of the activation energy spectra.

Acknowledgement

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