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Comparative study of amorphous and partially crystalline poly(ethylene-2,6-naphthalene dicarboxylate) by TSDC, DEA, DMA and DSC

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Abstract

A comparative study of the relaxational behavior of amorphous and partially crystalline poly(ethylene-2,6-naphthalene dicarboxylate) (PEN), has been carried out by thermally stimulated depolarization currents (TSDC), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and dynamic electric analysis (DEA). As received, PEN (partially crystalline) shows, in the temperature range from −150 to 200°C, four relaxations located, in increasing temperature order, around −70°C (β), 60°C (β^*), 130°C (α) and 170°C (ρ). Amorphous PEN has been crystallized thermally heating up to different temperatures between 170 and 200°C. The DSC measurements of these samples show a small endothermic premelting peak, once the crystallization of the sample is completed. This peak increases and shifts towards higher temperatures as the sample is further thermally treated. Associated with the presence of this endothermic peak, the ρ relaxation passes through a maximum and presents a sharp decrease as it is further thermally treated. The α-relaxation, detected by dynamic mechanical as well as dielectric (ac) measurements, shifts to higher temperatures and broadens as the crystallinity degree increases. The kinetic parameters of the observed relaxations have been determined fitting experimental data to standard models.

Keywords: Crystallinity; Thermostimulated depolarization current; Dynamic mechanical analysis

1. Introduction

Interest in the study of polyesters, showing high-performance physical and chemical properties, arises from growing electronics and electrical engineering demands. From this family of polymers, poly(ethylene-2,6-naphthalene dicarboxylate) (PEN), is a new aromatic polyester that differs from poly(ethylene terephthalate) (PET) in the double aromatic ring of naphthalate group instead of the single one present in PET. Its properties improve those of PET. For example, among other physical properties PEN is characterized [1–3] by a melting point of $T_m = 267$°C that is about 10°C higher than the one of PET, and a glass transition temperature $T_g = 122$°C that is 50°C higher than the one of PET [4]. This polymer, as in the case of PET, can be obtained in a state with a low crystallinity degree (≈5%) by quenching in iced water. Because of the increased stiffness of the polymer backbone, PEN exhibits superior thermal stability and better mechanical and tensile properties than other polyesters. These improved properties give response to high demanding mechanical and electrical engineering requirements, as insulating in surface mounted technology, miniaturization of capacitors or, for instance, as base film for long-playing videotapes. These applications require however a wide knowledge of the electrical relaxations that the material can undergo, and its electrical behavior in a broad spectrum of environmental conditions. In this sense, thermally stimulated currents technique [5,6] (TSDC) combined with other characterization techniques such as dielectric spectroscopy analysis (DEA), dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) represent powerful experimental tools in order to characterize the material.

The aim of the present work is to study the effect of the crystallinity degree on different electrical and mechanical relaxations present in commercial semicrystalline PEN (Kaladex) by TSDC, DSC, DMA and DEA. From the complete spectrum obtained for each high temperature relaxation, various kinetic parameters have been determined fitting the curves to the usual empirical models. The

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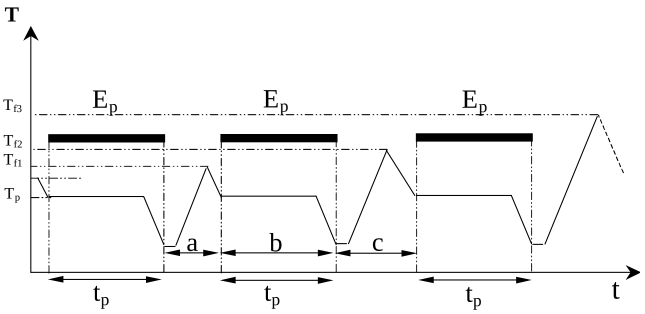

Fig. 1. Schematic representation of the electric field and temperature program developed in the TSS process: (a), (c) TSDC measurements and partial crystallization; (b) polarization.

evolution of these relaxations with the crystallinity degree of the material is analyzed in partially crystallized samples obtained from the amorphous state.

2. Experimental

Commercial PEN (Kaladex) sheets were used for the experiments. Low crystallinity degree samples were prepared quenching the molten material in water at room temperature. By this procedure mainly amorphous samples (≈5% crystallinity) are obtained and subsequently will be referred as amorphous samples. Calorimetric measurements (DSC) were performed with a Mettler TC11 thermoanalyzer equipped with a Mettler-DSC20 Differential Scanning Calorimeter module. DSC curves were obtained from 10 mg samples, sealed in aluminum pans, at 10°C/min controlled heating rate.

Depolarization current measurements (TSDC) were carried out on 130 μm thick circular samples, 2 cm diameter Al electrodes were prepared on both sides of the sheet by vacuum deposition. A Kottermann-2715 air forced circulation oven, controlled by an Eurotherm-818 programmer was used for the measurements. Temperature during annealing and measurements was measured to an accuracy of 0.1°C by Pt-100 probes located near to the sample. Current intensity measurements were performed by means of a Keitheley-610C electrometer. The full description of the TSDC experimental setup technique has been reported in previous works [7].

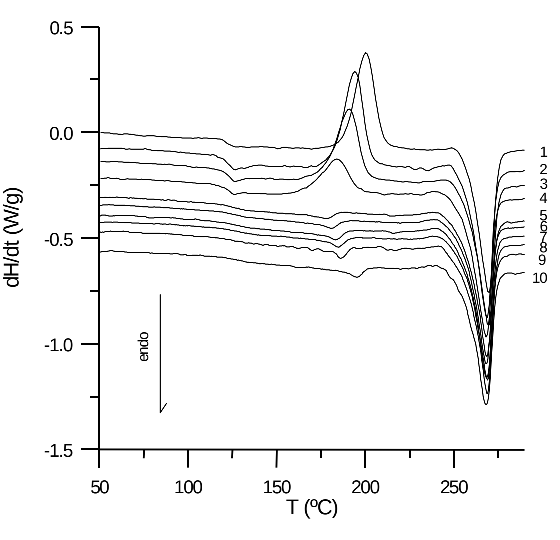

Fig. 2. DSC scans at 10°C/min for different samples of PEN treated by the TSS method (see Table 1 for details).

Dielectric measurements were performed in the frequency range from 10^1 to 10^4 Hz with a dielectric analyzer DEA 2970 from TA Instruments. The samples used were prepared in the same way as for TSDC measurements. Data were collected between −150 and 100°C at a constant heating rate of 1°C/min. From 100 to 200°C, the isothermal step method was used, in which data is collected isothermically at several frequencies, increasing the temperature at 5°C steps.

PEN samples of $0.13 \times 6.5 \times 2$ mm were investigated in a range from 0.1 to 30 Hz using a dynamic mechanical thermal analyzer DMTA-MARK II. The heating rate was 1°C/min up to 100°C. As it was done with DEA measurements, from 100 to 200°C, the isothermal step method was used, increasing the temperature at 5°C steps.

Amorphous sheets of PEN were prepared quenching the molten material in water at room temperature. Different degrees of crystallization were obtained by subsequent heating processes up to different final temperatures. This method, called *Thermal Step Stimulation* (TSS) [8,9], is represented schematically in Fig. 1. During the first heating process (section “a” of the figure) the amorphous sample is heated up to a temperature T_{f1} that produces some degree of crystallinity in the material. The partially crystallized sample is then cooled down to temperatures below T_g (section “b”) and heated up again to $T_{f2} > T_{f1}$ (section “c”), increasing further the crystallinity degree. This process is repeated to ever increasing final temperatures (T_{f3},T_{f4},…) raising gradually the crystallinity degree of the material. One interesting advantage of this method is that when the sample is at low temperatures (around T_g) it can be polarized in the usual way, and the TSDC discharge, DEA and DMA measurements can be performed during the heating ramps.

3. Results and discussion

3.1. DSC

Previous to TSDC, DEA and DMA studies, DSC measurements have been carried out from 30 to 300°C, in order to characterize the glass transition, melting point and the crystallinity degree of the material. Fig. 2 shows results obtained for samples treated by the TSS method up to different final temperatures. The glass transition, clearly observable in the scan corresponding to the amorphous sample, lies at $T_g = 125$°C approximately.

During the crystallization of the material a phase

Table 1
Calculated crystallinity degree as a function of T_f. T_{exo} and T_{endo} refer to the temperature of the maximum value of the crystallization exothermic peak and the first endothermic peak, observed by DSC

Curves	T_f (°C)	T_g (°C)	T_{exo} (°C)	T_{endo} (°C)	χ_c (%)
1	158	119.8	200.5		5.4
2	160	119.8	194.6		9
3	163	120.9	191.1		11.5
4	166	121.4	183.9		29
5	172	124.6		179.1	≈48
6	175	124.8		180.2	≈48
7	177	128.7		183.7	≈48
8	178	128.4		184.8	≈48
9	180	130.7		186.0	≈48
10	190	132.0		195.3	≈48

transformation occurs in which the polymer chains move towards a lower energy configuration. These transformations involve important heat transfer processes between sample and environment, which can be measured by DSC. If the sample is heated at a constant rate and the heat flow measured, an exothermic peak will arise whose area is directly related to the amount of crystallized polymer. The exothermic crystallization process of amorphous PEN (probably due to a cold crystallization process), can be observed in curves 1–4 located at Fig. 2 (T_f up to 166°C) at temperatures around 180°C, previous to the melting process located at 270°C approximately. Curves 5–10 (T_f from 172 to 190°C) do not show ulterior crystallization process. This indicates that these samples have already the highest crystallinity degree achievable by TSS. From the area of the crystallization exothermic and the melting endothermic peaks the crystallinity degree of each sample can be estimated and is reproduced in Table 1. For this calculations an extrapolated fusion heat for a pure PEN crystal of $\Delta H_f = 103.3$ J/g has been used. Table 1 is subsequently used to relate the final temperature of any experiment to the corresponding degree of crystallinity.

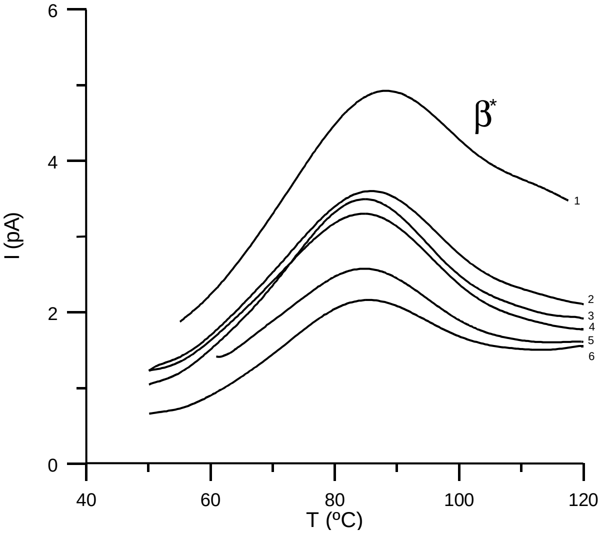

Fig. 3. TSDC scans of the β^* relaxation for samples with different crystallinity degree: (1) $T_f = 160$°C; (2) $T_f = 166$°C; (3) $T_f = 169$°C; (4) $T_f = 172$°C; (5) $T_f = 177$°C; (6) 182°C. ($T_p = 67$°C, $V_p = 1.5$ kV, $t_p = 30$ min.)

The presence of a small endothermic peak around 180°C in the highly crystalline samples can be noted in Fig. 2. This endothermic peak increases in area and shifts towards higher temperatures as T_f is increased. This behavior is related to important changes in the ρ relaxation (associated to free charge trapped in the material) as will be discussed below.

3.2. TSDC

Amorphous PEN shows, in the temperature range from 20 to 200°C, three relaxations located, in increasing temperature order, at 80°C (β^*), 130°C (α) and 150°C (ρ) [1]. It is interesting to compare these results with those obtained with a similar polymer as PET [8]. For PET only two relaxations, the α peak corresponding to the glass transition of the material and the ρ relaxation associated to free charge, are observable. The absence of the β^* peak suggests that this relaxation is probably due to the relative motion of the two naphthalene rings present in the PEN polymer chain and not present in PET.

Amorphous PEN has been crystallized to different crystallinity degrees by the TSS process. TSDC discharges of partially crystallized samples are reproduced in Fig. 3 for the β^* relaxation and in Fig. 4 for α and ρ relaxations. In these figures the plotted spectra correspond to conventionally polarized samples. The polarization temperature has to be carefully chosen in order to observe the desired relaxations. In the case of the β^* relaxation, the employed polarization temperature was 67°C, since in a previous work [1] it was found to be the optimal polarization temperature T_{po} for this relaxation. To observe simultaneously α and ρ relaxations, a polarization temperature of 130°C was used, which is located between their respective T_{po} (α: 120°C, ρ: 150°C).

It can be seen in these figures a decrease in area and in intensity of the β^* and α relaxations. This decrease is associated to the decrease of the total amorphous fraction in the sample. Somehow more interesting is the behavior of the ρ relaxation, associated to free charge detrapping in the material, that increases at the beginning (curves 1–3 of Fig. 4), decreasing afterwards as T_f is increased. In this case the maximum in intensity is observed for samples heated up to temperatures between 166 and 172°C, that are already fully crystallized. This increase must be associated to an important increase in the number of trapping centers present in the material at the end of the crystallization process. When T_f is further increased the sample stays fully crystallized but, however, the ρ relaxation decreases drastically. This behavior occurs at the same time as a small endothermic peak appears in the DSC measurements, and as this peak shifts towards higher temperatures. This evolution

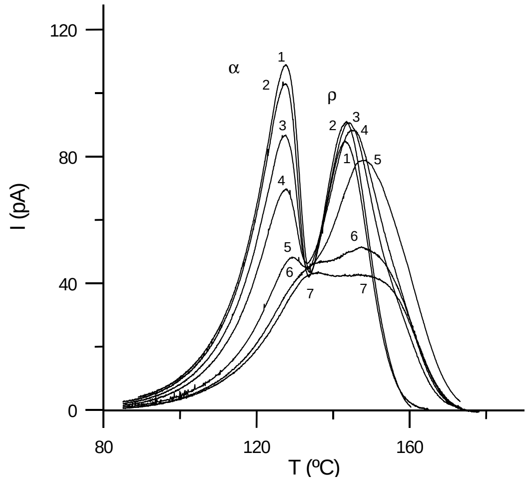

Fig. 4. TSDC scans of the α and ρ relaxations for samples with different crystallinity degree: (1) $T_f = 160$°C; (2) $T_f = 166$°C; (3) $T_f = 172$°C; (4) $T_f = 175$°C; (5) $T_f = 177$°C; (6) $T_f = 178$°C; (7) $T_f = 179$°C. ($T_p = 130$°C, $V_p = 1.5$ kV, $t_p = 30$ min.)

can be associated to the improvement of the amorphous–crystal interphases.

It can be noted, in the α and ρ relaxations, a slight shift of the temperature of the peak maximum towards higher temperatures. This behavior can be seen more clearly in Fig. 5 where the peak maximum is plotted versus the final temperature of each relaxation. In fact, the α peak is made up of contributions coming from dipoles placed in two different amorphous regions (the interspherulitic and the interlamelae regions). As shown for other polymers as PET [10], each one of these amorphous fractions has its own T_g, which is lower in the case of the interspherulitic than in the case of the interlamelae region. Therefore, a shift of the α peak towards higher temperatures can be explained in terms of an increase of the amount of the interlamelae fraction with respect to the interspherulitic one. The ρ peak also shifts to the right, due to an increase in the depth of the traps. From $T_f = 179$°C onwards it is difficult to distinguish between the α and the ρ relaxations due to the broadening of their TSDC peaks.

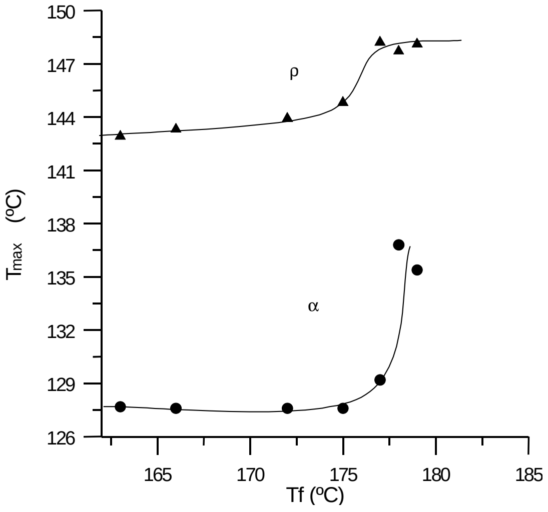

Fig. 5. Evolution of T_{max} for α and ρ relaxations versus the final temperature T_f reached in the TSS process.

3.3. DEA

In order to compare with the results obtained by TSDC, we have carried out similar DEA measurements with an initially amorphous PEN sample, crystallized by the TSS method (increasing the final temperature in steps of 10°C).

In Fig. 6 we can see the evolution of the loss permittivity at a frequency of 10^3 Hz as the final temperature of the scan increases gradually. This evolution implies an increase in the crystallinity degree according to Table 1. In the experimental range of temperatures and frequencies studied we have detected the presence of three relaxations, located at ~ -40°C (β) (not plotted), ~ 90°C (β^*) and ~ 145°C (α), however no ρ relaxation can be observed in this case. Again a decrease in the intensity of β^* and α relaxations is observed, associated to the decrease in the crystallinity degree. The temperature of the peak maximum shift as well to higher temperatures as the crystallinity degree increases, accordingly to the results obtained by TSDC.

3.4. DMA

We have reported previously [1] results obtained on amorphous PEN. This material presents three peaks in tan δ (1 Hz), located at ~ -70°C (β), ~ 60°C (β^*) and ~ 130°C (α), respectively. Moreover, at about ~ 180°C, a strong increase of E' is observed as temperature increases, which is correlated with a further small maximum in tan δ.

Fig. 7 shows the evolution of tan δ at 10 Hz for a sample of amorphous PEN heated up to progressively higher final temperatures. We can observe that the maximum in tan δ, corresponding to the dynamic glass transition at about 135°C, is not modified when the final temperature is smaller than 180°C. However, when the sample is heated to final temperatures higher than 180°C, the maximum of the α relaxation decreases, its width increases and an additional small maximum appears as a shoulder at ~ 165°C. This peak has to be attributed to the crystalline fraction of the polymer [11]. When the sample is heated at higher temperatures we cannot clearly observe this additional peak but since the width of the peak increases we can assume that these two peaks overlap. Thus, in this case, also the intensity of β^* and α relaxations decrease when the crystallinity increases. As it was done in the case of mechanical measurements, we correlate the final temperature of the scan with the crystallinity degree according to Table 1.

3.5. Kinetic parameters

The activation energies (E_a) for the dipolar relaxations (α and β^*), can be evaluated from TSDC curves assuming for

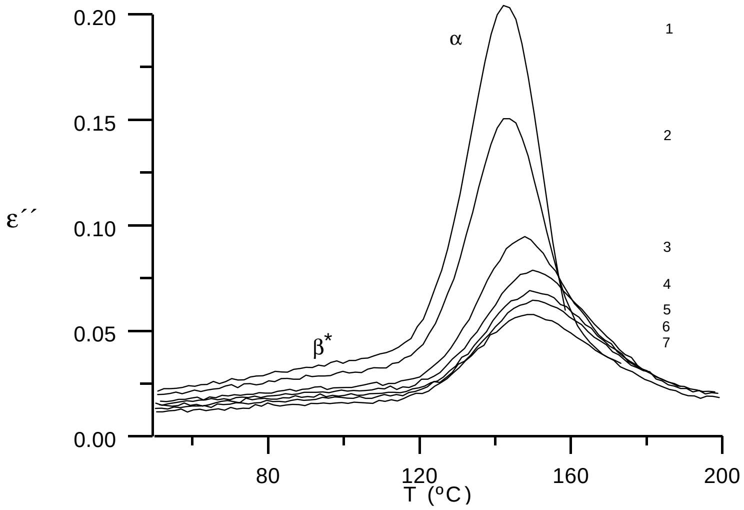

Fig. 6. Dielectric loss for PEN at 1000 Hz for samples after heated to different final temperatures: (1) $T_f = 158$°C; (2) $T_f = 173$°C; (3) $T_f = 189$°C; (4) $T_f = 198$°C; (5) $T_f = 219$°C; (6) $T_f = 228$°C; (7) $T_f = 238$°C.

the discharge process a first order kinetic model, according to the Bucci and Fieschi equation [12,13]:

$$I(t) = \frac{SP(\infty)}{\tau_0}\exp\left(-\frac{E_a}{kT}\right)\exp\left(-\frac{1}{\nu\tau_0}\int_{T_0}^{T}\exp\left(-\frac{E_a}{kT}\right)dT\right). \tag{1}$$

In this model the intensity of depolarization is expressed by Eq. (1), where S is the area of the sample, $P(\infty)$ is the equilibrium polarization, $1/\tau_0$ is the natural frequency, T the temperature, k the Boltzmann constant and v is the heating rate. Mathematical fitting of the calculated discharges to the experimental ones allows to determine some kinetic parameters of the process, such as E_a and τ_0.

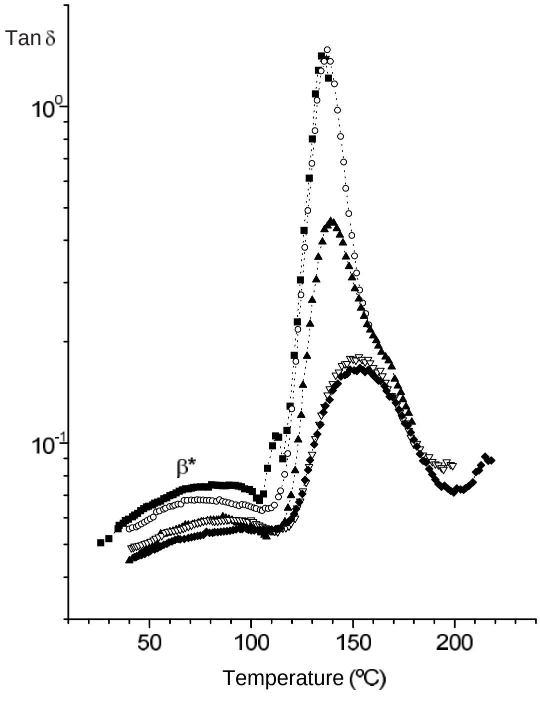

Fig. 7. tan δ for PEN at 10 Hz for samples after heated to different final temperatures: (■) 150°C; (○) 170°C; (▲) 200°C; (▽) 210°C; (◆) 240°C.

Within this model, E_a was calculated from discharges obtained for the β^* relaxation, and is reproduced in Fig. 8. We can observe a significant tendency of its value to decrease as T_f is increased. We can understand this behavior assuming that long polymer chain segments motion is restricted in the interlamelae amorphous regions, in which the polarization is mainly due to short polymer chain segments. When crystallization proceeds in the material, interlamelae amorphous regions increase respect to the interespherulitic amorphous regions, and thus the observed discharge is mainly due to short segments with lower E_a. In the case of α relaxation the value of $E_a = 1.5$ eV is approximately constant.

For the β^* relaxation, it is possible to calculate E_a from DEA measurements assuming an Arrhenius law for the relaxation time of the dipoles and the Fuoss–Kirkwood equation [14,15] for ε'':

$$\varepsilon''(T) = \frac{\frac{m}{2}(\varepsilon_s - \varepsilon_\infty)}{\cosh\left[\frac{mE_a}{R}\left(\frac{1}{T} - \frac{1}{T_{max}}\right)\right]}, \tag{2}$$

where ε_s and ε_∞ are respectively the static and optic dielectric constants, the parameter m $(0 < m < 1)$ gives account for the broadness of the relaxation and T_{max} is the temperature at which ε'' has the maximum. These parameters are frequency dependent and have to be calculated for each curve obtained at a fixed frequency.

In this way, E_a was calculated for the β^* relaxation from measurements performed with different samples (see Fig. 6), and the results are reproduced in Fig. 9. We can observe a significant tendency to decrease E_a with the crystallinity degree, as in the case of the TSDC measurements. On the

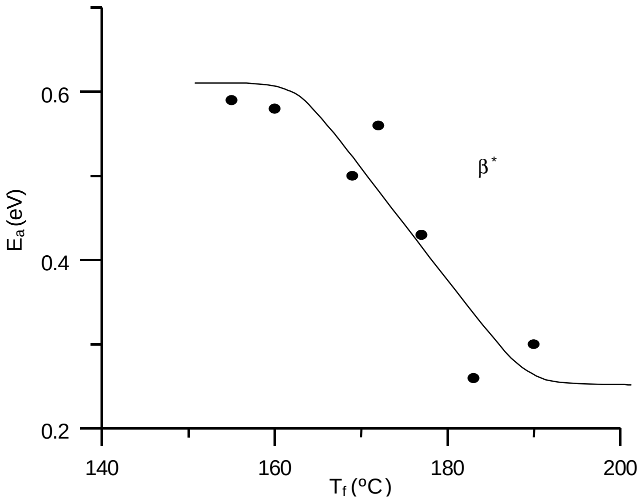

Fig. 8. Calculated activation energies versus T_f for the β^* relaxation measured by TSDC.

other hand, the parameter m increases from 0.25 for the amorphous material to 0.42 for the polymer containing the highest crystallinity degree (48%).

It is interesting to study the effect of the crystallinity degree in the value of the activation energy associated to the α process. For this reason we have represented in Fig. 10 ln *f* vs. 1/*T*. We can observe that, as the slope of the curves decreases, the value of T_f (and consequently the degree of crystallinity) increases, as it was observed in the case of the β^* relaxation.

Moreover, the effect of an increase of the degree of crystallinity on E_a is less important in the case of the α-relaxation. This result is in accordance with the TSDC analysis reported previously.

We could also carry out a similar analysis of the results obtained by DMA. However, by this technique we only have a narrow range of frequencies and this study is, therefore, not reported.

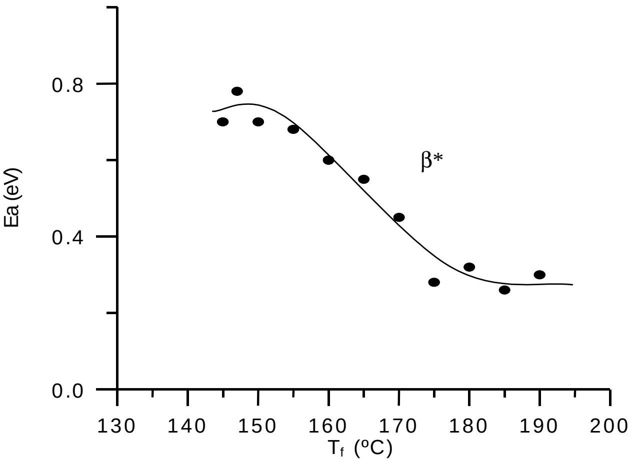

Fig. 9. Calculated activation energies versus T_f for the β^* relaxation measured by DEA.

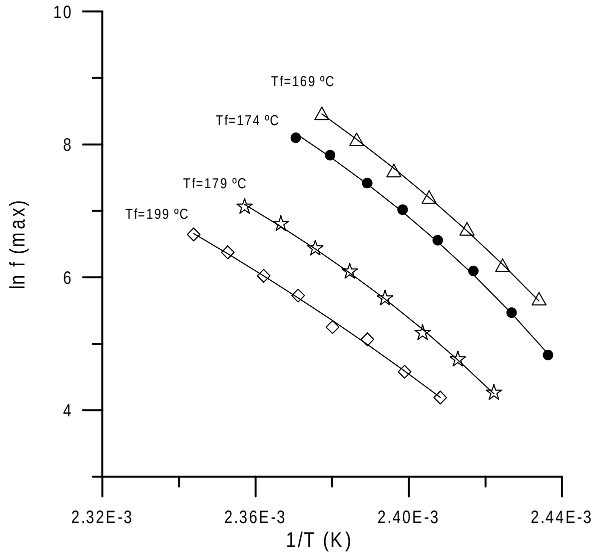

Fig. 10. α relaxation dielectric map (ln *f* versus 1/*T*) of partially crystallized PEN in the studied temperature and frequency range.

4. Conclusions

TSDC, DEA and DMA measurements of as received PEN Kaladex (R) (partially crystalline) show in the temperature range from –150°C to 200°C four relaxations located, in increasing temperature order, around −70°C(β), 60°C(β^*), 130°C(α) and 170°C(ρ). The evolution of these relaxations with the crystallinity degree of the material was investigated in samples thermally crystallized to different degrees from the amorphous state.

The β^* and α relaxations show a decrease in the peak area and intensity of the maximum as the crystallinity degree increases in the material. This behavior is explained in terms of the decrease of the total amorphous fraction present in the material, where the β^* and α relaxations are active. In the case of the α relaxation a slight shift of the peak maxima temperature towards higher values is observed when the crystallinity degree increases. This evolution is explained assuming for the partially crystallized polymer two separated amorphous zones, one between the growing spherulites and the second one between the crystalline lamellae inside the spherulites. The amorphous fraction within the spherulites presents a higher glass transition temperature than the amorphous fraction between them, resulting in the shift of the α peak.

The fit of experimental TSDC and DEA data to conventional models for the β^* peak, shows a significant tendency to decrease in E_a as the crystallinity degree increases in the material. The obtained values range in both cases from approximately 0.7 eV for the amorphous material to 0.3 eV for the fully crystallized material (≈48%). In the case of the α relaxation, the activation energy calculated from the TSDC results lies around 1.5 eV, and is approximately independent from the crystallinity degree.

The ρ relaxation, only detectable by TSDC, shows a complex evolution with an initial increase in the peak area that reaches its maximum value when the crystallization process (detected by DSC) concludes. This fact indicates an important increase in the number of trapping centers in the material while the crystallization takes place. Further thermal treatment of the sample produces a sharp decrease of the peak, at the same time as a small endothermic peak appears in DSC measurements.

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