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Behaviour of amorphous poly(ethylene terephthalate) annealed at $T < T_g$ by thermally stimulated currents

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Thermally stimulated current (TSC) discharges in open circuit of amorphous poly(ethylene terephthalate) (PET) corona-charged electrets show a heteropolar relaxation at 87 °C, ρ_1, between α and ρ peaks. This relaxation tends to become homopolar when the sample is annealed at temperatures below the glass transition temperature. This is due to the formation of a trapped charge density on the surface of the material that originates, during the TSC discharge, a current that counteracts the one that results in ρ_1. This trapping effect, which initially is null, increases with annealing due to the rise in resistivity. On the other hand, TSC discharges in short-circuited annealed samples result in a heteropolar peak, ρ^*, that corresponds to ρ_1. The area of ρ^* increases with the annealing time in a bounded way. This peak is related to the formation of thermal nuclei (embryos) in the bulk of the material that act as heterogeneities. This suggests that ρ_1 is associated with a barrier-type polarization. If the annealed sample is heated to temperatures above the glass transition temperature, the tendency to the inversion of ρ_1 vanishes and ρ^* disappears, whereas α and ρ are modified. This suggests that ρ relaxation is related to a Maxwell–Wagner–Sillars effect.

1. Introduction

The thermally stimulated currents (TSC) technique consists of depolarizing samples (of polymeric material in this case) by thermal stimulation. These samples are previously polarized by an electric field. The process of polarization takes place at a temperature above the room temperature at which the polarizing field is applied to the sample. This field activates both free and bound charges and when the sample is cooled the activated charge is frozen.

One of the fundamental aspects of this technique is related to the nature of the contact between the electrodes and the surfaces of the samples. It is possible to polarize (and depolarize) the sample either in short circuit or in open circuit. In the first case the measured current is associated with polar and free charge movements in the bulk of the material, and in the second case there is added the ohmic current response [1].

The TSC technique has been used to study the relaxations of amorphous poly(ethylene terephthalate) (PET-a) [2–4], the physical ageing [5] and the effects of cold crystallization [6] on this material. In all these studies the samples have been metallized on both sides and discharged in short circuit. These kinds of discharge have been applied to electrets conventionally formed, that is, applying an electric field E_p at a temperature of polarization T_p for a time t_{pi} and then cooling the sample to a temperature $T_f < T_p$ while the field remains applied.

The TSC discharges in short circuit of electrets of PET-a polarized in short circuit show two relaxations in the range of temperatures between 30 and 100 °C. One is a polar relaxation (α) which presents its maximum at approximately 82 °C. The other one (ρ), which is associated with free charge, shows its maximum at approximately 94 °C and takes place over the range of temperatures between 84 and about 100 °C.

The discharges in open circuit of corona-charged electrets of PET-a show three peaks: α, ρ_1 and ρ_2. The first one, α, corresponds to the polar peak observed in short-circuit processes. The peak ρ_1 appears at about 87 °C and some of its characteristics have been explained in a previous report [7]. This peak is clearly heteropolar (even with an increase of the polarizing field), it shows symmetry with the inversion of the polarity of the electrodes, and it also varies linearly with the applied field. This effect indicates that the mechanism that activates this relaxation is uniform. On the other hand, as it takes place in the range of temperatures that corresponds to ρ relaxation in short-circuit processes, it should be more consistent with a free charge mechanism.

Although electronic conductivity has been associated with the range of temperatures between 87 and 90 °C [8], to impute the activation of ρ_1 to a mechanism of free charge seems to be contradictory with the fact that in no case does this peak tend to acquire a homopolar sign in open-circuit processes, and with

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the properties previously explained. The third peak (ρ_2) appears at the same temperature that ρ does in short-circuit processes and it has a homopolar sign. This inversion of sign shows that ρ relaxation is activated by free charge, but the presence of ρ_1 seems to indicate that ρ could be overlapped by another mechanism.

The aim of this work is to obtain information about the mechanism that originates ρ_1, adding to the aforementioned results the effect of annealing at temperatures below the glass transition temperature (T_g). To make this study the TSC technique has been used to discharge electrets either in short circuit or in open circuit.

2. Experimental procedure

Experiments were carried out on commercial PET with a number-average molecular weight M_n of 20 000. Its determination was performed by viscosimetric measurements using o-chlorophenol at 25 °C as solvent and the Marshall and Todd equation [9] as the relation between M_n and [η]:

$$[\eta] = 6.56 \times 10^{-4} M_n^{0.79}$$

which is valid for the molecular weight range between 12 000 and 25 000.

T_g was determined in a previous paper [4] by differential scanning calorimetry (DSC) measurements and resulted in a value of 72 °C.

Films of PET-a of approximately 250 μm thickness and 2 cm diameter were prepared by melting the material in moulds and quenching them into ice-cooled water afterwards. Then the samples were conditioned in a vacuum chamber at 40 °C to dry them, and they were heated to a temperature lower than 90 °C to eliminate internal stresses. Density measurements after this heating process, using a density gradient column with carbon tetrachloride and n-heptane at 23 °C as solvent, resulted in a degree of crystallinity lower than 5% in all cases.

The samples were polarized to form electrets. The formation of an electret consists of two steps: a first one, isothermal, during which an electric field is applied to the sample, and a second one during which the sample is cooled at a controlled rate. During both steps the field activates the mechanisms of conduction which are temperature-dependent, and during the second one those mechanisms are frozen. If the field remains applied during this second step a conventional electret is formed, but if the field is switched off during the cooling a windowing polarized electret is formed. Cooling of the samples was carried out at a rate of 2 °C min^{-1} in all cases.

Aluminium electrodes were vaporized on both sides of the samples used in short-circuit (SC) processes. In the case of samples used in open-circuit (OC) processes aluminium electrodes were vaporized only on one side. The OC charging process is called corona charging. Corona-charged electrets were discharged in open circuit and an air gap of 1 mm was left between the high-voltage electrode and the non-metallized surface of the sample in both processes, charge and discharge. The metallized surface was grounded.

Once the samples had been polarized, they were discharged by TSC in this study. The heating rate of thermal stimulation was always 2 °C min^{-1}. The experimental equipment used was composed of a measuring cell placed in a forced-air Heraeus oven controlled by a Setaram PID RT-3000 temperature programmer. The temperature was measured by a digital thermometer (Mettler TM-15) with Pt-100 probes located very close to the sample. The discharge current was measured by a Keithley 616 digital electometer and recorded as a function of temperature by an HP 7046 A x–y recorder.

3. Results and discussion

The TSC spectrum of a PET-a sample conventionally charged in the open-circuit process is shown in Fig. 1. It can be observed that the discharge of a sample polarized at $T_p = 60$ °C shows the polar peak (α), ρ_1 relaxation (heteropolar) at approximately 87 °C and ρ_2 relaxation (homopolar) at about 94 °C. This figure also shows the discharge of a conventionally polarized electret in the short-circuit process (curve f), in which only α and ρ relaxations appear, in order to compare their shape.

For $T_p < T_g$ the temperature at which the maximum of α appears increases with T_p until it reaches a value of 84 °C. The peak ρ_1 increases with T_p and presents its maximum at slightly higher temperatures than α.

The peaks α and ρ_1 seem to become mixed in single peak at a temperature of polarization $T_p = 72$ °C which corresponds to T_g. For $T_p > T_g$ they can be distinguished again, as ρ_1 can be detected at the beginning of the intensity drop (at approximately 87 °C) whereas α, more pronounced, remains at 84 °C.

Samples of PET-a, annealed at temperatures (T_a) below T_g for several values of the annealing time (t_a), were subjected to both SC and OC processes. In the case of SC processes, as t_a increases, α relaxation, which appear clearly defined, decreases in intensity whereas the temperature at which the maximum appears increases in a sigmoidal way and it tends to a

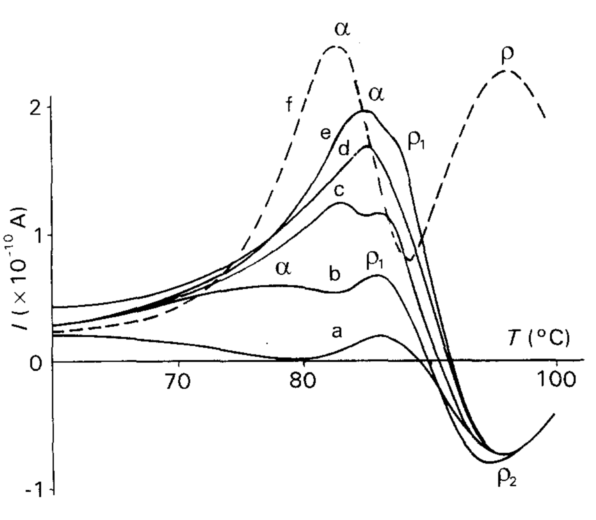

Figure 1 TSC curves of conventional electrets of amorphous PET in OC processes at several values of T_p. $E_p = 31\ \text{kV cm}^{-1}$, $t_{pi} = 30$ min, $T_f = 40$ °C; T_p (°C) = (a) 40, (b) 62, (c) 67, (d) 72, (e) 75; (f) TSC curve in SC process.

constant value that depends on the annealing temperature [5]. If t_a is very large it is difficult to fix the temperature of the maximum since the peak is very weak.

If the charge and discharge of the sample are carried out in open circuit, α relaxation appears very flattened and it is difficult to follow the changes of its maximum with annealing. However, as α is a polar peak, its behaviour in this kind of process must be similar to that observed in short-circuit ones.

Since in SC processes and for $T_p < T_g$ the peak ρ is very weak, we chose a temperature of polarization at which this relaxation could be distinguished in order to study its variations with the annealing. The value of T_p chosen was 60 °C. For this temperature of polarization the peak ρ shows a very flattened maximum between 90 and 93 °C (Fig. 2). As t_a increases it can be observed that another peak, ρ^*, appears in the range of temperatures that corresponds to peak ρ (at about 87 °C). This peak increases in intensity with t_a, but its increase is bounded: the peak obtained for $t_a = 7$ days is similar to the one obtained for $t_a = 3$ days although the first appears at higher temperatures. After ρ^* relaxation, ρ relaxation appears, which shifts to higher temperatures and decreases in intensity with t_a. Once the annealed sample had been discharged, a new reference TSC discharge was obtained immediately afterwards. ρ^* could not be observed in this new discharge whereas α decreased and ρ increased in intensity, in accordance with the time of annealing (Fig. 3).

In the case of OC processes, if $T_a < T_g$ it can be observed that ρ_1 tends to acquire a homopolar sign with t_a. Fig. 4 plots the discharges of a corona-charged PET-a sample for several values of t_a.

When the sample is annealed, a current of opposite direction to the one that originates ρ_1 causes the sign inversion of this peak. The new peak, $\rho_{1\,\mathrm{homo}}$, is sensitive to the polarity of the applied field so that it is larger when it is negatively biased for the same value of t_a (Fig. 5). The size of $\rho_{1\,\mathrm{homo}}$ increases with polarizing field for the same annealing conditions.

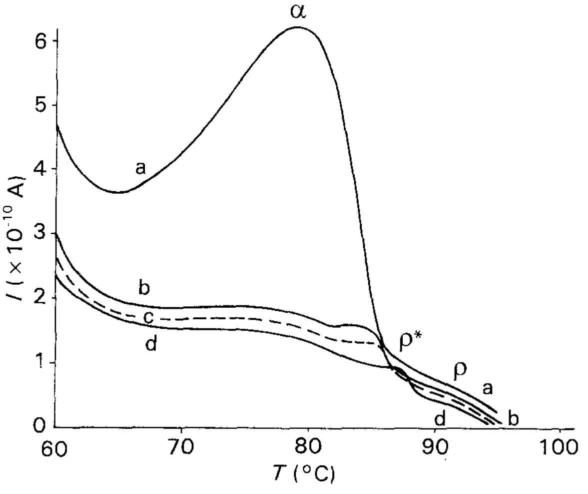

Figure 2 Annealing time effect in SC processes. $T_a = T_p = T_f = 60\,°\mathrm{C}$, $E_p = 88\,\mathrm{kV\,cm^{-1}}$, $t_{pi} = 30$ min; t_a (days) = (a) 0, (b) 1, (c) 3, (d) 7.

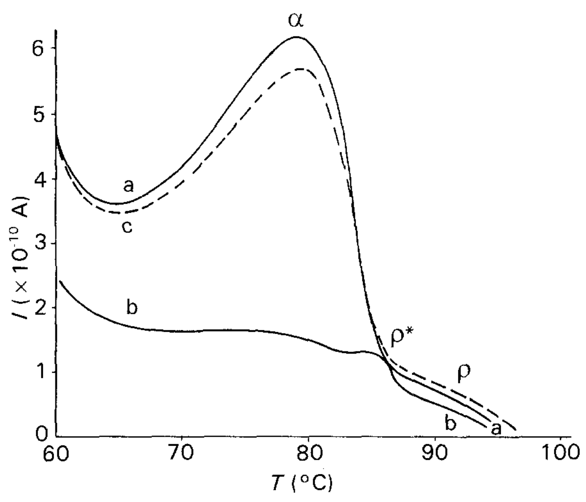

Figure 3 TSC curves in SC processes. $T_a = T_p = T_f = 60\,°\mathrm{C}$, $E_p = 88\,\mathrm{kV\,cm^{-1}}$, $t_{pi} = 30$ min; (a) $t_a = 0$ days, (b) $t_a = 3$ days, (c) $t_a = 0$ days, polarized after heating to 95 °C of a sample annealed 3 days at 60 °C.

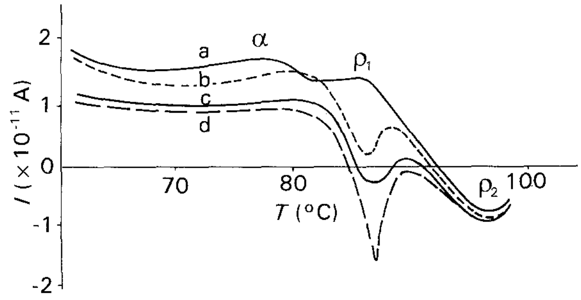

Figure 4 Annealing time effect on the ρ_1 relaxation in PET-a samples (OC processes). $T_a = T_p = T_f = 60\,°\mathrm{C}$, $E_p = 35\,\mathrm{kV\,cm^{-1}}$, $t_{pi} = 30$ min; t_a (days) = (a) 0, (b) 1, (c) 4, (d) 7.

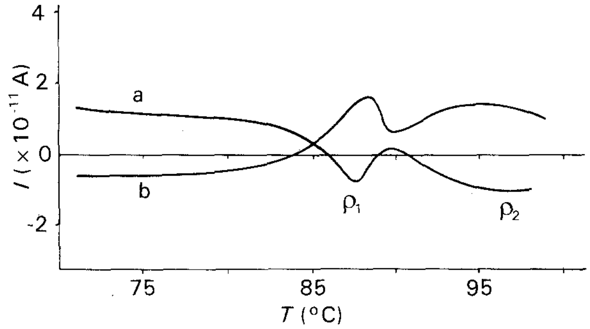

Figure 5 Bias polarity effect on the peak $\rho_{1\,\mathrm{homo}}$ obtained after annealing at $T_a = 60\,°\mathrm{C}$, for $t_a = 2$ days. $T_p = 60\,°\mathrm{C}$, $t_{pi} = 20$ min and E_p (kV cm^{-1}) = (a) + 24, (b) − 24.

One characteristic of the aforementioned process is that, once the annealed sample is heated to a temperature above T_g, a new TSC reference spectrum does not show $\rho_{1\,\mathrm{homo}}$ (as happened with ρ^* in SC processes). The change in the sign of ρ_1 agrees with the fact that there is injected charge from the electrodes which is trapped on the surface of the material. The trapped charge increases with annealing time. Since initially in no case does the current tend to change in sign, one concludes that initially there is no surface trapping in PET-a and that the formation of traps is conditioned by the increase in the resistivity that happens during the annealing [10]. The increase in the resistivity allows the charges to remain trapped for a longer time because the relaxation of homocharge is due to ohmic conductivity [1].

The formation of trapping centres on the surface of PET-a as a consequence of annealing seems to agree with the results obtained by Yeh and Geil [11]. They explain that, in the amorphous sample, ball-like regions with paracrystalline order are formed. When the sample is annealed they join to form larger structures which are the basis of the later formation of spherulites. These structures could be responsible for surface trapping in corona-charged samples. The fact that $\rho_{1\,\mathrm{homo}}$ tends to acquire a constant value with t_a (Fig. 6) should be related to the bounded development of the aforementioned structures. These are unstable and disappear when the sample is heated to temperatures above T_g.

The formation of trapping centres should be detected in all annealed samples, whether they are studied by SC or by OC processes. In the case of SC processes, the formation of these centres can only be observed in the bulk of the material. This is confirmed by the presence of ρ^* that appears at 87 °C with a heteropolar sign in SC processes. On the other hand, if ρ^* relaxation is due to free charge, its mechanism should agree with uniform behaviour [7], as is possible in the case of a barrier-type mechanism [12].

The formation of trapping centres in the bulk of the material, associated with interphases, should agree with the results obtained by Stuart [13] and Miller [14] with respect to the existence of molecular order in PET-a, which cannot be measured by X-ray diffraction, that increases when the material is annealed. On the other hand, Illers [15] indicates that, when the sample is annealed, thermal nuclei (embryos) can be added to the athermal ones coming from melting and to the ones originated during quenching from the melted to the amorphous state. The presence of ρ^* in the spectrum confirms the possibility of the formation of these embryos that act as trapping centres.

The behaviour of ρ^* and ρ indicates that during the annealing new embryos are formed which, added to the ones that were previously in the material, grow and form small heterogenities that act as Maxwell–Wagner–Sillars (MWS) capacitors. These structures turn out to be unstable, but the new embryos, thermally originated, remain in the material. This fact explains the increase of ρ relaxation after annealing: the number of embryos is larger than it was before the annealing. We do not impute the increase of ρ to the creation of impurities, as they are not affected by annealing. On the other hand the fact that ρ is sensitive to the number of embryos suggests that this peak could be associated with a mechanism of MWS type.

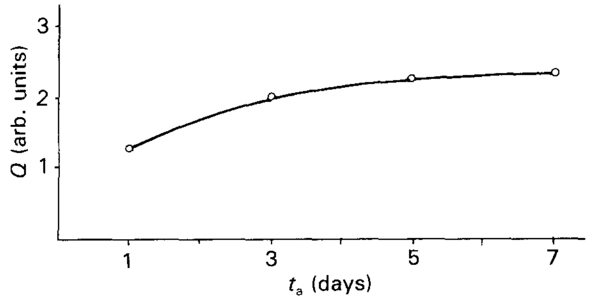

Figure 6 Charge of peak $\rho_{1\,\mathrm{homo}}$ versus t_a in samples annealed at 60 °C. $T_p = 60$ °C, $t_{pi} = 30$ min and $E_p = 24$ kV cm^{-1}.

4. Conclusions

TSC discharges of PET-a electrets in OC processes show at 87 °C a heteropolar peak, ρ_1, which is associated with a uniform mechanism. This relaxation is related to barrier-type polarization and it expresses the charge trapping in the interphases that are in the material as a consequence of its low initial crystallinity (about 5%), and the presence of athermal nuclei coming from melting and those originated during quenching from the melted to the amorphous state. The TSC discharges in OC of electrets of annealed material give rise to a progressive inversion of this peak, which finally takes a homopolar sign. This is due to the formation of surface traps that during the discharge give rise to a current with opposite sign to the one that originates ρ_1, which finally causes its inversion.

The discharges in SC of electrets of annealed material give rise to a heteropolar peak, ρ^*, that corresponds to ρ_1, whose area increases with t_a in a bounded way because it is related to the formation of embryos, the development of which is also bounded.

In both cases (SC and OC processes) the mechanism that originates the changes in ρ^* and ρ_1 vanishes if the sample is heated to temperatures above T_g, whereas α and ρ are affected.

The effect of annealing on ρ relaxation indicates that this relaxation, besides being associated with the presence of impurities in the material, is sensitive to the heterogeneities that give rise to the formation of embryos, and in consequence it could be related to an MWS mechanism.

References

1. J. VAN TURNHOUT, "Thermally Stimulated Discharges of Polymer Electrets" (Elsevier, Amsterdam, 1975).
2. J. BELANA, P. COLOMER, S. MONTSERRAT and M. PUJAL, *Anales Fisica Serie B* **78** (1982) 8.
3. *Idem, ibid.* **78** (1982) 142.
4. *Idem, J. Macromol. Sci. Phys.* **B 23** (1984–85) 467.
5. S. MONTSERRAT, P. COLOMER and J. BELANA, *J. Mater. Chem.* **2** (1992) 217.
6. J. BELANA, P. COLOMER, S. MONTSERRAT and M. PUJAL, *Polymer* **29** (1988) 1738.
7. J. BELANA and P. COLOMHER, *J. Mater. Sci.* **26** (1991) 4823.
8. R. A. CRESWELL and M. M. PERLMAN, *J. Appl. Phys.* **41** (1970) 2365.
9. J. MARSHALL and A. TODD, *Trans. Faraday Soc.* **49** (1953) 67.
10. P. COLOMER, J. CALAF, J. BELANA and S. MONTSERRAT, in Proceedings of 7th International Symposium of Electrets (ISE-7), Berlin, September 1991, edited by R. Gerhard-Multhaupt, W. Künstler, L. Brehmer and R. Danz (IEEE Electrical Insulation Society, New York, 1991) p. 199.
11. G. S. YEH and P. H. GEIL, *J. Macromol. Sci.* **B1** (1967) 235.
12. P. MÜLLER, *Phys. Status Solidi* **A23** (1974) 165.
13. H. A. STUART, *Angew. Chem.* **6** (1967) 844.
14. G. W. MILLER, *J. Polym. Sci, Polym. Phys. Edn* **13** (1975) 1831.
15. K. H. ILLERS, *Kolloid-Z. Z. Polym.* **245** (1971) 393.

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