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Influence of orientation in the amorphous phase of poly(ethylene terephthalate) [α]

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Abstract

A comparative study of amorphous, uniaxially and biaxially oriented films has been performed by thermally stimulated current (TSC) spectroscopy. The study of the TSC peak observed around the glass transition temperature (T_g) has been undertaken. In amorphous poly(ethylene terephthalate), a TSC peak is observed at 82 °C. Under uniaxial orientation, it is shifted to 88 °C, and under biaxial orientation, it reaches 100 °C. The shift of this T_g peak under stretching indicates a stiffening of the amorphous chains. The analysis of the fine structure of these complex peaks shows the existence of compensation phenomena. For uniaxially and biaxially oriented poly(ethylene terephthalate) this analysis reveals lower and upper temperature components of the glass transition. This phenomenon indicates the existence of two segregated phases.

INTRODUCTION

Poly(ethylene terephthalate) (PET) films have been widely used in electrical engineering. Numerous works have been devoted to uniaxially [1] or biaxially [2] oriented films. Fewer papers have been focused on a comparative study of these two films. The aim of this work is to characterize the influence of uniaxial and biaxial orientation on the amorphous phase of PET. Thermally stimulated current (TSC) spectroscopy has been applied to the study of unoriented, uniaxially and biaxially oriented films.

MATERIALS AND METHOD

Measurements reported here were carried out on a biaxially oriented PET film (10 μm thick) manufactured by Rhône-Poulenc (TERPHANE®) with 39.5% crystalline. The properties of the film were anisotropic because it was

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produced with a two-step stretching process, the first in the travel direction and the second of greater strain in the transverse direction. During and after the stretching the PET crystallized. Note that the crystallization temperature was 125 ° C, in normal conditions. The film was then heat-set at 180 ° C.

We have compared the biaxially oriented PET with a uniaxially oriented sample (50 μm thick and 4% crystalline). Uniaxially oriented film corresponds to the first process in the travel direction. We have chosen as reference an unoriented amorphous PET film of 150 μm thickness.

Thermally stimulated current (TSC) experiments were performed on a Solomat TSC/RMA spectrometer.

The principle of the TSC technique is as follows: the sample is polarized by a static electrical field E at the temperature T_p. When the polarization P has reached its equilibrium value, the temperature is decreased until $T_0 \ll T_p$ in order to freeze this configuration. Then, the field is cut off. The polarization recovery is induced by increasing the temperature in a controlled manner. The depolarization current j flowing through the external circuit is measured by an electrometer and gives the "dynamic conductivity" $\sigma = j/E$.

If the isothermal polarization varies exponentially with time, then its relaxation time τ is deduced from

$$\tau = \frac{P}{\sigma E} \tag{1}$$

From the recording of the TSC spectra of such an elementary process, the temperature dependence of the relaxation time, $\tau(T)$ can be deduced in the corresponding temperature range.

In polymers, the polarization P is associated with a distribution of relaxation times so that P can be written as

$$P = \sum_i P_i$$

with

$$\frac{\mathrm{d}P_i}{\mathrm{d}t} = -\frac{P_i}{\tau_i}$$

where τ_i is the relaxation time and t is the time. The advantage of TSC spectroscopy is to allow the experimental resolution of the contribution of P_i by using the procedure of fractional polarizations [3]. Then, the analysis of the corresponding elementary spectra gives $\tau_i(T)$.

EXPERIMENTAL RESULTS

The polarization phenomena of the amorphous, uniaxially and biaxially oriented PET were at the origin of the complex TSC spectra, which were resolved by the fractional polarization technique.

Complex TSC spectra

Experimental procedure

Experimental conditions to record the spectra of the amorphous, uniaxially and biaxially oriented PET samples (Figs. 1, 2 and 3) were as follows:

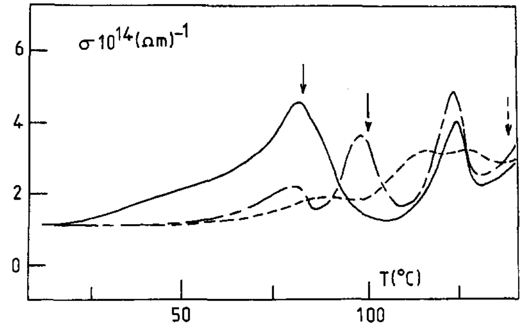

Fig. 1. Complex TSC spectra of amorphous unoriented PET after polarization at the temperatures indicated by the arrows.

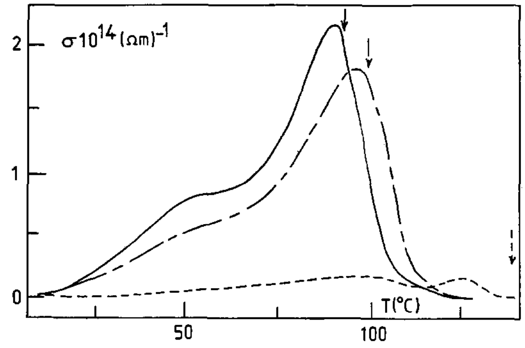

Fig. 2. Complex TSC spectra of uniaxially oriented PET after polarization at the temperatures indicated by the arrows.

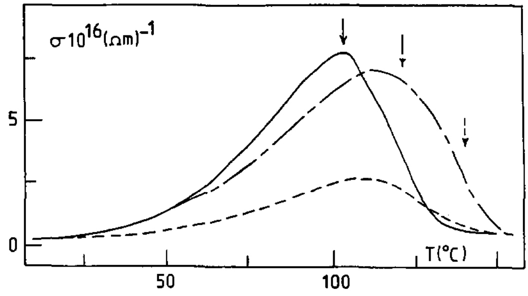

Fig. 3. Complex TSC spectra of biaxially oriented PET after polarization at the temperatures indicated by the arrows.

samples were not submitted to thermal treatment before the TSC run; an electric field of 2×10^6, 6×10^6 and 3×10^7 V m^{-1} was applied at the polarization temperature T_p indicated by the small arrows on Figs. 1, 2 and 3, respectively; when the polarization reached its equilibrium value, the sample was quenched. Then, the field was cut off. The polarization recovery was induced by increasing the temperature at a rate of 7 K min^{-1}.

In order to avoid the evolution of the material, the polarization was applied at the glass transition temperature (T_g) for 2 min. These conditions were adopted to record the reference spectrum (solid lines in Figs. 1, 2 and 3).

For investigating the influence of thermal treatment on PET films, samples were annealed at temperatures T_a for 2 min. The polarization was applied during the annealing time. Two values of T_a were used: $T_g < T_a <$ 125 ° C (dotted lines in Figs. 1, 2 and 3); $T_a = 140$ ° C (dashed lines in Figs. 1, 2 and 3).

Amorphous PET

The TSC spectra presented in Fig. 1 were recorded after polarization at various temperatures on an amorphous PET sample: after polarization at 80 ° C, the reference spectrum showed two peaks at 82 and 125 ° C (see solid line). After polarization at 100 ° C, a new additional TSC peak appeared at 96 ° C (see dotted line). This peak disappeared after annealing at 140 ° C (see dashed line). Note the broad peak at 120 ° C.

Uniaxially oriented PET

TSC spectra of uniaxially oriented PET are presented in Fig. 2. The reference spectrum, recorded after polarization at 90 ° C, showed only one peak at 88 ° C (solid line). With this uniaxially oriented sample, the increase of thermal treatment to 140 ° C induced a shift of the peak to 100 ° C with a decrease of its magnitude. A new peak appeared at 125 ° C (dashed line).

Biaxially oriented PET

Figure 3 shows the TSC spectra of the biaxially oriented PET sample. The reference spectrum (solid line) was recorded after polarization at 100 ° C. The increase of annealing temperature to 140 ° C induced an increase of the peak temperature to 110 ° C.

Fine structure of TSC spectra

Experimental resolution

The complex TSC spectra of three series of PET samples were resolved by using the fractional polarization technique [3]. Elementary spectra were recorded with the same polarization field as complex spectra with a "temperature window" of 5 ° C. Each elementary spectrum were recorded on

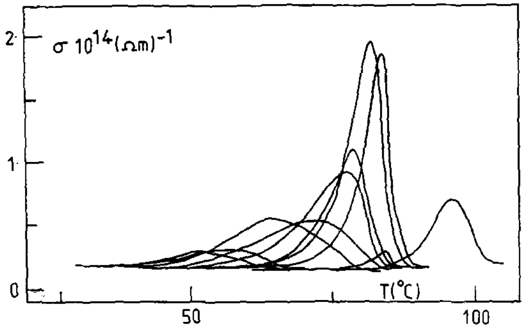

Fig. 4. Elementary TSC spectra of amorphous unoriented PET.

samples with the same initial procedure. In those conditions, the elementary TSC peaks were uniform shifted along the temperature axis. Figure 4 shows, as an example, the elementary peaks isolated in amorphous PET around the glass transition indicating a wide distribution of relaxation times.

ANALYSIS OF ELEMENTARY TSC SPECTRA

Each elementary peak has been analyzed and the relaxation times have been deduced from eqn. (1). The experimental points have been plotted on an Arrhenius diagram: Figs. 5, 6 and 7 correspond respectively to amorphous unoriented PET, uniaxially oriented PET and biaxially oriented PET.

Amorphous unoriented PET

Arrhenius relaxation times

At the lowest temperatures the variation $\tau(T)$ (Fig. 5), isolated in the region of the glass transition, are characterized by relaxation times following an Arrhenius equation

$$\tau(T) = \tau_{0A} \exp\frac{\Delta H}{kT} \tag{2}$$

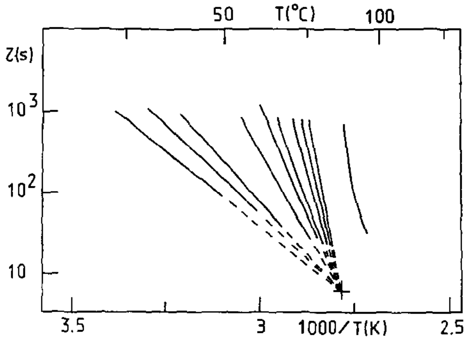

Fig. 5. Arrhenius diagram of dielectric relaxation times of amorphous unoriented PET.

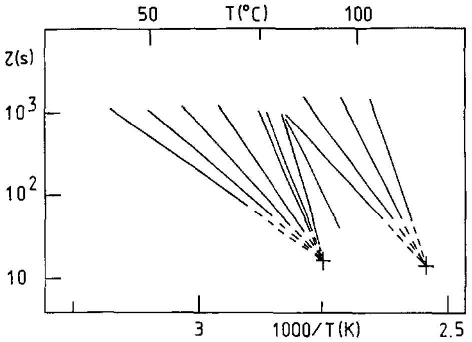

Fig. 6. Arrhenius diagram of dielectric relaxation times of uniaxially oriented PET.

where τ_{0A} is the pre-exponential factor, ΔH is the activation enthalpy, and k is the Boltzmann constant.

Compensation law

For nine elementary processes, the corresponding relaxation times have the same $\tau_c = 6.2$ s at a $T_c = 87\,°\mathrm{C}$. In other words, they obey a compensation law

$$\tau(T) = \tau_c \exp\left\{\left(\frac{\Delta H}{k}\right)\left(T^{-1} - T_c^{-1}\right)\right\} \tag{3}$$

In this case, the relaxation times are only dependent upon one parameter, the activation enthalpy ΔH. This relaxation mode has been associated with the dielectric manifestation of the glass transition (T_g).

Vogel relaxation times

The peak, isolated at 96 °C, can be described by a Vogel–Tamman–Fulcher (VTF) equation

$$\tau(T) = \tau_{0\nu} \exp\{\alpha_f (T - T_\infty)\}^{-1} \tag{4}$$

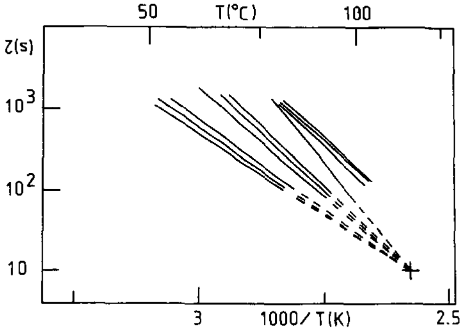

Fig. 7. Arrhenius diagram of dielectric relaxation times of biaxially oriented PET.

where $\tau_{0\nu}$ is the pre-exponential factor. The free volume theory of Cohen and Turnbull [4] allowed a description of the temperature dependence of τ. Those authors suppose that the fractional free volume is given by

$$T < T_\infty \qquad f = 0$$

$$T > T_\infty \qquad f = \alpha_f (T - T_\infty)$$

Below the critical temperature T_∞ any molecular motion is frozen; above T_∞ the free volume expands linearly with an expansion coefficient α_f. The corresponding parameters were $T_\infty = 57\,^\circ\mathrm{C}$, $\alpha_f = 2.5 \times 10^{-3}\ \mathrm{K}^{-1}$ and $\tau_{0\nu} = 1.2 \times 10^{-3}$ s. This peak has been associated with the dielectric manifestation of the liquid–liquid transition (T_{ll}).

Uniaxially oriented PET

The elementary peaks isolated in uniaxially oriented PET are characterized by relaxation times following an Arrhenius equation (eqn. 2). The Arrhenius diagram of uniaxially oriented PET (Fig. 6) shows the existence of two compensation laws. The corresponding compensation temperatures T_c were, respectively, 91 °C and 120 °C. For the compensation times τ_c, we obtained, respectively, 17 s and 15 s. These two compensation laws have been related to the apparent double glass transition of uniaxially oriented PET.

Biaxially oriented PET

The analysis of TSC elementary peaks gave relaxation times obeying the Arrhenius equation (eqn. 2). On the Arrhenius diagram of biaxially oriented PET (Fig. 7) we observed only one compensation law. For the corresponding elementary processes, the relaxation time was the same value $\tau_c = 10$ s at the $T_c = 115\,^\circ\mathrm{C}$. The characteristics of this relaxation mode can be attributed to the dielectric manifestation of the glass transition.

DISCUSSION

Reference TSC spectra recorded on unoriented and oriented films showed several relaxation modes. The analysis of these modes will allow us to specify their molecular origin.

Crystallization

On the reference spectrum of amorphous PET we can see a TSC peak at 125 °C. This temperature corresponded to the crystallization region observed by differential scanning calorimetry (DSC). This DSC peak has been associated with the dielectric manifestation of crystallization. This phenomenon is strongly dependent on thermal history and can be observed only in amorphous samples due to experimental conditions.

Liquid–liquid transition (T_{ll})

For amorphous PET, Fig. 1 has a TSC peak at 96 °C located before the crystallization region. The analysis of this mode shows that it is not distributed. The relaxation time corresponding to this peak is well described by a VTF equation (eqn. 4). Such a TSC peak has also been observed above the glass transition for other amorphous polymers, e.g. polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(cyclohexyl methacrylate) (PCHMA) [5]. It has been associated with the dielectric manifestation of the liquid–liquid transition (T_{ll}).

Volumetric and enthalpic measurements allowed us to observe the thermodynamic manifestation of this transition. Several papers concerning the observation of this transition in polystyrene by dynamic techniques have been published: measurements of the viscosity and elasticity during melting [6]; a study of the diffusion and solubility of organic liquids [7]; measurements of the mechanical energy loss (low frequencies) [8]; and spectroscopic studies (high frequencies) by NMR, FTIR, fluorescence polarization and EPR [9].

The liquid–liquid transition has been associated with disentanglements of macromolecular chains. The disappearance of this relaxation after crystallization supports this hypothesis. Crystallites act like cross-links of a network, inhibiting movements of the entire amorphous chains.

Glass transition

Lower temperature component (T_{gl})

Reference spectra of the amorphous, uniaxially and biaxially oriented PET films (see Figs. 1–3) show a lower temperature component of the glass transition (T_{gl}) at 82 °C, 88 °C and 100 °C, respectively. We observed that the temperature of the peak increased and its magnitude decreased for an increasing crystallization rate. The crystalline phase progressed versus the amorphous phase. This is confirmed by thermal treatments performed on all films. This low temperature sub-mode corresponded to a distribution of relaxation times. These relaxation times obeyed a compensation law defining the structure of the amorphous phase. In the case of amorphous and uniaxially oriented PET film, $T_c - T_g = 4$ °C, while for biaxially oriented film $T_c - T_g = 15$ °C. This relationship agrees with $T_c - T_g = 20$ °C obtained in other materials such as polyethylene (PE) [10] and polyamide (PA) [11] where the crystallinity was about 50%. This relationship is related to the degree of crystallinity of the material.

For uniaxially oriented PET the structure was slightly crystalline. The contribution of crystallites does not modify the behaviour of the amorphous phase. The relaxation processes were comparable to the ones observed in amorphous PET. On the contrary, in biaxially oriented PET the crystalline phase induced a modification of the amorphous phase.

Upper temperature component (T_{gu})

Reference spectra of uniaxially and biaxially oriented PET (see Figs. 2 and 3, solid lines) show a broadening of the high temperature spectra. Their analysis confirmed the existence of a distributed sub-mode corresponding to an upper temperature component of the glass transition (T_{gu}).

In the case of uniaxially oriented PET, the isolated relaxation times follow a compensation law. This phenomenon was explained by the existence of an additional segregated amorphous phase.

On the contrary, for biaxially oriented PET, the experimental peaks cannot be fitted by a compensation line. The amorphous chains were not deprived of constraints from crystallites and constitute an interphase between the amorphous and crystalline phases.

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