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Glass transition studies in physically aged partially crystalline poly(ethylene terephthalate) by TSC

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Abstract

Physical ageing in poly(ethylene terephthalate) (PET) was studied by differential scanning calorimetry (DSC), thermally stimulated depolarization currents (TSDC) and thermally stimulated polarization currents (TSPC) as a function of the material crystallinity degree. Calorimetric measurements confirm the presence of two separated glass transitions in partially crystallized samples ($x_c = 27\%$), associated with the presence of two different amorphous regions: the interspherulitic region and the interlamellar region within the spherulites. The α peak obtained by TSDC shows the progressive decrease of the chain segments mobility in the amorphous fraction as ageing progresses. The increase in the crystallinity degree of the material also produces a decrease of the mobility in the amorphous fraction. In this case the decrease observed is associated with the interlamellar conformation of these regions. However, TSDC measurements do not show evidences of a double glass transition. TSPC measurements on aged samples show a current peak, which is directly related to the polarization of the amorphous regions when mobility is recovered above the glass transition. The study of these peaks in aged partially crystallized samples shows evidences of a double glass transition associated with theinterspherulitic and interlamellar amorphous regions. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate); Glass transition; Thermally stimulated currents

1. Introduction

When a molten polymer is cooled below its glass transition temperature (T_g), becoming an amorphous solid, it is not in a true thermodynamical equilibrium state and many properties (free volume, enthalpy, entropy, and other mechanical and electrical properties) are different than they would be in the equilibrium state. Below T_g, only slow changes which attempt to establish equilibrium can take place, in a process of structural relaxation known as physical ageing [1]. During physical ageing many properties of the material, such as the free volume (closely related to the mobility of the chain segments), change in large time-scales relative to the experimental time-scale. The decrease in the mobility of the polymer chain segments, resulting from this evolution, influences the glass transition of the material that shifts towards higher temperatures and takes place in a more definite temperature range. The presence of crystalline regions in semicrystalline polymers is also known to affect the glass transition of the material, that usually is broader than in the case of the amorphous one [1]. The mobility of the polymer chain segments close to the crystals will be constrained, extending the glass transition range to higher temperatures. Depending on the morphology of the crystalline regions a double T_g can be obtained. This happens if real isolated amorphous domains are present in the material. This double T_g has already been detected for some polymers as reported by R.F.Boyer [2]. In the case of poly(ethylene terephthalate), (PET), crystallization takes place in a spherulitic morphology in which crystalline lamellae, amorphous layers between the lamellae and amorphous regions between the growing spherulites coexist [3]. Corresponding to this morphology two T_gs are expected in partially crystallized PET (c-PET): one corresponding to the amorphous regions between the spherulites, and another, at higher temperatures, corresponding to the amorphous interlamellar regions.

Differential scanning calorimetry (DSC) has been widely used to study the glass transition and the enthalpy relaxation during physical ageing in amorphous PET (a-PET) [4]. By this technique an endothermic peak appears around T_g when the sample is aged at temperatures below T_g. The position, height, and area of this endothermic peak vary with the ageing condition of the material, increasing the area and

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the temperature of its maximum as annealing proceeds. This behavior is because of the decrease of the chain segments mobility, required to promote the recovery of enthalpy, which occurs during the ageing process. Recent works have dealt with the study of enthalpy relaxation in aged semicrystalline PET by DSC [5]. In these studies a double endothermic peak appears for low crystallinity samples aged at different temperatures for different times. The first endothermic peak is observed at temperatures close to the glass transition of amorphous PET (labelled P1 in Ref. [5]) and the second one (P2), of lower intensity, merged at higher temperatures as a shoulder of P1.

Thermally stimulated depolarization currents (TSDC) and polarization currents (TSPC) have proved to be most useful in studying relaxations of polymeric materials [6,7]. In the case of TSDC, bound and free charges in the material are activated by a polarizing field above room temperature, and then are frozen by cooling down the sample. The sample is then depolarized at a constant heating rate while the resulting current intensity is recorded as a function of temperature. In the case of TSPC, the sample is polarized by an applied electric field while heating at a constant rate, and the polarization current is recorded as a function of temperature. These measurements reveal the existence of different relaxations processes, such as the dipolar α relaxation related to the glass transition of the material. This relaxation is originated by the cooperative motion of the main polymer chain segments, when they regain full mobility at T_g. This is a kinetic process and therefore it must be affected by the ageing condition of the material. The polarization and depolarization processes in TSDC and TSPC have been widely described in the literature [8–11].

Previous studies of the α dipolar relaxation measured by TSDC in a-PET demonstrated the progressive decrease and shift towards higher temperatures of this peak with physical ageing [4]. More recently, TSPC measurements in physically aged a-PET show the appearance of a polarization peak directly related to the ageing condition of the material [12]. The origin of this peak (labelled α_a in Ref. [12]) is attributed to the complete polarization of the polymer chain dipoles of the aged material, when the sample is heated through the T_g range. At temperatures below T_g the restricted mobility of the aged material prevents the complete polarization of the polymer chain dipoles, that become fully polarized when mobility is recovered above the glass transition. This work showed the possibility of study physical ageing in the polymer by analyzing the evolution of this peak, that changes in a way similar to that of the endothermic peak detected by DSC. Thermally stimulated currents techniques have been applied to the study of partially crystallized PET (c-PET), although in a more limited way. TSDC measurements performed by Belana et al. and other groups [13,14] in c-PET of different crystallinity degrees displayed a double α relaxation in the high crystallinity samples. These relaxations were initially attributed to the amorphous interspherulitic region and to the amorphous interlamellar region respectively, however more experimental data was necessary. In this way, TSPC measurements of physically aged PET can be a convenient method to obtain separated glass transition in c-PET, as the recovery of mobility produces an enhanced current peak in these measurements.

The aim of this work is, following the aforementioned works, to study the glass transition and the influence of physical ageing in partially crystallized PET. To make this study DSC, TSDC and TSPC techniques were used in a complementary way. The effect of ageing and the crystallinity degree in the evolution of the α and α_a relaxations were analyzed. Different treatments and polarization conditions were employed for this purpose.

2. Experimental

Experiments were carried out on commercial poly(ethylene terephthalate) (PET) provided by Hoechst Ibérica S.A. in amorphous sheets (Hosta PET (R)) 500 μm thick. The crystallinity degree measured by DSC was less than 8% in the as-received material. Samples of 14%, 21%, 27% and 32% crystallinity degree were prepared by annealing the polymer for 15 min at 105°C, 107°C, 110°C and 115°C, respectively. Circular samples were prepared for current measurements by coating 2 cm diameter Al electrodes on both sides of the sheet by vacuum deposition. All the samples were pre-treated by heating, in a controlled way, up to 100°C to suppress any possible memory effect from the formation process (internal stress, etc.). Physical ageing of the samples was performed annealing at $T_a = 65°C$ for different times t_a (between 0 and 21 600 min). In all cases the samples were cooled down in a controlled way from 100°C to the ageing temperature, in order to erase any previous thermal history.

Calorimetric measurements were made with a Mettler TC11 thermoanalyzer equipped with a Mettler-20 Differential Scanning Calorimeter module. The calorimeter was previously calibrated with metallic standards (indium, lead, zinc). DSC curves were obtained from 10 mg samples, sealed in aluminum pans, at 10°C/min controlled heating rate. Thermally stimulated currents were carried out in a Kottermann-2715 forced air circulation oven, controlled by an Eurotherm-818 temperature programmer. Temperature during the annealings and the measurements, was measured to an accuracy of 0.1°C by Pt-100 probes located close to the sample. A Keithley-610C electrometer was employed for the current intensity measurements. The heating and cooling rates used, in all the ramps, was 10°C/min for DSC measurements and 2.5°C/min for TSDC measurements.

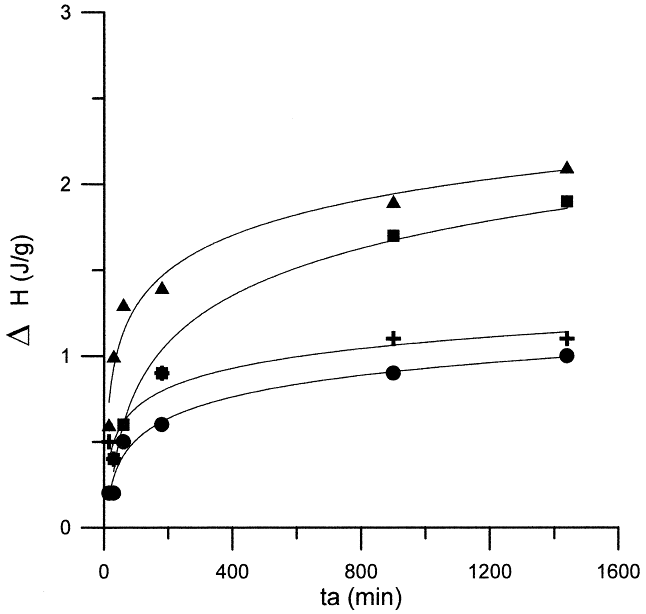

Fig. 1. Dependence of the enthalpy relaxation on the ageing time t_a for samples with different crystallinity degrees aged at $T_a = 65$°C (15°C below T_g). $x_c =$ 14% (▲), $x_c = 21$% (■), $x_c = 27$% (+), $x_c = 32$% (●).

3. Results and discussion

3.1. Calorimetric results

Previous to the electrical measurements, the material was studied by DSC in order to characterize the glass transition, crystallinity degree and the evolution of physical ageing in commercial sheets of a-PET (HOSTA PET(R)) studied in this work. The main purpose of these preliminary measurements was to obtain the optimum conditions (crystallinity degree and ageing condition) to detect a double glass transition in our polymer.

The glass transition temperature (T_g) measured at 10°C/min heating rate was $T_g = 80$°C. The crystallization degree, evaluated from the melting endothermic peak of various samples, was in all the cases less than 8%. Samples of 8%, 14%, 21% 27% and 32% crystallinity were aged at 65°C (15°C below T_g) for annealing times between 15 and 1000 min. The measured DSC thermograms of these samples show, as expected, an endothermic peak around T_g associated with the enthalpy recovery the material undergoes. In a manner similar to results obtained by other groups, our results show a relative increase in the endothermic peak area and a shift in the temperature of the maximum as t_a is increased. The total amount of excess enthalpy falls as the crystallinity degree grows in the material, as a result of the decrease of the amorphous fraction that can be aged.

The dependence of the excess enthalpy relaxation ΔH, calculated from these measurements, on t_a is represented in Fig. 1 for several crystallinity degrees. The slope of this curve is a measure of the relaxation rate, and for a given x_c is high at the beginning but falls with t_a because of the decrease in the free volume of the system, and therefore in the molecular mobility of the chain segments. Its remarkable that the slow down in the relaxation kinetics (indicated by the slope of the curve) is observed also when x_c increases. This fact indicates a decrease in the molecular mobility of the chain segments of the amorphous fraction when x_c increases.

The previous results can be explained assuming the presence of two different kinds of amorphous regions within the partially crystallized PET, already suggested by Illers and Breuer [15]: a less restricted interspherulitic amorphous region, predominating in the low x_c samples, and a more restricted interlamellar amorphous region, that prevails in high x_c samples. A result indicative of the presence of two different amorphous regions within the material is a double T_g, already reported for aged partially crystalline PET [5,13]. For the material studied in the present work, similar experiments show the appearance of a double T_g in the $x_c =$ 27% sample after annealing times equal or greater than 900 min (not shown).

3.2. TSDC results

Thermally stimulated discharge currents technique (TSDC) has not been applied extensively to the study of physical ageing, although the effect of ageing in the α relaxation is well suited for this purpose [4,12]. The decrease in mobility of the chain segments results in a decrease in the polar response of the material, that can be analyzed as a function of the annealing (or ageing) temperature (T_a) and time (t_a).

For this study, partially crystallized samples were aged at $T_a = 65$°C (15°C below T_g) for times between 15 and 1000 min. The aged samples were later polarized by the

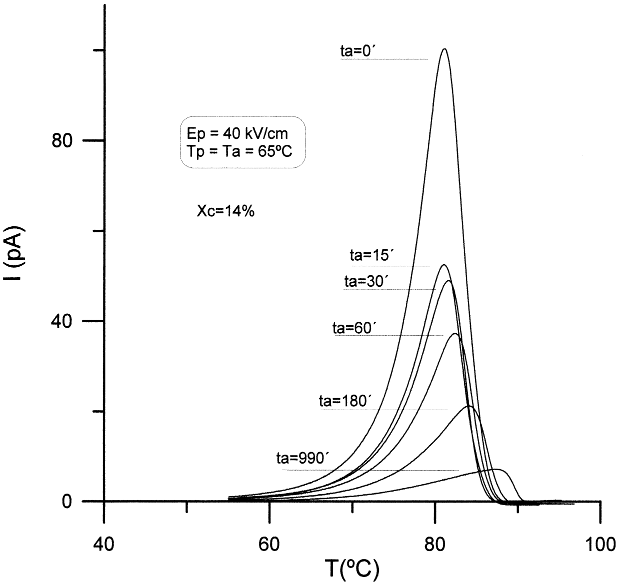

Fig. 2. TSDC curves of 14% crystallinity PET aged at $T_a = 65$°C (15°C below T_g) for different times ($T_p = 65$°C, $t_p = 15$ min., $E_p = 40$ kV/cm).

window polarization method (WP) [16], which was carried out as follows: the sample was polarized for 15 min. at $T_p =$ 65°C, and then it was cooled down to the initial temperature of the scan (50°C) with no electric field applied. It must be pointed out that by this poling procedure only those dipoles that respond to a definite temperature (the polarization temperature) are activated, and thus not suited to detect, in the same discharge, 'different kinds' of amorphous regions.

Fig. 2 shows the evolution of the α peak, associated with the glass transition of the material, for the 14% crystallinity sample as a function of the ageing time t_a. The α peak shifts towards higher temperatures with t_a and a significative decrease in its maximum current and area occurs. This behavior is explained by the decrease in the mobility of the molecular chains, which is also related to the reduction of free volume in the sample. In addition, the height of the peak decreases with x_c in the range of t_a used. This fact also indicates a decrease in the mobility of the molecular chains, in this case associated with an increase in the crystallinity degree.

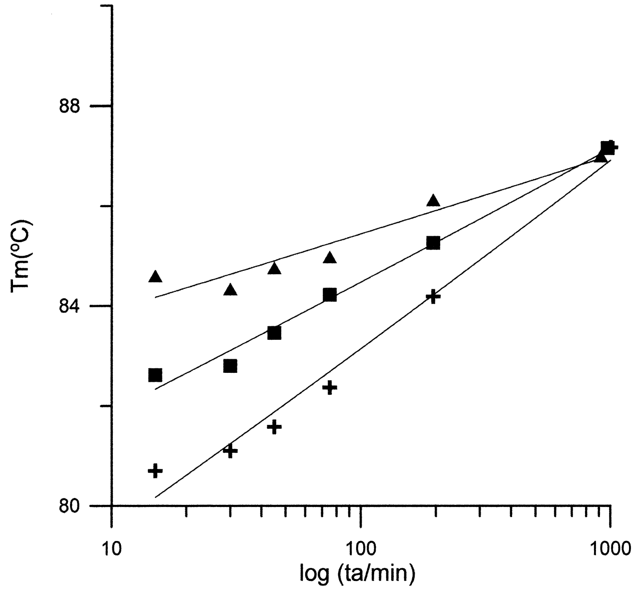

Fig. 3. Dependence of the temperature of the maximum in the TSDC spectrum on the ageing time t_a for samples with different crystallinity degrees aged at $T_a = 65$°C (15°C below T_g) $x_c = 32\%$ (▲), $x_c = 27\%$ (■), $x_c = 14\%$ (+).

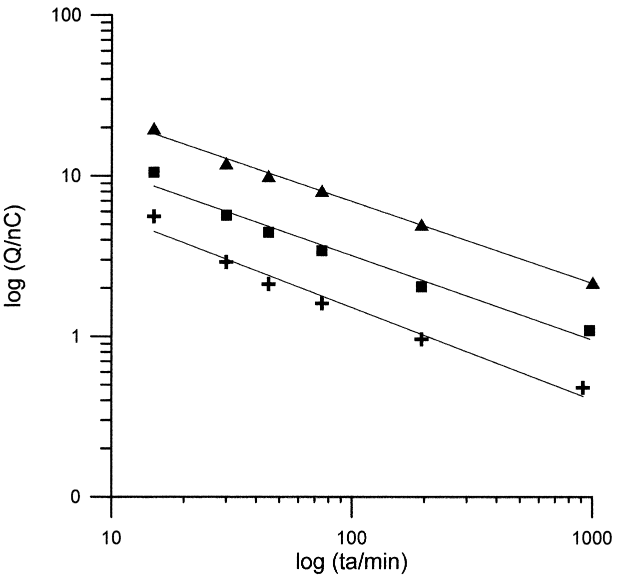

Fig. 4. Dependence of the total charge associated to the α relaxation on the ageing time t_a for samples with different crystallinity degrees aged at $T_a =$ 65°C (15°C below T_g) $x_c = 14\%$ (▲), $x_c = 27\%$ (■), $x_c = 32\%$ (+), (TSDC measurements).

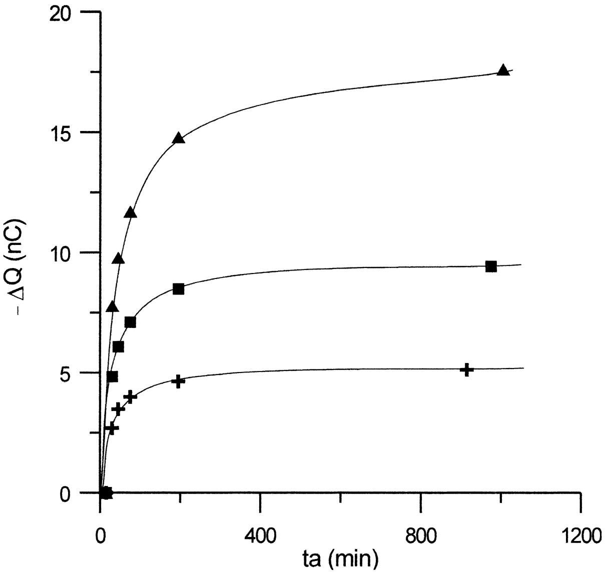

Fig. 5. Decay of the induced charge $\Delta Q = Q_0 - Q$ associated to the α relaxation of the TSDC spectrum versus the ageing time t_a for samples with different crystallinity degrees aged at $T_a = 65°\text{C}$ (15°C below T_g) $x_c = 14\%$ (▲), $x_c = 27\%$ (■), $x_c = 32\%$ (+).

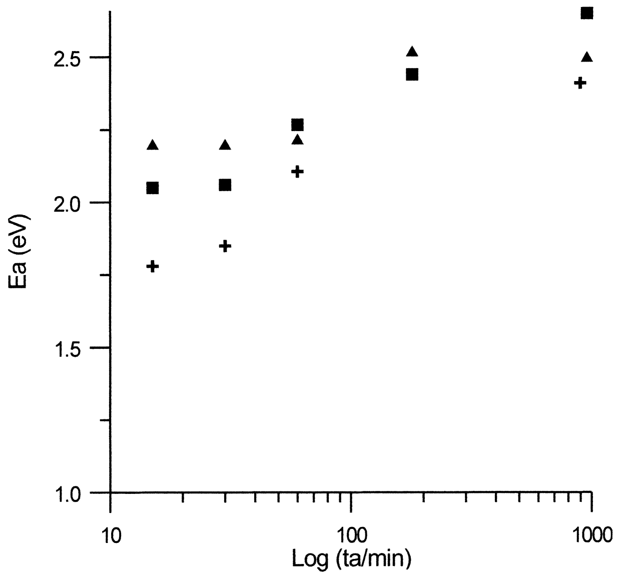

Fig. 6. Dependence of activation energy of the α relaxation on the ageing time t_a for samples with different crystallinity degrees aged at $T_a = 65°\text{C}$ (15°C below T_g) $x_c = 32\%$ (▲), $x_c = 27\%$ (■), $x_c = 8\%$ (+), (TSDC measurements).

Fig. 3 shows the temperature of the peak maxima (T_m) versus log(t_a) for the different samples. It can be noted in this plot that T_m increases as physical ageing proceeds in the material, however this effect is much more evident in the samples with lower crystallinity degree. At a given annealing time, T_m is always higher in samples with higher x_c, and tends in all the cases to a maximum value of approximately 87°C.

Simultaneously to the increase in T_m, the total area of the peak (or induced polarization in the material) decreases with t_a and with the crystallinity degree. This behavior is represented in Fig. 4 where a linear dependence between log(Q) versus log(t_a) is observed.

For the different x_c samples and for each ageing time we calculated the absolute difference between the initial induced charge Q_0 and the induced charge Q ($\Delta Q = Q_0 - Q$). The slope of these curves ($d\Delta Q/dt_a = -dQ/dt_a$) reflects the relaxation rate in a way similar to $d\Delta H/dt_a$, since they show the rate at which the capacity of polarization is lost. Fig. 5 reproduces these plots where we can observe that $d\Delta Q/dt_a$ decreases with t_a for a given x_c, in a way similar to that obtained for ΔH (Fig. 1).

Table 1
Pre-exponential factor of the relaxation time, τ_0, for the α relaxation calculated from the TSDC measurements

t_a (min)	$x_c = 8\%$	$x_c = 27\%$	$x_c = 32\%$
15	1.4×10^{-26}	1.2×10^{-30}	1.0×10^{-32}
30	1.4×10^{-27}	9.7×10^{-31}	1.4×10^{-32}
60	3.3×10^{-33}	1.4×10^{-33}	6.6×10^{-33}
900	6.2×10^{-36}		
960		2.9×10^{-39}	5.9×10^{-37}

We can explain the decrease in $d\Delta Q/dt_a$ by the decrease in the segmental mobility of the polymer chains with ageing. This decrease reduces the possibility of dipolar orientation by the application of an electric field, and the material can then be polarized to a lower degree for the same polarization conditions. This behavior is also obtained when the crystallinity degree increases in the material for a given ageing condition.

The activation energy (E_a) and the pre-exponential factor of the relaxation time (τ_0) can be evaluated from the TSDC curves assuming for the discharge process the Debye's equation:

$$I(t) = S \cdot \frac{dP}{dt}. \tag{1}$$

In this model the intensity of the depolarization (Eq. (1))

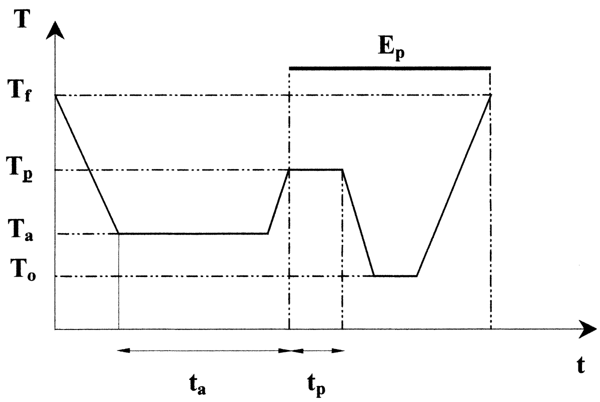

Fig. 7. Schematic representation of the field and temperature program developed in the TSPC measurements. (Fixed parameters: $T_a = 65°\text{C}$, $T_p = 70°\text{C}$, $t_p = 15$ min, $E_p = 8$ kV/cm, $T_0 = 60°\text{C}$, $T_f = 97°\text{C}$.)

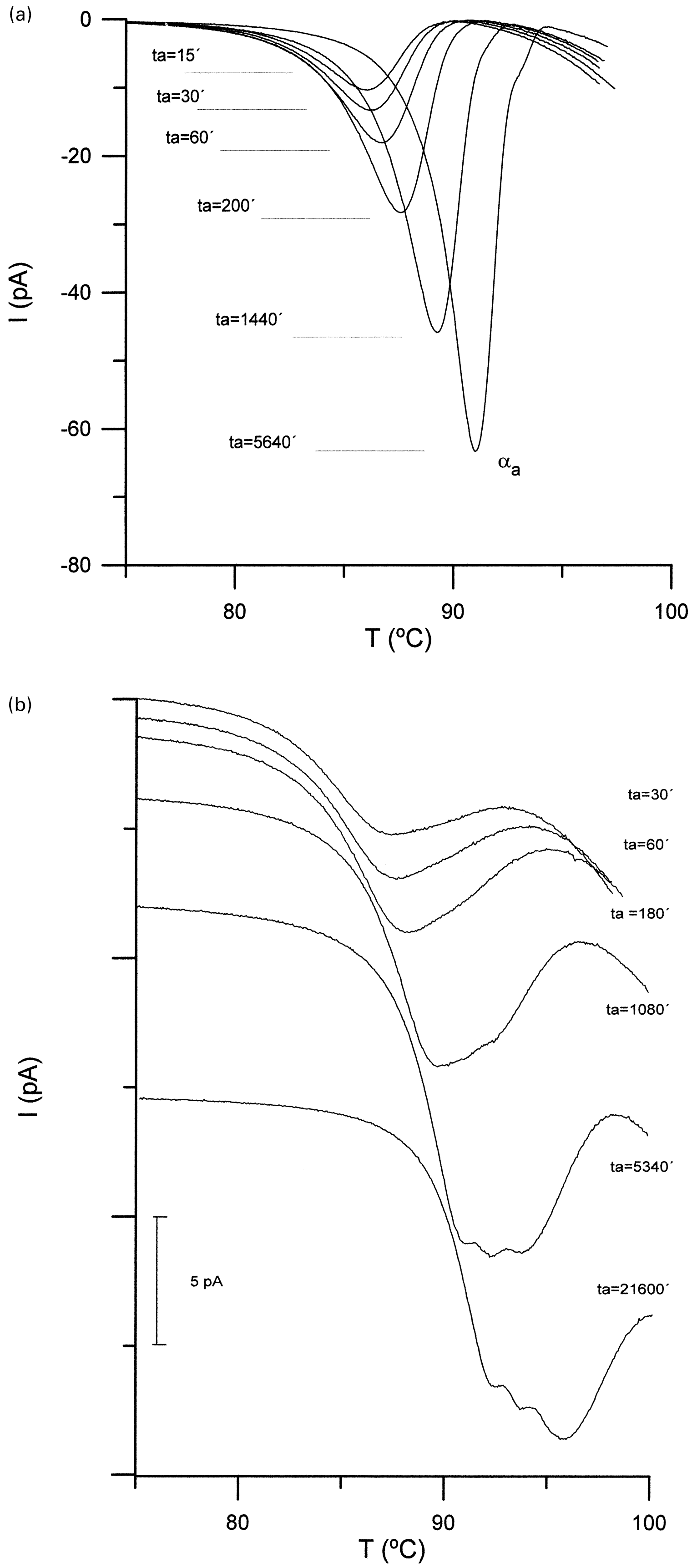

Fig. 8. Short circuit TSPC curves of PET samples aged at $T_a = 65$°C (15°C below T_g) for different times. (a) $x_c = 8\%$, (b) $x_c = 27\%$ and (c) $x_c = 45\%$ (α dipolar peak cleaning was performed by the polarization of the sample prior to the scan at $T_p = 70$°C for $t_p = 15$ min, $E_p = 8$ kV/cm).

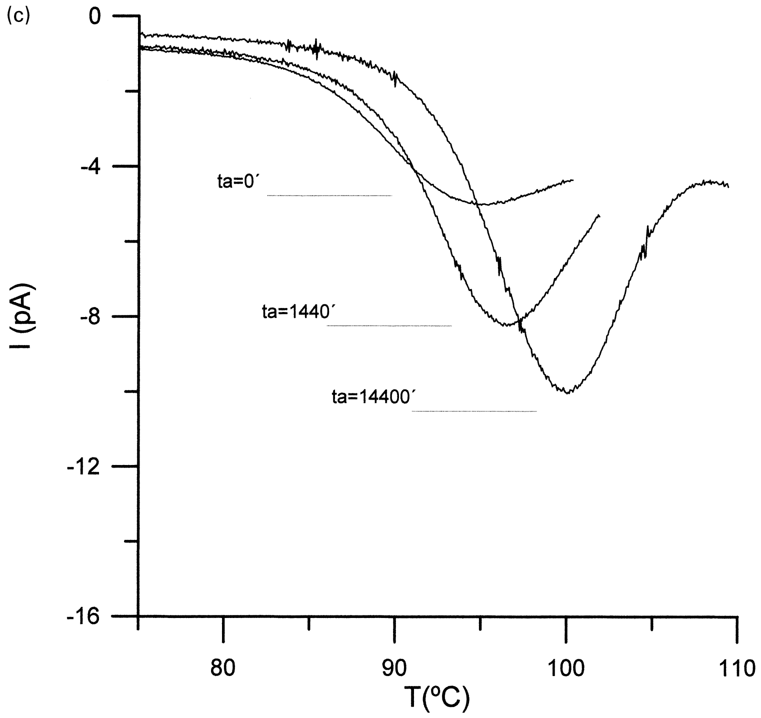

Fig. 8. (*continued*)

is obtained assuming for dP/dt a first order linear dependence on P (Eq. (2a)), were S is the area of the sample, P the induced polarization and τ the relaxation time of the process. For τ an Arrhenius behavior is assumed (Eq. (2b)), were E_a is the activation energy of the relaxation, T the temperature and τ_0 a pre-exponential factor.

$$\frac{\mathrm{d}P}{\mathrm{d}t} = -\frac{P}{\tau}, \tag{2a}$$

$$\tau = \tau_0 \exp\left(\frac{E_a}{kT}\right). \tag{2b}$$

Combination of Eqs. (1) and (2a,b) leads, for the initial steps of depolarization, to a linear dependence of ln(I) versus 1/T (Eq. (3)). This equation was first proposed by Garlick and Gibson and is known as the 'initial rise method' [17];

$$\ln(I) = \ln\left(\frac{SP_0}{\tau_0}\right) - \left(\frac{E_a}{kT}\right). \tag{3}$$

Within this model E_a and τ_0 were calculated from the measured discharges, and are reproduced for x_c equal to 8%, 27% and 32% in Table 1 and Fig. 6. We can observe a slight increasing trend of E_a as ageing proceeds in the material, which becomes more significant in the low crystallinity samples. We can understand this behavior assuming that, as ageing proceeds, mobility of polymer chain segments decreases. With the decreased mobility more energy is necessary to activate the depolarization process. This tendency is less evident in the high x_c samples that show almost a constant value of E_a of approximately 2.4 eV, irrespective of the ageing condition of the material. These results indicate that chain segment motions are already restricted in these samples, probably as a result of the interlamellar conformation of the amorphous regions within the spherulites. The calculated values for τ_0 show a progressive decrease as t_a and/or x_c increases. We can explain this result again in terms of the reduction of mobility of the polymer chains, associated either with physical ageing or with the interlamellar conformation of the amorphous regions in partially crystallized samples. Effectively, with the decrease in mobility the material behaves as an elastic system with enhanced stiffness, and it results in higher natural oscillation frequencies or lower relaxation times. Similar evolution in τ_0 with physical ageing has been observed in poly(ether imide) (PEI ULTEM 1000(R)) [18] and is consistent with the increase in the dynamic flexural modulus reported for PEI by Biddlestone et al. [19].

3.3. TSPC results

As we mentioned previously, no double peak was detected in the TSDC scans, because, by the WP method only those dipoles that respond to a definite temperature are activated. Different amorphous regions can however be conveniently analyzed by the thermally stimulated polarization currents (TSPC) technique. In this technique the sample is heated at a constant rate while an electric field is applied between the electrodes, and the charge intensity current is measured versus temperature. As all processes leading to dipolar orientation and free charge polarization in the material are thermally activated, these measurements will result in different peaks related to relaxations that the material undergoes.

An interesting characteristic of these measurements for the study of physical ageing is that when enthalpy is recovered at T_g the mobility of the amorphous regions suddenly increases, resulting in a current peak in the TSPC spectrum [12]. This peak is usually superimposed to the end of the dipolar charge current peak corresponding to the non-aged amorphous polymer, and is thus difficult to study. To perform these measurements a kind of 'dipolar charge peak cleaning' was developed as follows; The aged samples were, prior to the TSPC measurement, polarized for 15 min at $T = 70$°C in the same field applied during the TSPC scans. This temperature, just above the static glass transition of non-aged PET-a, corresponds to the 'optimum polarization temperature' [20] at which the chains in the non-aged glassy polymer are mobile. During this process the dipolar chains that remain mobile after ageing will polarize. The polarization field is not removed during the rest of the experiment, and so these dipoles will not produce a charge peak in the TSPC spectra. A more detailed description of this procedure can be found in Ref. [12]. Fig. 7 represents schematically this process, showing the temperatures and times involved.

Representative curves obtained in these measurements are plotted in Fig. 8 for x_c equal to 8%, 27%, 45% and different ageing times. This plot shows the presence of a polarization process (labelled α_a) associated to the recovery of mobility in the amorphous regions, that appears previous to the ρ charge current peak (not completed in these measurements). The evolution of the α_a polarization peak shows, for a given x_c, a shift towards higher temperatures and a significative increase in area as t_a increases. This behavior is related to the decrease in the mobility of the amorphous fraction, associated with the increase in the ageing condition of the material. The resemblance of this evolution with that of the endothermic peak associated with the enthalpy recovery process at T_g is remarkable. The total area of the α_a peak should be related to the total amount of dipoles polarized by the applied field once the mobility is recovered above T_g. This area is thus related to the 'degree of packing' of the chains in the polymer, being an alternative way to monitor the evolution of ageing in the material as discussed in previous works [12].

Besides the commented evolution of this peak, the curves corresponding to the 27% crystallinity sample and long annealing times show a complex sub-structure of the polarization process with three separated peaks. To explain this result we must consider, as we commented earlier, that in these measurements the polarization process of the material was scanned continuously in a wide temperature range, and this should be able to detect temperature separated relaxations in the material. The presence of different amorphous regions with different glass transition temperatures, already detected by other techniques [5], should produce in the material separate polarization processes, each of them associated to the recovery of mobility of the aged sample at the different glass transitions.

Within this hypothesis, the first polarization peak of Fig. 8b (located at 92°C in the sample aged for $t_a = 21\ 600$ min) should correspond to the polarization of the interspherulitic amorphous fraction when mobility is recovered above the first glass transition process that the material undergoes. The following two polarization processes, located at 94°C and 96°C, should correspond to the polarization of the more restricted interlamellar amorphous fraction, that takes place at higher temperatures. The presence of two different peaks associated to this amorphous fraction can be explained attending to two considerations: (a) the ageing condition of the interlamellar amorphous regions is not very high as the ageing temperature is far from the T_g of these regions; (b) the 'dipolar peak cleaning' procedure carried out (see an explanation of this procedure at the beginning of the TSPC results section) will not clean the α peak associated to the interlamellar amorphous regions, as the polarization temperature used ($T = 70$°C) corresponds to the optimum polarization temperature of the interspherulitic amorphous regions. Taking this into consideration, the first of the last two peaks should correspond to the polarization of the non aged portion of the interlamelar amorphous fraction. The last peak should be related to the complete polarization of this amorphous fraction, that will occur when it recovers full mobility at temperatures above the second T_g of the material.

To check this interpretation of the polarization processes observed, another TSPC experiment was carried out as follows: an $x_c = 27\%$ sample was aged for 10 800 min at $T_{a1} = 73$°C (near the glass transition of the interlamellar amorphous regions) and next aged for 1380 min more at $T_{a2} = 65$°C. Prior to the TSPC measurement a 'dipolar peak cleaning' process was performed by polarizing for 15 min at $T_p = 73$°C (the electric field is not removed during the rest of the experiment), cooling down afterwards the sample to the initial temperature of the scan where the TSPC measurement starts. By this ageing-polarization procedure a high degree of ageing of the interlamellar amorphous regions will be obtained. This should produce, within the hypothesis, a decrease of the second peak observed in the curve of Fig. 8b for $t_a = 21\ 600$ min, corresponding to the polarization of the non-aged portion of the interlamellar amorphous fraction.

Fig. 9 reproduces the TSPC spectrum obtained in the experiment described previously, where the second peak located at $T = 94$°C is already not observable. Consistent with the explanation discussed earlier, each one of the observed peaks corresponds to the polarization of the interspherulitic and interlamelae amorphous regions when mobility is recovered above their respectives glass transitions.

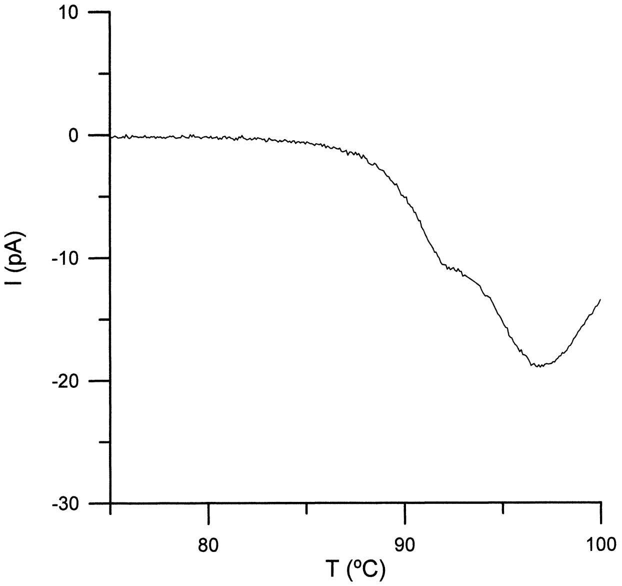

Fig. 9. Short circuit TSPC curve of a $x_c = 27\%$ PET sample aged 10 800 min at $T_{a1} = 73°C$ and then 1380 min at $T_{a2} = 65°C$. α dipolar peak cleaning was performed by the polarization of the sample previous to the scan at $T_p = 73°C$ for $t_p = 15$ min ($E_p = 8$ kV/cm).

4. Conclusions

TSDC measurements of partially crystallized and physically aged PET show a decrease in the capacity of polarization when the crystallinity degree and/or the ageing condition of the material increases. This behavior is explained in terms of the decrease in the mobility of the chain segments, that is associated to the ageing condition of the material or to the interlamellar conformation of the amorphous regions. Fit of TSDC data to conventional models shows, associated to this decrease in the mobility, a slight increasing tendency in the activation energy of the process. However, TSDC measurements do not show evidences of a double glass transition in c-PET.

Physical ageing of partially crystallized PET have proved to enhance both DSC and TSPC response at the glass transition of the material, and can be used to obtain more detailed data of the transitions the material undergoes.

TSPC measurements in aged PET show a charge current peak directly related to the polarization of the amorphous regions when mobility is recovered above the glass transition. The study of this peak shows, for the first time by TSPC, a real double glass transition in partially crystallized PET ($x_c = 27\%$) associated with the interspherulitic and the interlamellar amorphous regions.

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