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Origin of the α_c relaxation in poly(ethylene–terephthalate) by thermally stimulated currents

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The thermally stimulated depolarization currents of poly(ethylene–terephthalate) electrets with a reduced degree of crystallinity ($\simeq$ 4%), corona-charged at polarization temperatures between 65 and 100 °C, show a heteropolar α^* relaxation placed between the α relaxation (heteropolar) and the ρ relaxation (homopolar). This α^* relaxation is associated with a uniform mechanism and has been observed in the discharge of electrets with shorted evaporated electrodes, which have been formed using the windowing polarization method at polarization temperatures between 76 and 79 °C. The intensity and position of α^* depend on the degree of crystallinity and the morphology. The application of the method of thermal stimulation by steps, which leads to a gradual crystallization of the sample, shows that the α_c relaxation of crystalline PET has its origin in α^*.

1. Introduction

The technique of thermally stimulated depolarization currents (TSDC) is most useful for studying the relaxation properties of dielectric materials in the solid state. These studies have allowed the evaluation and identification of dipole reorientation processes and of trapping levels of the free charges. The technique has been widely applied to polymer electrets [1–6] and particularly to study poly(ethylene–terephthalate) (PET) [7–17] in order to analyse the concrete mechanisms causing the relaxations and the effect of thermal treatments.

The conventional method of electret formation is the application of an electric field to a constant polarization temperature, T_p, followed by cooling until $T_0 < T_p$ at which moment the field is withdrawn. This process permits freezing the conduction mechanisms activated in the thermal range used. Further heating of the specimen, done at a constant rate, originates a depolarization current or TSDC curve where one or a few peaks, associated with the various activated mechanisms, occur.

Amorphous PET films, polarized and discharged with shorted evaporated electrodes show, between room temperature and 100 °C, two heteropolar relaxations: α, polar, associated with the T_g of the material, and ρ, of the free charge [18–21].

Should there be a blocking electrode during the charge and discharge, with air between the electrode and the sample, three relaxations will be observed in the same temperature range when specimens are polarized at $T_p > 65$ °C: α, heteropolar, as mentioned in the case of discharges in short circuit; α^*, also heteropolar, visible from $T_p \simeq 68$ °C; and, finally, ρ relaxation associated with the free charge injected from the electrodes, with homopolar character [22].

On increasing the polarization temperature, α^* relaxation makes more apparent its heteropolar character and spreads progressively in the zone of peak ρ which, in turn, becomes smaller when temperatures are higher [23].

This relaxation, α^*, has apparently no correspondence with any originated in the case of discharges in short circuit which can be only interpreted, either way, as associated with a mechanism not occurring in this type of discharge or which is overlapped with that of α or ρ.

One inconvenience in electret formation by the conventional method is that should there be in the thermal range various mechanisms depending on temperature – all with the same character, for instance heteropolar – cooling would affect them all and, hence, their differentiation would not be possible from the recorded TSDC curve.

"Windowing polarization" is a method introduced by Lacabanne and co-workers [24, 25], making possible the isolation of elementary Debye-type relaxation of the molecules over the entire spectrum of relaxation. This method isolates the elementary relaxation modes one by one and is used in building up the material's relaxation map. The usefulness of this method has been demonstrated in different papers [26–35] and facilitates the study of overlapped relaxations [20]. For this reason, its application to amorphous PET (PET-a) can be helpful and contribute to identifying and studying α^*.

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On the other hand, the effect of thermal treatment on relaxations is well known and sufficiently proved by the use of many experimental techniques [36–46]. In the case of PET-a when using the TSDC technique, the cold crystallization effect on α and ρ has been already studied by the method of thermal stimulation by steps (TSS) [21, 22]. With respect to α relaxation, a progressive increase of the degree of crystallinity leads to a decrease of its intensity as a consequence of the increase of restrictions in the amorphous region of the polymer. For crystallinities between 20 and 30%, the α relaxation occurs in the spectrum together with another which, later, with an increase of the degree of crystallinity, happens to be the α_c relaxation of crystalline PET (PET-c). The fact of appearing simultaneously proves that α_c does not derive from α and that its origin is caused by another relaxation associated from the start with the reduced crystalline phase of the material, whose mechanism is initially overlapped with α or ρ.

The objective of this paper is, on the one hand, to analyse α* and prove it to be a uniform relaxation as well as to establish it in the discharge of electrets with shorted evaporated electrodes using the windowing polarization method; and the other hand, to study the influence of crystallinity on the relaxation and see whether the origin of α_c of PET-c is in α*.

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 a solvent and the Marshall and Todd [47] equation as the relation between M_n and [η]:

$$[\eta] = 6.56 \times 10^{-4} M_n^{0.73}$$

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

Films of PET-a were prepared with a diameter of 2 cm and thickness of $\simeq 250\ \mu m$, by fusion and quenching in moulds. The samples were conditioned for a few days in a vacuum chamber at 40 °C to dry them, and 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 solvents, gave in all cases a degree of crystallinity $X_c < 5\%$.

The conditioned samples were metallized with aluminium on one side for the processes in open circuit and on both sides for short circuits.

Conventional elecrets were polarized by the traditional method which consists of the application of an electric field E_p at temperature T_p for a time t_{pi} and subsequent cooling to the temperature T_0 while the field is still applied. In the case of windowing polarization, the field is switched off during cooling. Such electrets are called in this paper "isothermic electrets". Cooling was carried out at 2 °C min^{-1} in all cases (Fig. 1).

Corona-charged electrets were made by leaving an air gap of 1 mm between the high-voltage electrode and the non-metallized surface of the sample. The metallized surface was connected to ground.

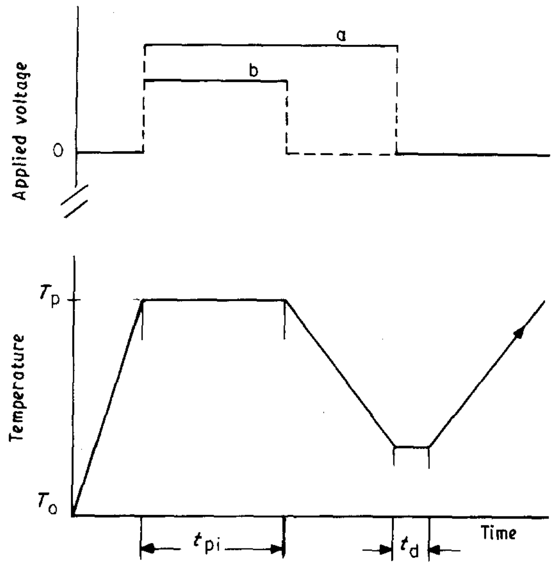

Figure 1 Electret formation. Field and temperature programme during charging, storage and TSDC: (a) conventional electrets, (b) isothermic electrets.

Once polarized, the TSDC technique was used in this study. Electrets metallized on both sides were discharged with the shorted evaporated electrodes, while the corona-charged electrets were discharged in open circuit under the same conditions of polarization. The heating rate was always 2 °C min^{-1}.

The TSS method was applied by increasing the crystallinity of the samples. The aim of this method is to produce electrets cyclically at a fixed T_p and then to apply to them a controlled heating to a final temperature T_f whose value increases by ΔT for each cycle. This increase should be as small as possible, < 1 °C in the temperature ranges where the most significant changes are expected. This process leads to gradual crystallization of the amorphous PET sample. The final temperatures attained, T_f, are between 90 and 140 °C. The crystallinity reached by the samples is determined by density measurements using a density gradient column.

The experimental equipment used included a measuring cell placed in a forced-air Heraeus oven, temperature-controlled by a Setaram PID RT-3000 temperature programmer. Temperature was measured by Pt-100 probes near to the samples with a digital thermometer (Mettler TM-15) to an accuracy of 0.1 °C. The discharge current was measured with a digital electrometer (Keithley 616) whose accuracy is 5% of the reading in the range 10^{-9}–10^{-11} A. The current was recorded as a function of temperature in an HP 7046 A. Previous experiments showed that the temperature gradients across the sample were lower than 0.2 °C in the temperature range used in this work.

3. Results and discussion

Thermally stimulated discharge curves for corona-charged isothermic electrets of amorphous PET are shown in Fig. 2 at different polarization temperatures T_p. At $T_p > 65\,^\circ C$ three relaxations can be observed in the thermogram. The first is evidently α and its sign is heteropolar. The second, α*, heteropolar as well, has a maximum at about 87 °C and the last, ρ, which has a maximum at 95 °C for $T_p = 82\,^\circ C$, is homopolar and always becomes exhausted at 105 °C (the temperature at which the current is reversed and turns again to have the heteropolar sign).

The intensity of the α relaxation, $I(\alpha)$, increases progressively as the polarization temperature increases, passing through a maximum at $T_p = 75\,^\circ C$. It decreases then without changing its position (Fig. 2, curves b–g).

The intensity of the α* relaxation, $I(\alpha^*)$, has a similar dependence to α, while that for ρ, $I(\rho)$, growing with no significant change of position at $T_p < 82\,^\circ C$, reaches its maximum at $T_p = 82\,^\circ C$ and decreases at the same time as the peak is displaced towards higher temperatures (Fig. 2, curves f and g).

ρ is known to be associated with charge injected from the blocking electrode to the sample and it occurs at the same temperature as the ρ peak of the electrets metallized on both sides. This injection is, of course, responsible for the inversion of the current and its homopolar character.

In Fig. 3, the behaviour of both α* and ρ relaxations for different applied electric fields is shown. It is to be noted that α* grows with the field with the heteropolar sign (without changing its position) while ρ increases as well, although with the homopolar sign. On the other hand, the discharge curves of conventional corona-charged electrets are shown in Fig. 4. For $T_p \leqslant 70\,^\circ C$, α and ρ are alone well defined.

On increasing the polarization temperature, α* becomes evident with heteropolar sign in the range occupied by ρ. For high polarization temperatures, the homocharge is always less activated while α* increases progressively in such a way that it cancels ρ (Fig. 4, curve f).

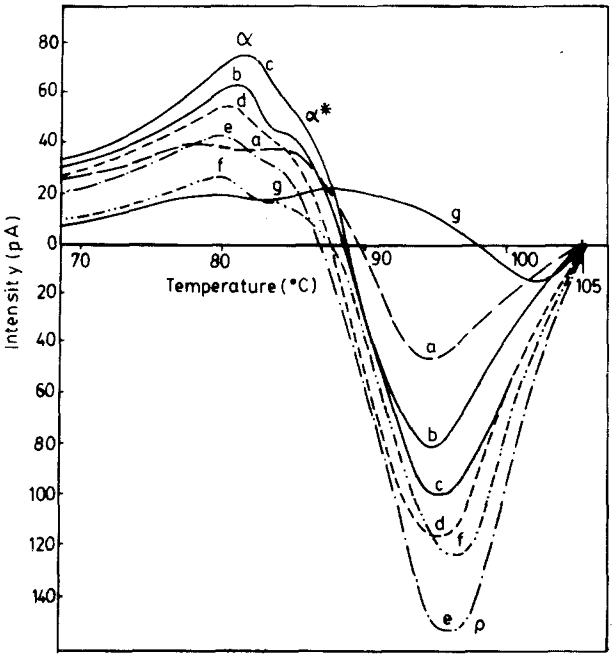

Figure 2 TSDC curves of amorphous PET isothermic electrets corona-charged at different polarization temperatures T_p; $E_p = 35\ \mathrm{kV\,cm^{-1}}$, $t_{pi} = 15$ min and $X_c \simeq 4\%$. T_p (°C): (a) 65, (b) 70, (c) 75, (d) 80, (e) 82, (f) 85, (g) 96.

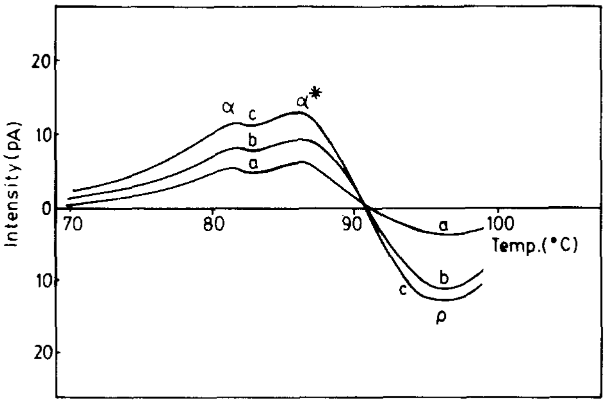

Figure 3 TSDC curves of isothermic electrets corona-charged at different polarization fields E_p; $T_p = 71.6\,^\circ C$, $t_{pi} = 30$ min and $X_c \simeq 4\%$. E_p ($\mathrm{kV\,cm^{-1}}$): (a) 24, (b) 36, (c) 48.

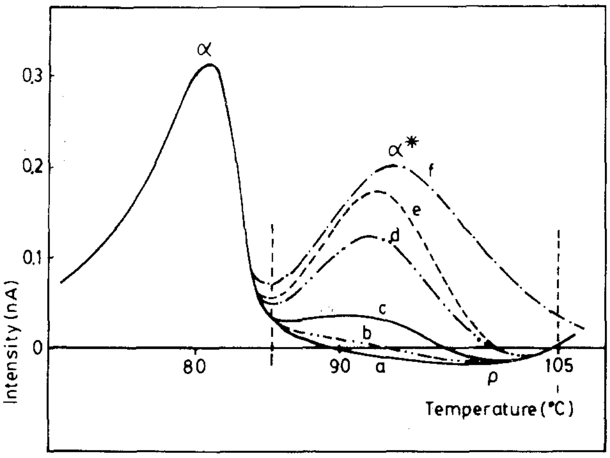

Figure 4 TSDC curves of amorphous PET conventional electrets corona-charged at different polarization temperatures T_p; $E_p = 41\ \mathrm{kV\,cm^{-1}}$, $t_{pi} = 5$ min and $X_c \simeq 4\%$. T_p (°C): (a) 70, (b) 75, (c) 80, (d) 85, (e) 90, (f) 100.

The behaviour of ρ, both in isothermic and conventional electrets (Figs 3 and 4) indicates that the value of T_p plays an important role in the trapping of the charge.

A peak cleaning technique has been used to analyse the mechanism associated with α* in the discharge of conventional electrets corona-charged at $T_p = 85\,^\circ C$ for different applied fields. This method [4] consists in heating from the lower-temperature peak (α) until a temperature T_a is reached, $T_m(\alpha) < T_a < T_m(\alpha^*)$, followed by cooling the sample again to T_f; the discharge of peak α*, which is total, is finally obtained. The results are shown in Fig. 5.

Fig. 6 shows the linearity of the stored charge $Q(\alpha^*)$ and the intensity $I(\alpha^*)$ versus the applied field E_p. Fig. 7 verifies the symmetry of the discharge current with the polarity of the electrodes. These results indicate that the α* relaxation is associated with uniform mechanism.

Since the temperature range occupied by the discharge is the same, it is evident that α* and ρ have

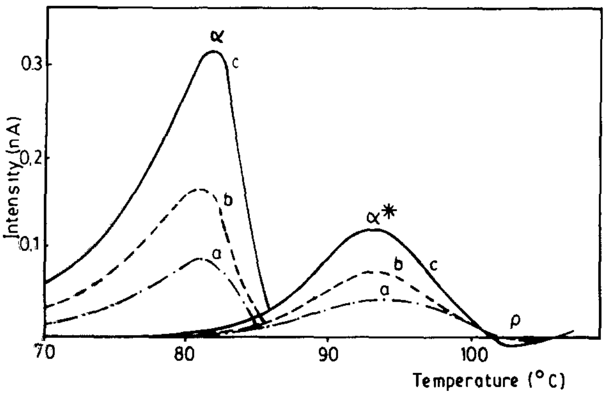

Figure 5 Peak cleaning at different polarization fields E_p in conventional electrets, corona-charged; $T_p = 85\,°C$ and $t_{pi} = 15$ min. E_p (kV cm^{-1}): (a) 9, (b) 18, (c) 31.5.

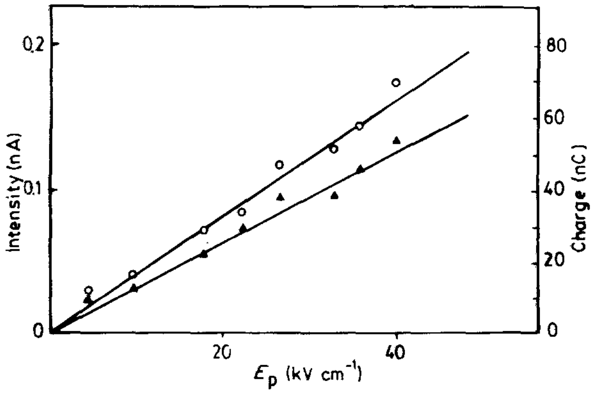

Figure 6 Plots of (▲) charge $Q(\alpha^*)$ and (○) intensity $I(\alpha^*)$ versus the polarization field E_p.

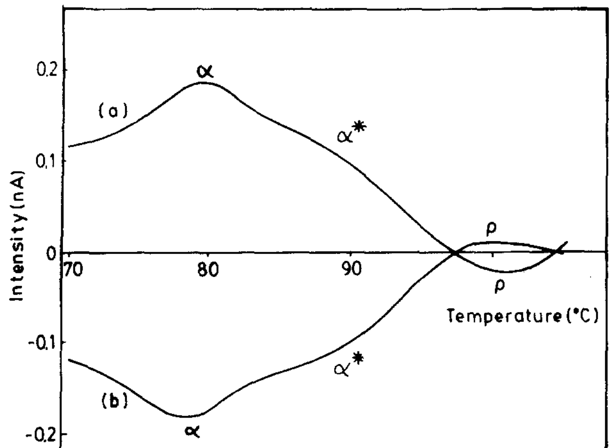

Figure 7 Effect of the polarity of the electrodes on the α, α* and ρ relaxations in conventional electrets, corona-charged; $T_p = 82\,°C$ and $t_{pi} = 15$ min. E_p (kV cm^{-1}): (a) -22.4, (b) $+22.4$.

similar activation energies and, therefore, α* is overlapped with ρ in the discharge of conventional electrets with shorted evaporated electrodes.

A total overlapping of α* and ρ leads to the conclusion that α* is not detectable in the discharges of conventional electrets with shorted evaporated electrodes; but, if the overlapping is partial, windowing polarization would perhaps be able to separate both contributions.

Fig. 8 shows the TSDC curves obtained at T_p between 70 and 80 °C for isothermic electrets of PET with a degree of crystallinity of 4–5%. For $T_p = 76\,°C$, the peaks α* and ρ are differentiated from the α relaxation. The first tends to move towards higher temperatures as T_p increases so that at 80 °C it remains overlapped with ρ. In this way and from this temperature, ρ is composed of two mechanisms: one polar and another of free charge.

On the other hand, the effect of crystallinity on the α* relaxation and its behaviour versus morphological changes of the samples (size and number of spherulites resulting from different treatments used to crystallize the amorphous samples) have been studied. Fig. 9 shows the relation between the α* relaxation and the

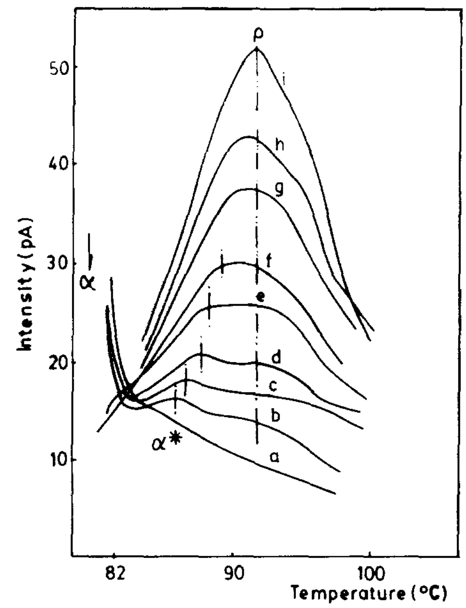

Figure 8 TSDC curves of an isothermic electret at different polarization temperatures T_p; $E_p = 70$ kV cm^{-1} and $t_{pi} = 30$ min. T_p (°C): (a) 70, (b) 75.7, (c) 76.4, (d) 77, (e) 77.8, (f) 78.4, (g) 79, (h) 79.4, (i) 80.

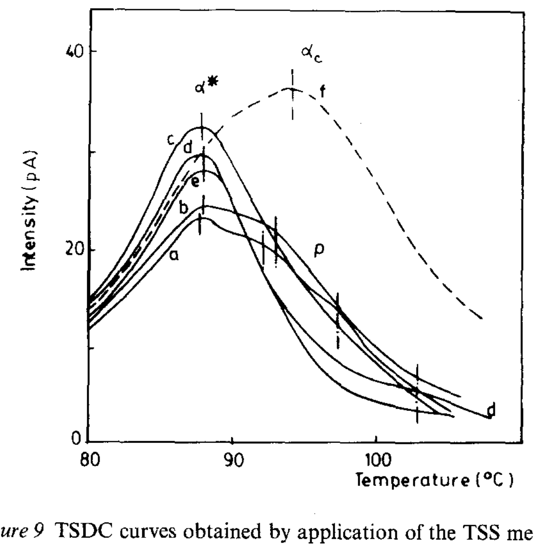

Figure 9 TSDC curves obtained by application of the TSS method to an isothermic electret; $T_p = 77\,°C$, $E_p = 70$ kV cm^{-1} and $t_{pi} = 30$ min. Final temperature of the previous discharge, T_f (°C): (a) 110, (b) 112, (c) 120, (d) 126, (e) 131. (f) Electret obtained after curve (e), polarized at $T_p = 90\,°C$ in the conventional way.

increase of the degree of crystallinity by applying the TSS method to an isothermic electret metallized on both sides. The forming conditions were $E_p = 70$ kV cm^{-1}, $t_{pi} = 30$ min and $T_p = 77$ °C, which allows the obtention of current curves with the α^* and ρ peaks sufficiently spaced and makes it possible to follow the evolution of α^* with the change of crystallinity.

In curve a of Fig. 9, the presence of the α^* and ρ relaxations, well differentiated, is evident. In curve b, α^* relaxation increases in intensity while ρ tends to displace towards higher temperatures. The discharge curve c, in which the final temperature of the previous discharge (T_f) is 120 °C, gives the maximum value of $I(\alpha^*)$. From this point the intensity of α^* decreases in the following discharges while its position does not change, and $I(\rho)$ falls while the peak is displaced to higher temperatures. In curves with $T_f > 131$ °C no changes have been observed either for α^* or for ρ, reaching X_c values of approximately 35%.

The displacement of ρ is the result of the higher thermal stability of the charges, which is strongly influenced by the degree of crystallinity. The progressive growth of α^* with T_f is related to an increase of the amorphous–crystalline interfaces as a result of the formation and initial growing of nuclei.

The fall in $I(\alpha^*)$ observed for higher values of X_c, is associated with an increase of restrictions in movement, only interlamellar movements being possible, which would originate α_c [21]. For $T_f > 131$ °C, the increase of the degree of crystallinity in the samples is very reduced and no shift is observed in the α^* peak position, which is fixed at 87 °C (Fig. 9, curve e).

It is known that for a distributed polarization, the course of the discharge current depends on the forming and storage conditions so that the values of maxima will depend on T_p. In this case, the conclusion that α^* is α_c can be easily demonstrated by conventional treatment at $T_p = 90$ °C of the crystalline sample resulting from the last experiment (Fig. 9, curve e).

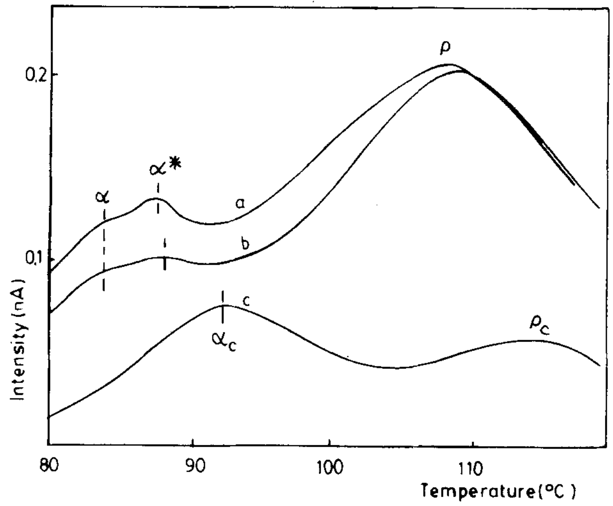

Figure 10 TSDC curves for samples crystallized in different ways. (a) Quenched and annealed 1 h at 220 °C; $T_p = 110$ °C, $t_{pi} = 1$ h, $E_p = 30$ kV cm^{-1} and $X_c = 27.9\%$. (b) Quenched and annealed 1 h at 110 °C; $T_p = 110$ °C, $t_{pi} = 1$ h, $E_p = 30$ kV cm^{-1} and $X_c = 27.4\%$. (c) Quenched and crystallized by non-isothermal method at constant heating rate (2 °C min^{-1}); $T_p = 90$ °C, $t_{pi} = 1$ h, $E_p = 20$ kV cm^{-1} and $X_c = 35\%$.

Fig. 9, curve f, shows the displacement of the α^* peak from 87 °C to 93 °C, which is the expected value of α_c for $T_p = 90$ °C in the samples of PET-c.

Fig. 10 shows the discharges of PET crystallized under several conditions to obtain different morphologies. In curves a and b, α^* is next to α and ρ although its size is related to the crystallization conditions used. In curve c, with the highest possible degree of crystallinity achievable with the treatment, only α_c is present.

These results suggest that in PET-a with $X_c \simeq 4\%$ an α^* polar relaxation exists, which in the discharge currents of shorted conventional electrets metallized on both sides is not evident, because there is overlap with the ρ relaxation. However, α^* can be attained in the discharge of corona-charged electrets as well as in the discharge of electrets with shorted evaporated electrodes by applying the windowing polarization method with T_p between 75 and 80 °C. This α^* relaxation, whose intensity and position depend on the degree of crystallinity and the morphology, evolves towards α_c on increasing the crystallinity, which is a relaxation of known polar character.

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