ELSEVIER

PII: S0032-3861(97)00623-X

Polymer Vol. 39 No. 13, pp. 2795–2801, 1998

0032-3861/98/$19.00+0.00

Comparative TSPC, TSDC and DSC physical ageing studies on PET-a

J.C. Cañadas*, J.A. Diego, M. Mudarra and J. Belana
Dept. de Física i Enginyeria, Nuclear. E.T.S Enginyers Industrials de Terrassa (U.P.C), C/Colon 11, Terrasa 08222, Barcelona, Spain
(Received 18 June 1996; revised 3 February 1997; accepted 14 May 1997)

In the present work a comparative study of physical ageing of poly(ethylene terephthalate) (PET) by thermally stimulated polarization currents (TSPC), thermally stimulated depolarization currents (TSDC) and differential scanning calorimetry (DSC), is presented. In all cases, physical ageing was carried out by annealing the sample at 60°C for several ageing times (from $t_a = 0$ to 264 h). Structural relaxation has been studied by DSC through the analysis of the endothermic peak superposed on the glass transition, which increases and shifts towards higher temperatures as the annealing time increases. Measured current spectra of annealed samples show the appearance of a relaxation peak which we named α_a. The evolution of this peak with the annealing time is presented, and it has been related directly to the endothermic peak obtained by DSC, and therefore directly associated with the physical ageing of PET. Experiments carried out show the dipolar origin of the α_a peak, related to the polarization of chains within the material when mobility is recovered above T_g. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(ethylene terephthalate); physical ageing; relaxations)

INTRODUCTION

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 volume, enthalpy and entropy are greater than they would be in the equilibrium state. Below T_g only slow processes which attempt to establish equilibrium (relaxation changes) can take place, in large time scales relative to typical experimental time scales in a process known as physical ageing[1]. During relaxation several temperature-dependent properties change in the same direction as during cooling through the T_g range, with a decrease in the enthalpy of the glass together with a decrease in mobility and free volume, that tend towards a metastable equilibrium value.

Physical ageing was experimentally studied in early years by measuring volume relaxation processes[2,3] and later, due to the ease with which enthalpy changes are monitored by differential scanning calorimetry measurements (DSC), they were extended to the study of enthalpy relaxation[4–8]. Using this technique, an endothermic peak around T_g appears when the sample is aged at a temperature below T_g. Enthalpy relaxation for different ageing conditions can be determined from the shape and position of this peak. One of the earlier studies by Petrie[4] establishes the equivalence between the energy absorbed during the heating through the glass transition and the enthalpy loss during the isothermal ageing process.

Thermally stimulated current techniques have been applied in more recent years to the study of physical ageing[9,10], although in a more limited way. In the case of thermally stimulated discharge current (TSDC), bound and free charges in the material are activated by a polarizing field above room temperature, and then frozen by cooling down the sample. The sample is then depolarized by heating at constant rate while the resulting current intensity is recorded as a function of temperature. In the case of thermally stimulated polarization current (TSPC) the sample is polarized while being heated at a constant rate, and the polarization current is recorded as a function of temperature. The polarization and depolarization processes in TSDC and TSPC have been widely described in the literature[11,12]. Apart from the internal charges activated during polarization, the material may acquire injected charges from the electrodes in a corona-charging process, if an air gap is present between them and the sample. The intensity measured by these techniques reveals the existence of different kinds of charge relaxations, such as the dipolar α relaxation related to the glass transition temperature T_g. This relaxation is generated by cooperative motion of the main polymer chain, when these chains regain full mobility above T_g, and therefore it must be affected by the ageing condition of the material.

Previous works have dealt with the study of physical ageing in amorphous PET (PET-a) by DSC and TSDC techniques[13,14]. Short-circuit discharges of PET-a polarized in short circuit showed a polar α relaxation around 82°C, followed by another one (ρ) associated with free charge around 94°C. Measurements in annealed samples showed the progressive diminution of the α relaxation as ageing increases, related to the drop in the mobility of the chains in the polymer. Open-circuit discharge of corona-charged electrets showed the appearance of a third peak, around 87°C, that is clearly affected by the annealing conditions of the material. This peak has been related in preliminary works to the probable formation of thermal nuclei in the bulk of the material, that act as heterogeneities and cause charge trapping in the interfaces. However several aspects of its behavior remain unexplained.

The aim of this work is, following these studies, to better understand the origin of this third relaxation induced by the

*To whom correspondence should be addressed

ageing condition of the material. To make this study, DSC, TSDC and TSPC techniques were used in a complementary way, dealing with the effect of ageing in the evolution of this peak. Different treatments and polarization conditions were employed for this purpose.

EXPERIMENTAL PROCEDURE

Experiments were carried out on a commercial poly(ethylene terephthalate) (PET) provided by Hoechst Ibérica S.A. in amorphous sheets (HostaPET (R)) of 250–500 μm thickness, cast by the 'electrostatic wire process'. The degree of crystallinity measured by DSC was in all cases less than 8%. Preliminary experiments have been carried on samples melted and then immediately quenched in cold water, lowering the degree of crystallinity to below 3%. Circular samples of 2 cm diameter were cut from the sheets in order to perform the TSDC and TSPC measurements.

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, trapped free charge, etc.). This temperature was never exceeded to avoid cold crystallization of the material. The annealing of the material has been performed at T_a = 60°C for different times t_a (between 0 and 264 h). In all cases the sample was cooled down from 100°C at 2.5°C/min to the ageing temperature.

Differential scanning calorimetry (DSC)

Calorimetric measurements were made with a Mettler TC11 thermoanalyser 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 2.5°C/min controlled heating rate.

Enthalpy relaxation Δh developed during ageing has been evaluated by integrating the output power of the aged specimen run (P_a) with respect to the reference sample (with no ageing) DSC run (P_{ref}), according to:

$$\Delta h = \frac{1}{\beta m} \int_{T_1}^{T_2} (P_a - P_{ref})\, dT \qquad (1)$$

where m is the sample weight, β is the heating rate, and T_1 and T_2 are the starting temperature and final temperature (above T_g), respectively. More detailed explanation of this method can be found in Ref. [13].

Thermally stimulated discharge currents (TSDC) and polarization currents (TSPC)

Thermally stimulated currents have been carried out in a Kottermann-2715 forced air circulation oven, controlled by an Eurotherm-818 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.

Two kinds of samples were prepared by vacuum deposition of aluminum electrodes on one side of the film (M1 samples) or on both sides (M2 samples), used in open-circuit and short-circuit measurements, respectively.

TSDC in coronal-charged electrets (M1 samples)

Open circuit measurements were performed on M1 samples, cooling down the material from 100°C at 2.5°C/min to the annealing temperate T_a = 60°C. After the sample was aged for different times from 15 min to 120 h, it was cooled down at 2.5°C/min to T_p = 50°C, where the polarization process took place.

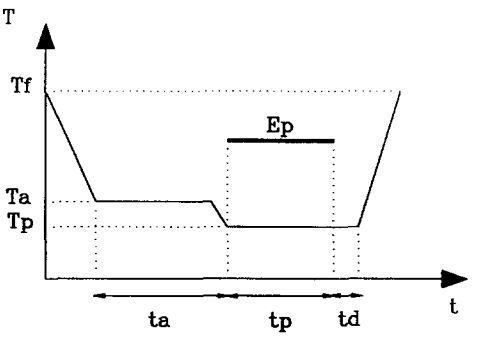

Figure 1 Schematic representation of the field and temperature program developed in the TSDC measurements of corona-charged electrets (fixed parameters: T_a = 60°C, T_p = 50°C, t_p = 15 min, t_f = 97°C)

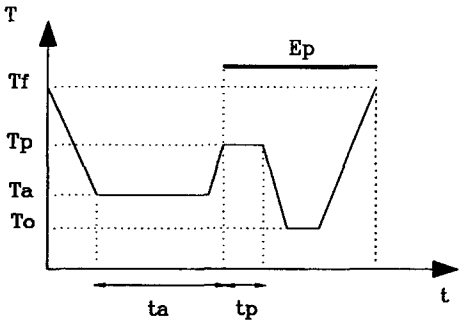

Figure 2 Schematic representation of the field and temperature program developed in the TSPC measurements in M2 samples (fixed parameters: T_a = 60°C, T_p = 70°C, t_p = 15 min, E_p = 4 kV/cm, T_o = 50°C, T_f = 97°C)

Corona-charged electrets have been produced by leaving a 1-mm air gap between the high-voltage flat electrode and the non-metallized surface of the sample. The metallized surface of the sample was grounded during polarization, applying in all the cases 3 kV potential difference between the electrodes for 15 min. The samples were discharged in open circuit, measuring the current intensity during the process. The whole procedure is represented schematically in *Figure 1*.

TSPC in annealed and polarized M2 samples

After cooling down the material from 100°C to the ageing temperature (T_a = 60°C), and annealing it for different times (between 0 and 144 h), polarization currents have been measured in M2 samples with a 4-kV/cm polarization field. In these measurements a kind of 'dipolar charge peak cleaning' was developed by the previous polarization of the aged samples in the same field (4 kV/cm) for 15 min at T_a = 70°C. This temperature, just above the static glass transition of non-aged PET-a, corresponds to the 'optimum polarization temperature' at which the chains in the glassy polymer are mobile and polarize in a convenient time scale [15]. During this process the dipolar chains that remain mobile after ageing will polarize, and will not produce a charge peak in the TSPC spectra as this field will not be removed during the rest of the experiment. *Figure 2* schematically represents this process, showing the temperatures and times involved.

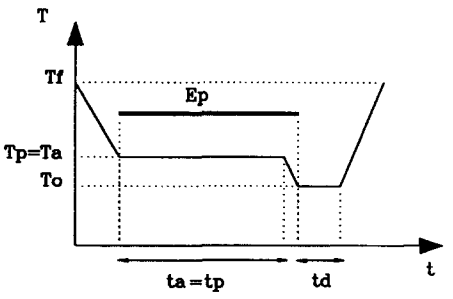

Figure 3 Schematic representation of the field and temperature program developed in the TSDC measurements of simultaneously annealed and polarized electrets (fixed parameters: $T_a = T_p = 60°C$, $E_p = 4$ kV/cm, $T_o = 50°C$, $t_d = 5$ min, $T_f = 97°C$)

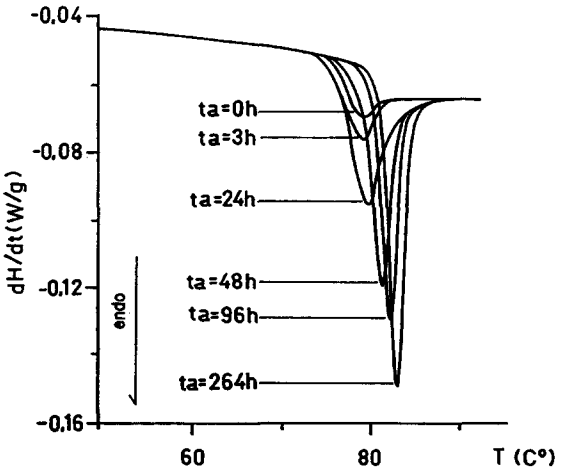

Figure 4 Endothermic peak in DSC curves of PET-a (3% crystallinity) annealed at $T_a = 60°C$ for different times t_a, obtained at 2.5 K/min heating rate

TSDC in simultaneously annealed and polarized electrets (M2 samples)

Short-circuit measurements were performed in M2 samples, cooling down the material from 100°C at 2.5°C/min to 60°C, where the sample was simultaneously annealed and polarized (with a polarization field of 12 kV/cm) for times between 1 and 144 h. Following a conventional polarization process, the field was also applied while the sample was cooled down to $T_o = 40°C$, where the discharge process started. The whole process is represented schematically in *Figure 3*.

RESULTS AND DISCUSSION

In order to characterize the evolution of ageing in the material, and prior to the current measurements, a preliminary study was carried out by differential scanning calorimetry. High amorphous samples were prepared for these measurements by melting the films and quenching them immediately in cool water. Using these procedures, the degree of crystallinity is lowered to values below 3%, however, the samples obtained show much less quality in the surfaces and less homogeneity. DSC curves obtained in aged samples show, as expected, an endothermic peak at T_g as a result of the structural relaxation process that the material undergoes. The curves obtained are represented in *Figure 4* for $T_a = 60°C$ and different annealing times. The position, height, and area of this endothermic peak vary with the ageing condition of the material, increasing the area and the temperature of its maximum as the annealing proceeds. The temperature of this endothermic peak (T_m) corresponds to the process of recovery of enthalpy during the heating of the aged sample. For a sample aged at a given T_a the endothermic peak takes place at higher temperatures as t_a increases, in a similar way to that reported in previous works[13,16]. This behavior is due to the decrease, with ageing, in the molecular mobility of the chain segments (required to promote the recovery of enthalpy).

The enthalpy relaxation Δh calculated according to equation (1) is represented in *Figure 5*. The slope of his curve is a measure of the relaxation rate, which is high at the beginning, but falls with t_a due to the decrease in the free volume of the system, and therefore in the molecular mobility of the chain segments. This behavior represents the slow down in the relaxation kinetics as a result of the system approaching a metastable equilibrium state.

Open-circuit TSDC measurements of corona-charged 3% crystallinity PET-a samples, polarized at $T_p = 50°C$, are presented in *Figure 6* for $T_a = 60°C$ and different annealing times. Several peaks are present in this diagram, identified as α, α_a and ρ.

The first heteropolar relaxation (α) is associated with the glass transition of the material and shows a considerable

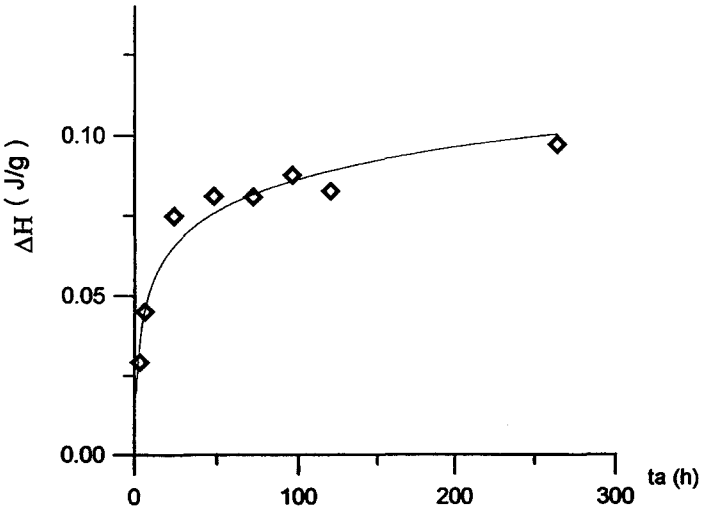

Figure 5 Dependence of enthalpy relaxation Δh on the ageing time t_a for $T_a = 60°C$

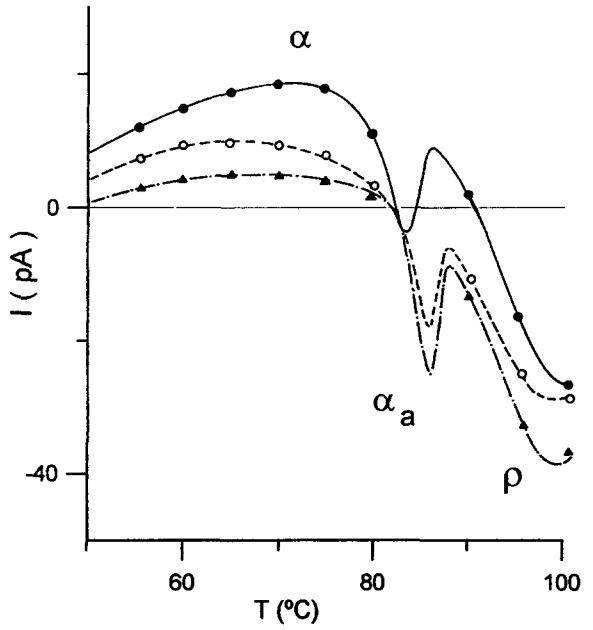

Figure 6 Open-circuit TSDC curves of corona-charged Pet-a (3% crystallinity) annealed for different times t_a (●, t_a = 24 h; ○, t_a = 96 h; ▲, t_a = 120 h) at T_a = 60°C (t_p = 15 min, T_p = 50°C, V_p = 3 kV)

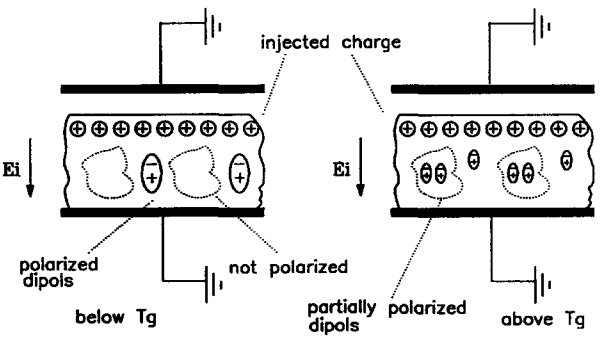

Figure 7 Schematic representation of the origin of the α_a peak when mobility is recovered above T_g in the aged material

decrease in intensity and area as the ageing time is increased. This behavior resembles that of other materials, such as PVC [10], and is explained by the decrease in the mobility of the molecular chains, which is also related to the reduction of the free volume in the sample.

We can see in the same figure, at temperatures above 90°C, the first part of the ρ relaxation, associated with ionic free charge in the material. The homopolar sign of this relaxation indicates that charges injected during the polarization process (from the air gap) in surface traps dominates those present in the bulk of the polymer. A noticeable fact is that complete discharge of the ρ peak cannot be achieved at the final temperature of the experiment (100°C), however, this temperature must not be exceeded in order to avoid the cold crystallization of the polymer.

Between the α and ρ relaxations discussed above, a third relaxation (α_a in figure) of homopolar sign appears superposed on the final part of the α relaxation at temperatures between 82 and 87°C. The position of this relaxation depends on the ageing condition of the polymer in a similar way to that observed for the endothermic peak detected by DSC, with a progressive increase in temperature as the annealing time increases. This relaxation corresponds to that related in preliminary works to the probable formation during ageing of nuclei in the bulk of the material[14] that act as trapping centers, however, the present study will show the dipolar origin of α_a.

As we mentioned previously, in the corona-charging process an injection of free charge takes place in the surface of the sample. This charge will release at temperatures above T_g (in the ρ peak), and generates an electric field that acts on the sample during the discharge. In aged samples, the decrease in the mobility of chains in the polymer prevents the complete activation of the α dipolar peak, the remaining part of the dipoles not being fully polarized (this effect causes the observed decrease in the α peak). When the sample is heated through the T_g range mobility is recovered, and the dipoles will be polarized by the effect of the electric field generated by the surface-injected charge (this process is represented schematically in *Figure 7*). This dipolar polarization during the TSDC scan will produce an homopolar charge current peak in the spectrum, which can explain the α_a peak observed. For short ageing times, the α_a relaxation starts and concludes before the α relaxation (which is usually a broad relaxation in polymers) is completed, which allows a possible net positive current after α_a, as shown in *Figure 6*. To check this model other experiments have been carried out and are related below.

The process described should not produce any result in a short-circuit TSDC measurement of an M2 sample, as no internal field is present during the measurement (these results have been reported previously[13]). However, the polarization current TSPC spectra should be affected by this charge current peak, as the polarization field acts during the whole scan in a similar way to the internal field in an open-circuit measurement.

To perform subsequent measurements the original 8% crystallinity PET-a film was used, as its better homogeneity and surface quality result in greater reproducibility of the curves. On the other hand, the only effect of lowering the amorphous fraction is a slight shift of the α_a peak towards higher temperatures, and a decrease in peak area, although it is still observable. For the TSPC measurements the aged samples have been polarized, previous to the scan, for 15 min at 70°C in the same field applied during the TSPC scan (that is never removed). This procedure avoids the presence of the α dipolar charge current peak below T_g (see Section 2). The curves obtained in these measurements are represented in *Figure 8* for T_a = 60°C, E_p = 4 kV/cm and different annealing times. The presence of the α_a polarization current peak prior to the ρ charge current peak can be seen in the figure. The peak corresponding to the α polarization is not present as expected.

The analysis of the measured α_a peak shows an evolution towards higher temperatures as ageing increases, the same behavior observed for the endothermic peak by DSC. Moreover, the total area of this peak should be related to the total amount of dipoles polarized by the applied (constant) 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. *Figure 9* represents the area of the α_a peak as a function of the annealing time, where a notably similar behavior is observed to that of the total Δh recovered in the sample during the ageing process (*Figure 5*).

The behavior of α_a relaxation in the TSPC measurements *versus* different polarization fields (E_p) is shown in *Figure 10*. In all cases the sample has been aged for 3 h at

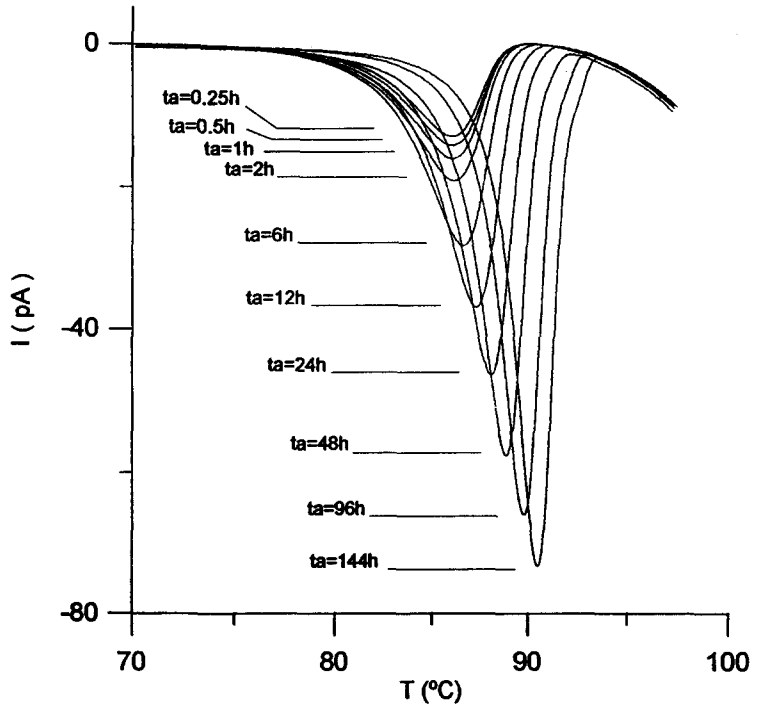

Figure 8 Short-circuit TSPC curves of PET-a (8% crystallinity) samples aged at $T_a = 60°C$ for different times. α dipolar peak cleaning was performed by the polarization of the sample previous to the scan. ($T_p = 70°C$, $t_p = 15$ min, $E_p = 4$ kV/cm)

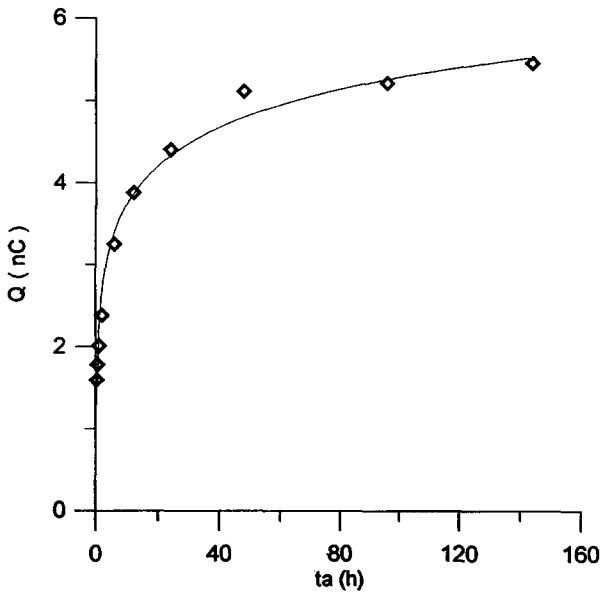

Figure 9 Dependence of the total charge associated to the α_a relaxation on the ageing time t_a for $T_a = 60°C$

60°C and measured after the previous polarization in the same field for 15 min at 70°C. This procedure will perform a kind of 'α peak cleaning', as explained above. It is remarkable to note from this figure the progressive increase in the total area of the α_a peak, together with an increase in the intensity corresponding to its maximum. *Figure 11* shows the total charge associated with the α_a relaxation *versus* the applied field E_p. The linear dependence shown in this curve is indicative of an uniform mechanism responsible for this peak, presumably of dipolar origin[10].

Another experiment indicative of the dipolar origin of α_a has been developed as follows. A complete polarization of the dipoles of a virgin sample (with no ageing) has been produced by a previous polarization at the optimum polarization temperature (70°C) for 90 min. Without removing the electric field, the sample has been aged for 18 h at 60°C and then the TSPC spectrum was measured (always without removing the electric field). The curve obtained in this case did not show any charge current peak. This is the expected behavior according to the dipolar origin of α_a, as all the dipoles had already been polarized before the ageing process.

The last experiment described above suggests the interesting possibility of ageing the sample in a polarized state, in this way stabilizing the polar conformation by the decrease in the overall mobility of the polymer chains. In order to characterize this process, we proceeded to analyze the effect of a constant electric field applied to an M2 sample during the ageing period. The results obtained in the TSDC measurements of these samples are represented in *Figure 12* for $T_a = T_p = 60°C$, $E_p = 4$ kV/cm, and polarizing-ageing times from 1 to 144 h.

The analysis of this figure shows the presence of an heteropolar discharge peak, that corresponds in the case of the 1 h ageing–poling time curve to the conventional α peak observed in PET-a. The space charge ρ peak is not present in the curves as the poling field and temperature are too low to activate these charges. As the ageing–poling time increases, a progressive evolution of the discharge peak towards higher temperatures is observed, together with an increase in the total area. For long annealing times, a notably sharp peak is obtained at temperatures corresponding to those of the α_a peak. We can thus conclude that the material has been really 'packed' (aged) in a polarized state (a fact which may lead to a stabilization of the electret charge).

CONCLUSIONS

Open-circuit TSDC measurements of corona-charged aged PET-a show the appearance of a homopolar current peak

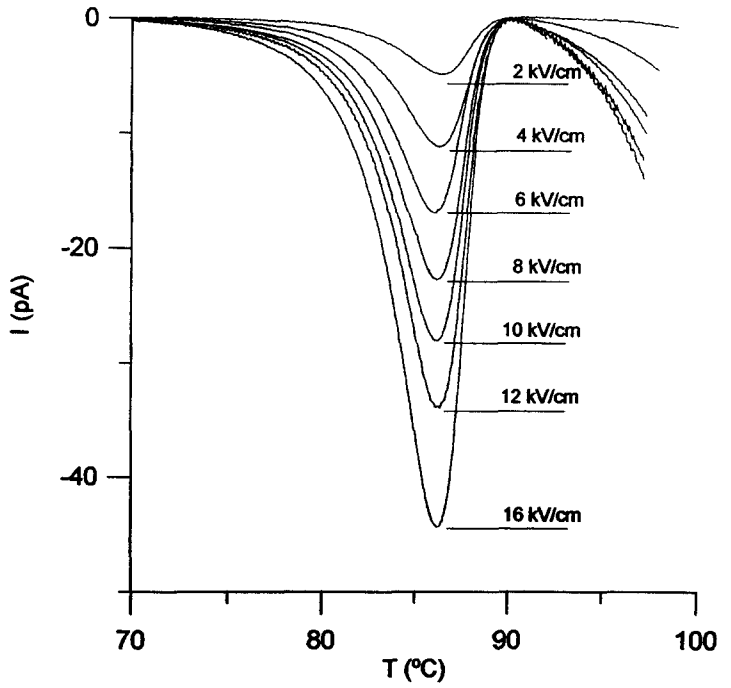

Figure 10 Short-circuit TSPC curves of PET-a (8% crystallinity) samples aged at $T_a = 60°C$ for 3 h *versus* different polarization fields (E_p). α dipolar peak cleaning was performed by the polarization of the sample previous to the scan. ($T_p = 70°C$, $t_p = 15$ min, $E_p = 4$ kV/cm)

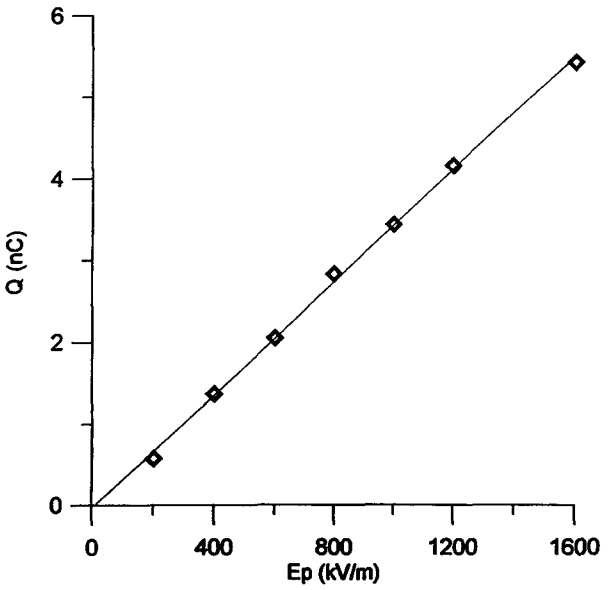

Figure 11 Linear dependence of the total charge associated to the α_a relaxation on the polarization field ($T_a = 60°C$, $t_a = 3$ h)

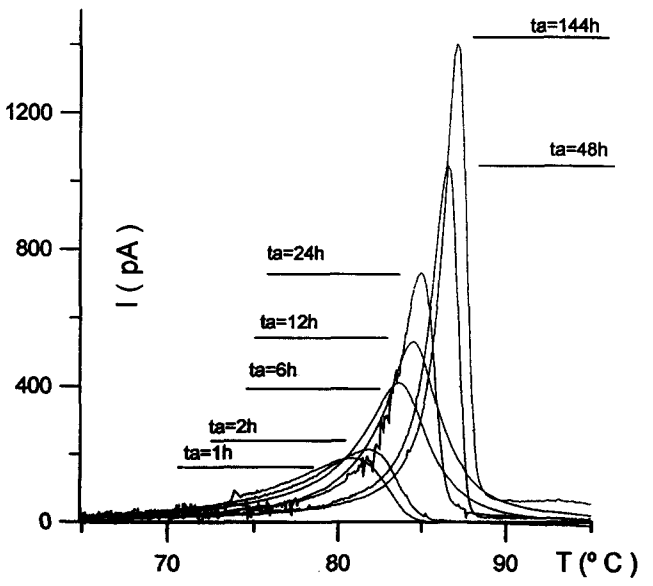

Figure 12 Short-circuit TSDC curves of PET-a (8% crystallinity) samples simultaneously aged and polarized at $T_a = T_p = 60°C$ for different times ($E_p = 4$ kV/cm)

(α_a), at temperatures between 82 and 87°C, directly related to the ageing condition of the material. Evolution of this peak shows a progressive increase in both the temperature of its maximum and its total area as ageing proceeds, in a similar way to that observed for the endothermic peak detected by DSC and associated to the recovery of enthalpy at T_g. the explanation of this peak in terms of the increase in the material polarization when enthalpy is recovered is discussed. In aged samples, the decrease in the mobility of chains in the polymer prevents the complete activation of the α peak, leaving some of the dipoles not fully polarized. When the sample is heated through the T_g range, mobility is recovered, and these dipoles will be polarized by the effect of the existing internal electric field. Evolution of the α_a peak in TSPC measurements, with a controlled polarizing electric field, show the possibility of the study of physical ageing in the polymer by means of this peak. TSDC measurements of simultaneously annealed and polarized samples show the viability of ageing the sample in a polarized state, thus stabilizing the polarization of the material.

ACKNOWLEDGEMENTS

Financial support for this work has been provided by the 'Centre de Transferencia de Tecnologia' of the UPC (Project: 'Projecte pre-competitiu PR9506')

REFERENCES

1. Struik L. C. E., in *Physical Ageing in Amorphous Polymers and Other Materials*. Elsevier Science, Amsterdam, The Netherlands, 1978.
2. Kovacs, A.J., *Adv. Polym. Sci.*, 1963, **3**, 394.
3. Hutchinson, J.M. and Kovacs, A.J., *J. Polym. Sci. Polym. Phys. Ed.*, 1976, **14**, 1575.
4. Petrie, S.E.B., *J. Polym. Sci. Part A-2*, 1972, **10**, 279.
5. Foltz, C.R. and McKinney, P.V., *J. Appl. Polym. Sci.*, 1969, **13**, 2235.
6. Kovacs, A.J., Akloins, J.J., Hutchinson, J.M. and Ramos, A.R., *J. Polym. Sci. Polym. Sci. Polym. Phys. Ed.*, 1979, **17**, 1097.
7. O'Reilly, J.M., *J. Appl. Phys.*, 1979, **50**, 6083.
8. Chen, H.S. and Wang, T.T., *J. Appl. Phys.*, 1981, **52**, 5898.
9. Fleming, R. J., in *Proc. 6th Int. Symp. Electrets*. Oxford (UK), IEEE Electrical Insulation Society, New York, 1988, p. 118.
10. Van Turnhout. J., in *Electrets, Topics in Applied Physics*, Vol. 33, ed. G. M. Sessler. Springer-Verlag, Berlin, 1980.
11. Sessler, G. M., in *Electrets, Topics in Applied Physics*, Vol. 33, ed. G.M. Sessler. Springer-Verlag, Berlin, 1980.
12. Hilczer, B. and Malecki, J., in *Electrets, Studies in Electrical and Electronic Engineering*, Vol. 14. Elsevier–PWN–Polish Scientific Publ., 1986.
13. Monsterrat, S., Colomer, P. and Belana, J., *J. Mater. Chem.*, 1992, **2**, 217.
14. Belana, J., Mudarra, M., Cañadas, J.C. and Colomer, P., *J. Mater. Sci.*, 1993, **28**, 3805.
15. Belana, J., Colomer, P., Pujal, M., Montserrat, S., *J. Macromol. Sci., Phys.* 1984–85, **B23**, 467.
16. Berens, A.R. and Hodge, I.M., *Macromolecules*, 1982, **15**, 756.