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Structural relaxation in a polyester thermoset as seen by thermally stimulated recovery

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Abstract

The thermally stimulated recovery technique (TSR), also known as thermally stimulated creep, is a low-frequency mechanical spectroscopic technique that is shown to enable the monitoring of the structural relaxation process in a polyester-based thermoset ($T_g \sim 95$°C). Thermal sampling experiments are able to isolate the contribution of a narrow window of relaxation times assigned to the strain of the material at different temperatures. Such experiments were performed after an ageing period at the same creep temperature. Three ageing temperatures and several ageing times were investigated. Characteristic parameters of the obtained TSR curves are observed to vary with T_a and t_a. Such variations are discussed on the basis of the general variation of the viscoelastic response upon structural relaxation, namely the shift of the distribution of relaxation times associated with the glass transition, towards longer times. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Physical ageing; Viscoelasticity; Compensation

1. Introduction

Many liquids can be transformed into glass, a solid phase without long-range positional order, by cooling them rapidly below their freezing temperature [1–3]. The change in molecular relaxation processes upon approaching the glass transition, continues to be the subject of much experimental and theoretical work [4,5]. Amorphous solids at temperatures below their glass transition T_g are not in a true thermodynamic equilibrium state. These materials are to be regarded as solidified supercooled liquids, whose relevant variables such as volume, enthalpy and entropy are greater than they would be in the equilibrium state [6]. Amorphous or low-crystallinity polymers are one of the most studied of such systems. In the metastable glassy state, the physical and mechanical properties of such materials change with time as the glass attempts to achieve equilibrium by slow changes in molecular configurations. This process has been commonly designated as the physical ageing or structural relaxation. Structural relaxation shows common behaviour: (i) non-linearity with respect to the magnitude of departure from equilibrium; (ii) asymmetry with respect to the sign of departure from equilibrium; and (iii) memory effects that are sensitive to the thermo-physical ageing behaviour.

A deep understanding of the time dependence of material properties is desirable if optimum material performance is required. In fact, taking into account only the change of the mechanical performances during ageing, it is observed that the yield stress and the elastic modulus of the polymer increase, whereas the impact strength, fracture energy, ultimate elongation and creep/stress relaxation rates decrease.

Most of the work done on the characterisation of the kinetics of the structural relaxation process has been based on the experimental determination of the dependence of enthalpy (measured by DSC) and volume on the annealing time at different temperatures. Any physical parameter, which depends on the conformational mobility, is affected by structural relaxation and its dependence on the thermal history can be used to characterise structural relaxation. Techniques, such as creep/recovery, dielectric or mechanical relaxation spectroscopies [7], and also more unusual techniques such as fluorescence [8], positron annihilation [9] or confocal microscopy in colloidal systems [10], have been used with this aim. However, the equivalence on the kinetics through equilibrium as measured with different variables is still controversial.

Thermally stimulated depolarisation currents (TSDC) have been shown also as an interesting technique to study

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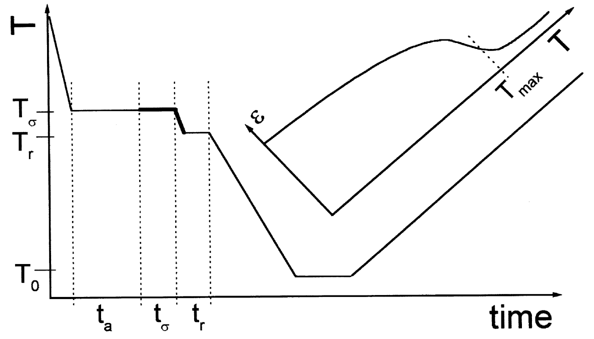

Fig. 1. Scheme of a typical TS experiment to study structural relaxation. The static stress is applied during the times t_σ and the cooling to T_r (thicker lines in the T vs time representation). Typical values of the experimental variables: $t_\sigma \sim 5$ min, $T_w = T_\sigma - T_r = 3$°C, $t_r \sim 2$ min, $\beta \sim 4$°C/min. T_{max} is the inflexion temperature of $\epsilon(T)$.

structural relaxation [11–15]. The low equivalent frequency of this technique [16] may be an advantage, if we pretend to investigate slow relaxations such as physical ageing. Moreover, this kind of techniques allows the individualisation of the complex processes, analysed by means of the so-called thermal sampling (TS) or thermal windowing procedure. Thermally stimulated recovery (TSR) is a similar technique, where the electric field is substituted by a static mechanical field. It was previously shown that these experiments can be carried out in commercial DMA (dynamic mechanical analyser) equipment [17,18]. This technique has the advantage of being able to study non-polar materials.

In this work we present the possibility of using TSR to study structural relaxation in polymeric systems.

2. Experimental

2.1. Material

All the experiments were carried out on a thermoset synthesised from a polyester resin based on orthophthalic acid — (Alpolic VUP 9731 from Hoechst). The preparation of the thermoset is presented elsewhere [18,19]. The advantage of using this material is related with its interesting thermal stability up to ~40°C above T_g and its negligible irreversible flow when subjected to mechanical stresses

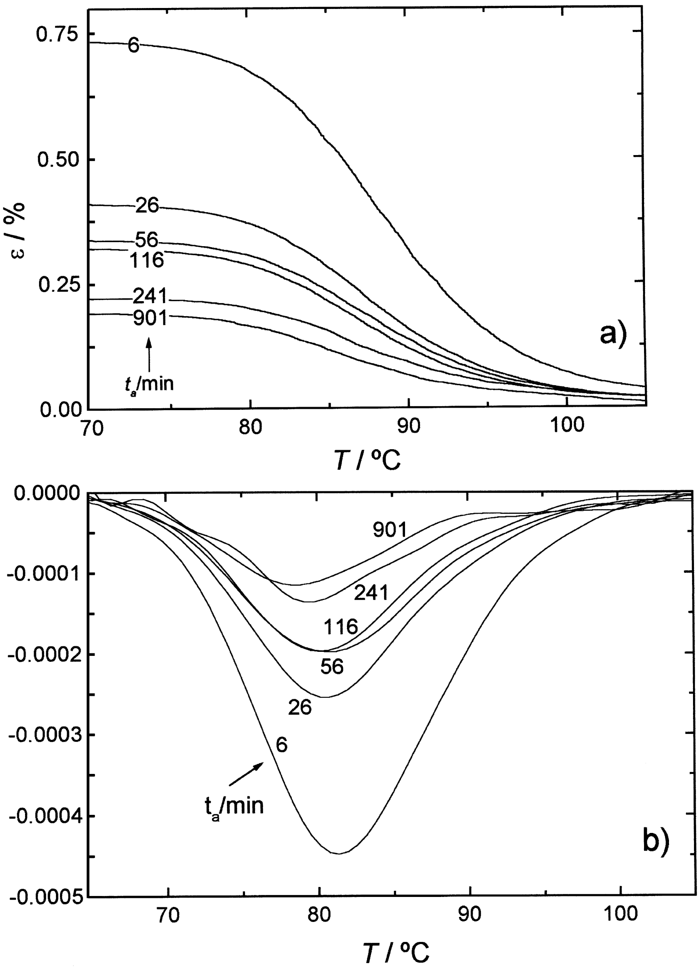

Fig. 2. TS curves obtained after an ageing period at $T_\sigma = 73$°C during different ageing times (shown over the curves). (a) Strain recovery; (b) dϵ/dT vs T.

[19]. Therefore, it was possible to use only one sample for all the mechanical experiments. In this case, a rectangular piece with dimensions of 1.45 × 5.47 × 18 mm, was used.

2.2. Thermally stimulated recovery studies

The dynamic mechanical apparatus used in this work was a DMA7e Perkin-Elmer analyser with controlled cooling accessory. Continuous flux of high-purity helium (flow rate of $\sim 25\ \mathrm{cm}^3\ \mathrm{min}^{-1}$) was used to improve heat transfer throughout the sample surroundings. The experiments on the polymer were carried out with the three-point bending mode. The sample was placed over a 15-mm bending platform, and a 5-mm knife-edge probe tip provided the mechanical excitation.

The physical ageing experiments with the TSR technique were carried out using the thermal sampling procedure (TS). In these experiments the mechanical stress is applied in a narrow temperature range within the glass transition region. A typical TS experiment is schematically explained in Fig. 1 and may be described as follows: (i) the sample is cooled from the equilibrium state ($T > T_g$) down to T_σ and is kept at that ageing temperature for a given ageing time t_a; (ii) a static stress σ_0 is applied at T_σ during a time period t_σ (T_σ varies from experiment to experiment in the region of the global process); (iii) the sample is quenched to $T_r = T_\sigma - T_w$ with the mechanical field on; (iv) the stress is removed and the mechanical strain is allowed to recover during a period of time t_r; (v) the sample is quenched to T_0, well below the temperature region of the global process (say 50°C below T_σ); and (vi) the position of the probe tip, always in contact with the sample, is monitored during controllable heating (β is the heating rate) from T_0 up to a final temperature well above T_σ.

In this study we use temperature windows, T_w, of 3°C and the creep and recovery times, t_σ and t_r, were 4 min. In all experiments the mechanical stress was $\sigma_0 = 5$ MPa and $T_0 = 50$°C.

2.3. DSC studies

The differential scanning calorimetry, DSC, experiments were carried out in a Perkin–Elmer DSC7 differential scanning calorimeter with controlled cooling accessory. The temperature of the equipment was calibrated with indium and lead standards and for the heat flow calibration only the same indium sample was used. All calibrations were carried out during heating, at 20°C/min. A single 20.069 mg polymer sample, sealed in an aluminium pan, was used for all the DSC experiments.

The enthalpy relaxation experiments were conducted as follows: (i) the sample was heated to above T_g (130°C) in order to erase any thermal history; (ii) the sample is then cooled at 100°C/min to the ageing temperature, $T_a = 73$°C, and aged during an ageing time, t_a, ranging from 0 to 5550 min; and (iii) after the ageing period the sample is cooled to 30°C. The results are subsequently collected during a heating ramp from 30 to 140°C, at 20°C/min.

3. Results

3.1. Thermally stimulated recovery results

The glass transition temperature of the studied thermoset is approximately 90°C [18]. The thermal sampling (TS) experiments were carried out at three different ageing temperatures: 73, 80 and 85°C. For each temperature, the TS experiments were performed after several ageing times, typically from 5 to 1000 min. In Fig. 2a some TS curves are presented, corresponding to experiments with $T_a = 73$°C and ageing times (t_a) between 6 and 901 min.

Each TS curve can be analysed as a thermally stimulated mechanical recovery process of an elementary mechanism. The Voigt–Kelvin model (parallel association of an elastic spring and a viscous dashpot) can be used in order to predict the dependence of the strain upon time or temperature. The corresponding constitutive equation is:

$$\epsilon(t) = \frac{\sigma_0/E - \epsilon(t)}{\tau(T)} \tag{1}$$

where σ_0 is the static strain, E is the Young modulus of the spring element and $\tau(T)$ is the retardation time of the process. The characteristic time is $\tau = \eta/E$, where η is the viscosity of the Newtonian dashpot.

Applying Eq. (1) to the mechanical recovery ($\sigma_0 = 0$) during heating at a constant rate β, the temperature dependence of the strain is

$$\epsilon(T) = \epsilon_0 \exp\left[-1/\beta \int_{T_0}^{T} \mathrm{d}T'/\tau(T')\right] \tag{2}$$

where $\epsilon_0 = \epsilon(T_0)$.It can be easily found from Eq. 2 that

$$\tau(T) = -\frac{1}{\beta}\frac{\epsilon(T)}{\mathrm{d}\epsilon(T)/\mathrm{d}T} \tag{3}$$

Fig. 2b shows the $\mathrm{d}\epsilon(T)/\mathrm{d}T$ curves calculated from $\epsilon(T)$ at different ageing times, at 73°C. These curves show a peak with the maximum appearing at $T = T_{\max}$.

Eq. (3) is often used to calculate the temperature dependence of the retardation time directly from the experimental results. This procedure, often called Bucci or BFG method, was first derived for the treatment of TSDC data [20]. The calculation of $\tau(T)$ by the BFG method is carried out between $\sim T_{\max} - 30$ and $\sim T_{\max}$. The experimental TS curve is never a pure elementary process and it was shown that due to this fact the validity of Eq. 3 should be lower for temperatures above $\sim T_{\max}$ [21–23].

From each of the performed TS experiments $\tau(T)$ was calculated up to $T_{\max}$. The temperature dependence of the retardation times of the elementary processes can be described with the Arrhenius equation:

$$\ln \tau(T) = \ln \tau_0 + E_a/\mathrm{R}T \tag{4}$$

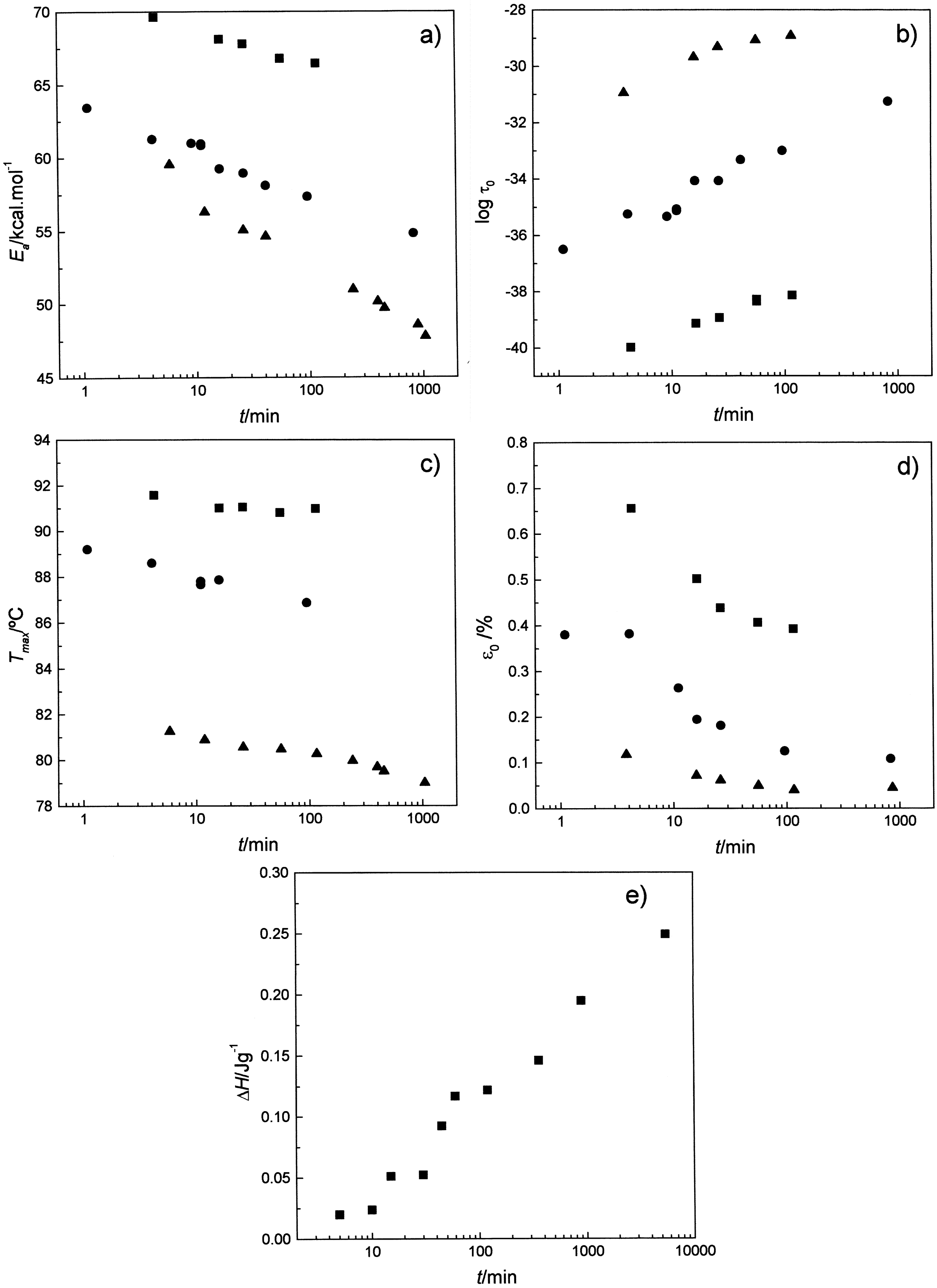

Fig. 3. Dependence of the parameters of the TS curve, on ageing temperature and time ((a) activation energy, (b) pre-exponential factor, (c) inflexion temperature, and (d) maximum strain recovered). Ageing temperatures, T_a: squares, 85°C; circles, 80°C; triangles, 73°C. (e) Enthalpy change during ageing at 73°C after different ageing times as seen by DSC.

where $\tau(T)$ is obtained at each temperature T using Eq. (3) on the experimental data, E_a is the apparent activation energy, τ_0 is the pre-exponential factor and R is the perfect gas constant. The thermokinetic parameters E_a and τ_0 are obtained by fitting ln $\tau(T)$ vs $1/T$. This assignment of the observed elementary process to a thermal-activated process has been popular in TSDC and TSR experiments. Fig. 3a and b shows the dependence of E_a and log τ_0 on the ageing time for the studied ageing temperatures. It is clear that a systematic decrease of E_a and an increase of log τ_0 is observed with increasing t_a.

Fig. 3c shows the ageing time dependence of T_{max}, the inflexion temperature of $\epsilon(T)$, i.e. the temperature of maximum of $d\epsilon/dT$(see Fig. 2b), which may be considered as the location of the processes in the temperature axis. The figure suggests that the elementary processes shift towards lower temperatures during ageing. It is easy to show from the analysis of Eqs. (2) and (3) that, in an Arrhenius situation, the thermokinetic parameters (E_a and τ_0) and T_{max} are not independent variables:

$$\tau_0 \ \exp \frac{E_a}{RT_{max}} = \frac{RT_{max}^2}{\beta E_a} \tag{5}$$

Fig. 3d shows the total strain of each elementary process that was stored at low temperatures and that was totally recovered during heating. This recovered strain corresponds to the pre-exponential factor in Eq. (2), ϵ_0.

3.2. DSC results

The structural relaxation process was also studied by DSC at 73°C. The results are shown in Fig. 4 for the case of ageing times between 0 and 5550 min.

Enthalpy changes during ageing were determined by subtracting the DSC curves of the annealed material ($T_a =$ 73°C, t_a) from that of the reference glass (cooled at 100°C/min from 140 to 30°C before the heating scan) [24,25]:

$$\Delta H(t_a) = \int_{T_1}^{T_2} ((C_{pa}(T) - C_{pr}(T))dT$$
$$= \frac{1}{\beta m}\int_{T_1}^{T_2}\left(\frac{dQ_a(T)}{dt} - \frac{dQ_r(T)}{dt}\right)dT \tag{6}$$

Here $C_{pa} - C_{pr}$ is the difference between the experimental heat capacities of the aged and the unaged sample. The integral is evaluated between T_1, a temperature low enough in the glassy state and a convenient temperature limit T_2 above T_g (in the equilibrium phase). $C_{pa} - C_{pr}$ can be obtained from the heat flux measured in the aged sample (dQ/dt) and the heat flux of the reference sample (unaged, i.e. $t_a = 0$) sample (dQ/dt), correcting for the heating rate, β, and the mass, m, as is shown in Eq. (6). The loss of enthalpy during ageing, at 73°C, for the studied thermoset is shown in Fig. 3e.

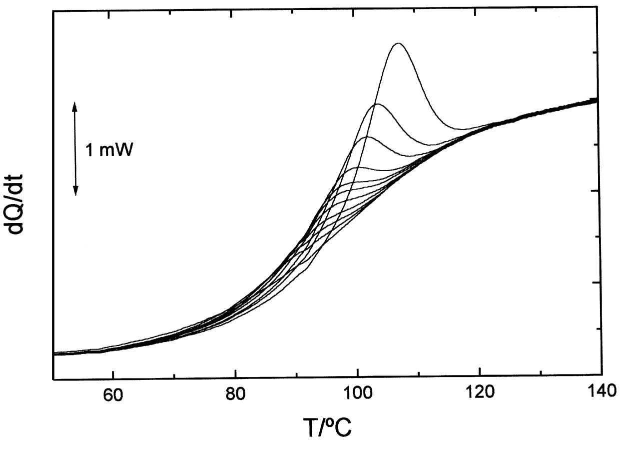

Fig. 4. DSC results obtained after ageing at $T_a = 73$°C and at different ageing times between 0 and 5550 min. The heating rate was 20°C/min. The sample weight was 20.069 mg.

4. Discussion

As explained in the experimental section, the thermal profile of the thermal sampling experiments in TSR selects a narrow window within the distribution of relaxation times. A stress σ_0 is applied to the polymer sample at a temperature T_σ for a time t_σ. Approximately, it can be said that the deformation of the sample in response to this stress is due to the contribution of molecular groups that relax in times smaller than t_σ, or that their relaxation time is smaller than a characteristic relaxation time τ_σ which depends on t_σ. Then, the temperature is decreased a few degrees to T_r and the stress made zero again. Under these conditions the sample is kept for a time t_r, which in our experiments is equal to t_σ, and a part of the deformation is recovered, this recovery is due to groups that at temperature T_r relax at times shorter than t_σ. Again, it can be said, approximately, that the remaining deformation of the sample at the end of this stage, and that will be monitored during heating, is due only to those molecular groups whose relaxation times are at T_σ shorter than τ_σ but at the temperature T_r are longer than τ_σ. This is a narrow window around τ_σ within the distribution of relaxation times, as shown in the schema of Fig. 5.

It is well known since the first works of Struik [26] that the ageing process shifts the distribution of relaxation times towards longer times.

The viscoelastic response, and in particular the result of a creep experiment, of the amorphous polymer in the temperature range in which the glass transition takes place can be characterised by a broad distribution of relaxation times $g(\log \tau)$. At least as a good approximation the viscoelastic behaviour is thermorheologically simple, as shown by the fact that the creep curves measured at different temperatures can be superposed with good approximation

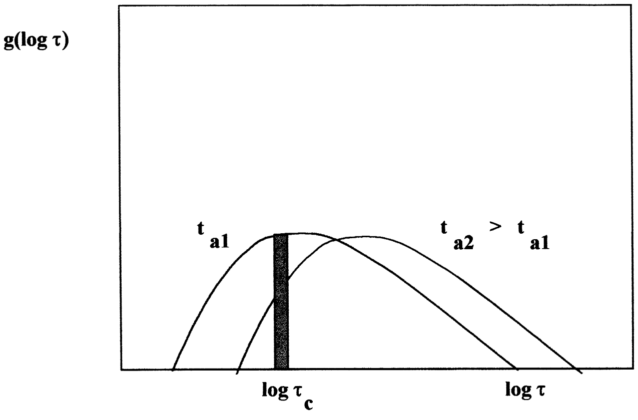

Fig. 5. Scheme of the distribution of relaxation times. The grey layer represents the window of relaxation times, which is responsible of the deformation of the sample after the deformation stage of the TS experiment. This window is shifted towards the left, i.e. towards shorter times, within the distribution of relaxation times as the ageing time increases.

by shifts in the time axis in a logarithmic scale. Thermorheological simplicity is also seen during ageing since creep recovery curves measured after successive creep experiments at the same temperature but after different ageing times can be superposed by shifts in the time axis (see Fig. 6). The behaviour, in this sense, can be described making reference to the schema of Fig. 7: at temperatures above the glass transition, in the rubber-like state, the sample is in thermodynamic equilibrium, with a distribution of relaxation times whose position in the time axis depends exclusively on temperature. The temperature dependence of the relaxation times in equilibrium states can be described by the Vogel equation. In the glass transition the relaxation times depart from the equilibrium line and in the glassy state the relaxation times of the polymer are much shorter than what would correspond to equilibrium at the same temperature. During physical ageing, at constant temperature T_a, the relaxation times shift to longer times trying to approach the equilibrium values.

As the ageing time increases, the distribution of relaxation times shifts towards longer times (see Fig. 5). As the parameters characteristic of the thermal sampling experiment σ, T_σ, T_r, and t_σ are the same for the experiments conducted after different ageing times, the relaxation time window, which is "activated" in the deformation stage of the TS experiment, corresponds to shorter times (with respect to the distribution of relaxation times) as the annealing time increases, as shown in Fig. 5. The molecular groups, which are responsible for the part of the distribution of relaxation times situated on the shorter times side of the distribution, relax more quickly and thus, the recovery of the deformation during the heating scan appears at shorter temperatures as the ageing time increases. This behaviour is, in fact, observed in the results in Fig. 3c, which shows how T_m decreases as the ageing time increases at constant ageing temperature. Fig. 3a shows a slight decrease in activation energy with increasing ageing time. In spite of the low magnitude of this process it is consistent over all studied temperatures and was also found in other systems in our laboratory. Thermal sampling experiments both in TSR and TSDC shows that, for a fixed temperature, the apparent activation energy is an increasing function of the relaxation

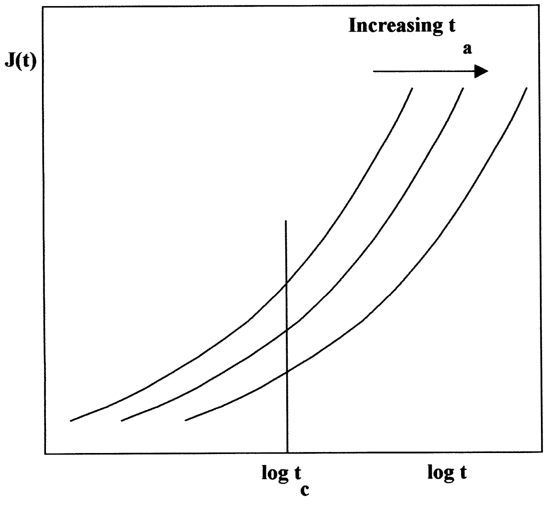

Fig. 6. Scheme of the influence of the ageing time on the creep compliance measured as a function of time in an isothermal creep experiment. The decrease of the sample deformation as the ageing time increases, for the same creep time, is shown.

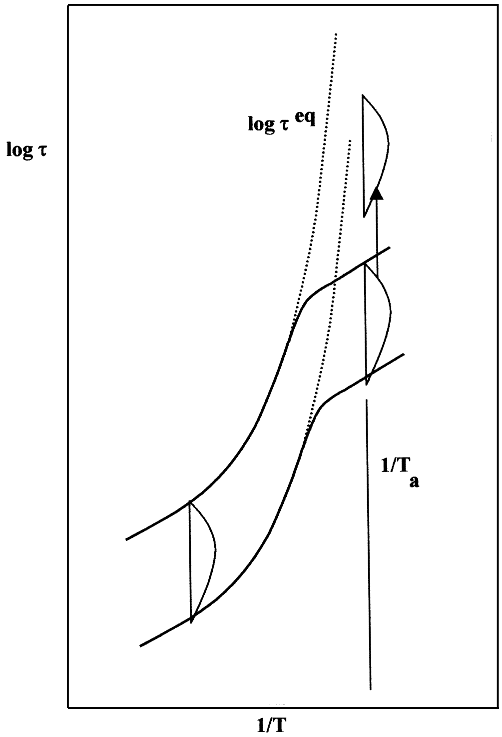

Fig. 7. Scheme of the dependence of the distribution of relaxation times with temperature both in the glassy and in equilibrium and its shift towards longer times with annealing at a temperature below the glass transition, in the glassy state.

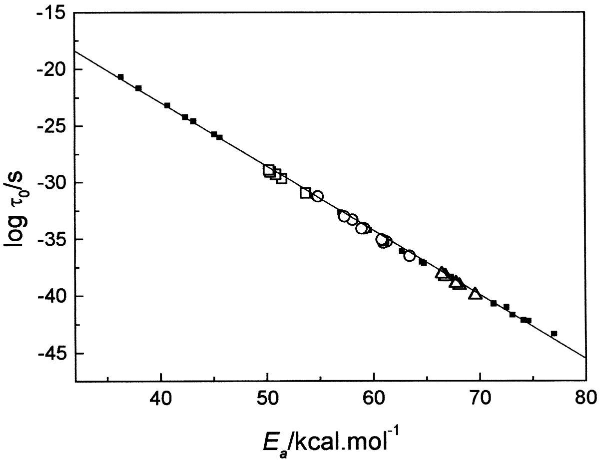

Fig. 8. Compensation plot of the studied thermoset. The solid squares are unaged TS results ($t_a = 0$ min) at different T_σ [18]. The solid line is a linear fitting of this data. The open symbols are for results at ageing times for three T_a (squares, 73°C; circles, 80°C; triangles, 85°C).

time within the relaxation times distribution [17,18]. Thus, the experimental feature of the decrease of the apparent activation enthalpy with increasing ageing time is closely related to the decrease observed in T_m.

It is interesting to note that Belana and his group found by TSDC an increase of the temperature of the depolarisation peak and the activation enthalpy with increasing annealing time in polyetherimide and semi-crystalline PET [13–15]. The discrepancy between TSR and TSDC could only be apparent because the way of conducting windowing in Refs. [13–15] is quite different from the one followed in this work; in particular, regarding the fact that stress is eliminated here at a temperature 3 degrees below T_σ, while in TSDC in Refs. [13-15] the electric field is switched off at the polarisation temperature immediately before cooling. The two charging profiles activate different relaxation times windows.

The deformation is smaller for increasing annealing times due to the shift of the creep curve towards longer times (Fig. 6). This stiffening of the material with physical ageing is clearly visible in the results in Fig. 3d: the recovered strain, ϵ_0, that reflects the short time creep occurred at T_a and the partial recovery at T_r after an ageing time t_a, decreases with increasing t_a at constant ageing temperature.

In a previous study, where the same thermoset was studied by TS at different temperatures a linear relationship was observed between E_a and $\log \tau_0$ [18]. This effect is the so-called compensation phenomenon, which is always observed in this kind of technique when the studies are carried out in the glass transition region (for the case of the TSDC technique see Ref. [27] and references therein).

Fig. 8 shows the compensation plot of the previous results [18] (solid symbols). The open symbols are for the results of this work, obtained at the different ageing temperatures and times. It can be observed that all the results of the ageing experiments lie on the compensation line of the non-ageing experiments, i.e. the compensation behaviour, given by the slope and the intercept of the linear fitting of E_a vs $\log \tau_0$, does not depend on the previous thermal history below T_g undergone by the material.

Fig. 3a–d shows that all the significant parameters of the TSR experiments (E_a, T_m, τ_0, ϵ_0) monotonously change with annealing time with no indication of approaching a steady or equilibrium state. For the sake of comparison, Fig. 3e shows that the enthalpy lost due to ageing at 73°C also monotonously increases with annealing time. As has been proved in extensive DSC studies in amorphous polymers [28,29] only annealing at temperatures very close to the glass transition allows to reach equilibrium within the experimental annealing range. It is worth noting that an accurate determination of the state attained at infinite time in an isothermal structural relaxation process is essential to characterise its kinetics. Thus, a comparison of the kinetics of structural relaxation as proved by the enthalpy and by the TSR parameters needs a more extensive experimental study, which is out of the scope of this work.

The changes in $\Delta H(t_a)$ reflect the gradual loss of excess configurational energy in the polymeric glass. The enthalpic ageing of a glass is believed to be a self-retarding phenomenon [30,31] in which the characteristic relaxation time (τ) for the process is a structure (or time) dependent parameter, i.e. at any $T_a < T_g : \Delta H(t_a) = f(\tau(\delta_H))$ where $\delta_H = H(t_a) - H_E$ is the distance of the instantaneous glass from the equilibrium glass (H_E). The evolution of the TSR parameters is a consequence of the shift of the distribution of the viscoelastic retardation times towards higher times as the annealing time increases.

5. Conclusions

A methodology has been described to probe structural relaxation by means of thermal sampling experiments in TSR. This technique is able to isolate the contribution of a narrow window of relaxation times assigned to the strain of the material and to study the recovery of the strain during a heating scan. The characteristic parameters of this recovery upon heating are found to be sensitive to the evolution of structural relaxation.

In all three studied ageing temperatures the TS characteristic parameters show consistent variation with ageing time. The activation energy decreases with increasing t_a. An opposite behaviour is observed for τ_0, which is in completely agreement with the general compensation behaviour observed for this material. The decrease of the stored strain, ϵ_0, was related with the stiffening of the material upon ageing, due to the decrease of free volume. The displacement of the process to lower temperatures, T_{max}, during structural relaxation was interpreted in terms of the shifting of the isolated retardation times towards lower values in the TS experiments.

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