

Relaxational study of poly(ethylene-2,6-naphthalene dicarboxylate) by t.s.d.c., d.e.a. and d.m.a.

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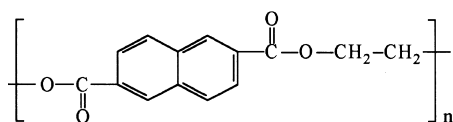
Abstract

A comparative study of the different relaxations present in poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) is carried out by thermally stimulated depolarization current (t.s.d.c.), dynamic mechanical analysis (d.m.a.) and dynamic electric analysis (d.e.a.). In the temperature range from -150 to 200°C , PEN shows four relaxations located, in increasing temperature order, around -70°C (β), 60°C (β^*), 130°C (α) and 170°C (ρ). The two sub-glass transition relaxations detected are attributed to dipolar motions of the polymer chain and their origin is discussed. Above the glass transition (α relaxation) the ρ peak is shown to be of non-dipolar origin and associated with free charge detrapping in the material. The kinetic parameters of the relaxations observed by these techniques in the aforementioned temperature range have been determined by fitting the experimental data to standard models. The activation energies calculated in this way vary from 0.5 eV for the β relaxation to 2.2 eV for the ρ relaxation. The β^* and α relaxations are distributed and it is shown that they follow the compensation law. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Relaxation; Depolarization current; Activation energies

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, poly(ethylene-2,6-naphthalene dicarboxylate) (PEN), with molecular structure



is a new aromatic polyester that differs from poly(ethylene terephthalate) (PET) in the double aromatic ring of the naphthalate group instead of the single one present in PET. The naphthalene moiety in PEN provides stiffness to the linear polymer backbone, leading to improved thermal resistance, excellent mechanical properties, such as tensile properties and dimensional stability, and outstanding gas barrier characteristics [1]. PEN has a melting point

temperature ($T_m = 267^{\circ}\text{C}$) obtained by differential scanning calorimetry (d.s.c.) that is about 10°C higher than that for PET and the glass transition temperature ($T_g = 122^{\circ}\text{C}$) is about 50°C higher than in the case of PET [2]; it is possible to obtain the material in the amorphous state by quenching from the melt at room temperature.

Because of the increased stiffness of the polymer backbone, PEN exhibits superior thermal stability, mechanical and tensile properties compared with other polyesters. These improved properties are useful in response to highly demanding mechanical and electrical engineering requirements, such as insulating in surface mounted technology, miniaturization of capacitors or as a base film for long-playing videotapes.

Thermally stimulated depolarization current (t.s.d.c.), dynamic mechanical analysis (d.m.a.) and dynamic electric analysis (d.e.a.), are complementary techniques suitable for performing a complete characterization of different relaxations present in dielectric materials. The t.s.d.c. technique allows us to detect molecular motions, associated with charge relaxations within the polarized material (electret) [3,4]. These relaxations originate from an off-equilibrium charge (bounded or free) conformation induced by the effect

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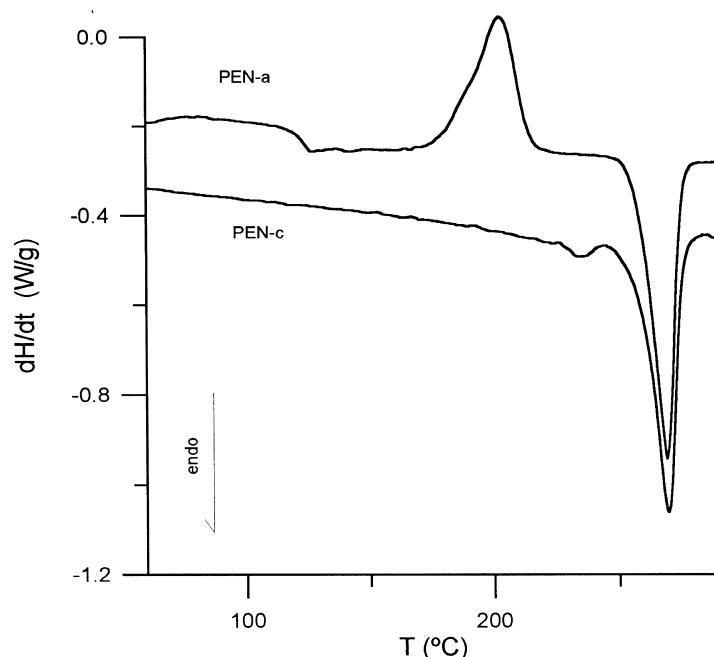


Fig. 1. D.s.c. scans of PEN film as-received (PEN-c) and after quenching at room temperature from the melt (PEN-a).

of an electric field. The subsequent heating of the sample results in a current, which is related to the charge motions tending to an equilibrium state, that is measured with a high sensitivity ammeter as a function of the temperature. Each relaxation results in a current peak in the t.s.d.c. spectrum. A more extensive description of this technique can be found in the literature [5–7].

The purpose of the present work is to make a comparative study of the different relaxations present in PEN by t.s.d.c., d.m.a. and d.e.a. in the temperature range from -150 to 200°C . The kinetic parameters of the relaxations observed by these techniques in this temperature range were determined by fitting the experimental data to standard models.

2. Experimental

D.s.c. measurements were carried out with a Mettler DSC-20 calorimeter. Amorphous PEN samples (Kaladex 1030 from Cadillac Plastics and Chem Co., USA), used in the preliminary studies, were prepared by quenching the molten film in water at room temperature. Depolarization current measurements were carried out on commercial PEN films of thickness $130\ \mu\text{m}$ from room temperature up to 180°C . Disc samples were prepared by coating Al electrodes of diameter 2 cm on both sides of the film by vacuum deposition. The experimental set-up and a full description of the t.s.d.c. technique have been reported previously [3,4]. All the measurements were carried out on samples as-received, thus some degree of crystallinity is present in them as described in Section 3. The effect of crystallinity on the relaxational behaviour of this polymer will be discussed in a following paper.

Dielectric measurements were performed at 21 experimental frequencies in the range from 10^{-1} to 10^4 Hz with a dielectric analyser DEA 2970 from TA Instruments. The samples used were films of thickness $130\ \mu\text{m}$ between gold sputtered electrodes of diameter 5 mm. The samples were coated with aluminium on both sides to improve the electric contact with the electrodes. Data were collected between -120 and 100°C at a constant heating rate of $1^{\circ}\text{C}\ \text{min}^{-1}$. From 100 to 200°C , the isothermal step method was used, in which data were collected isothermally at all the frequencies increasing the temperature in 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 analyser of type MARK II (DMTA-MARK II) in double cantilever mode. The heating rate was $1^{\circ}\text{C}\ \text{min}^{-1}$ up to 100°C . From 100 to 200°C , the isothermal step method was used, in which data were collected isothermally at several frequencies increasing the temperature in 5°C steps.

3. Results

3.1. D.s.c. results

D.s.c. measurements have been carried out from 30 to 300°C , in order to characterize the glass transition, melting point and crystallization degree of the material. Fig. 1 shows the results obtained with the as-received material as well as with the amorphous one. The glass transition, clearly observable in the scan corresponding to the amorphous sample, lies at approximately $T_g = 125^{\circ}\text{C}$ (measured at a heating rate of $10^{\circ}\text{C}\ \text{min}^{-1}$). This amorphous sample crystallizes between 160 and 220°C , preceding the fusion of the material

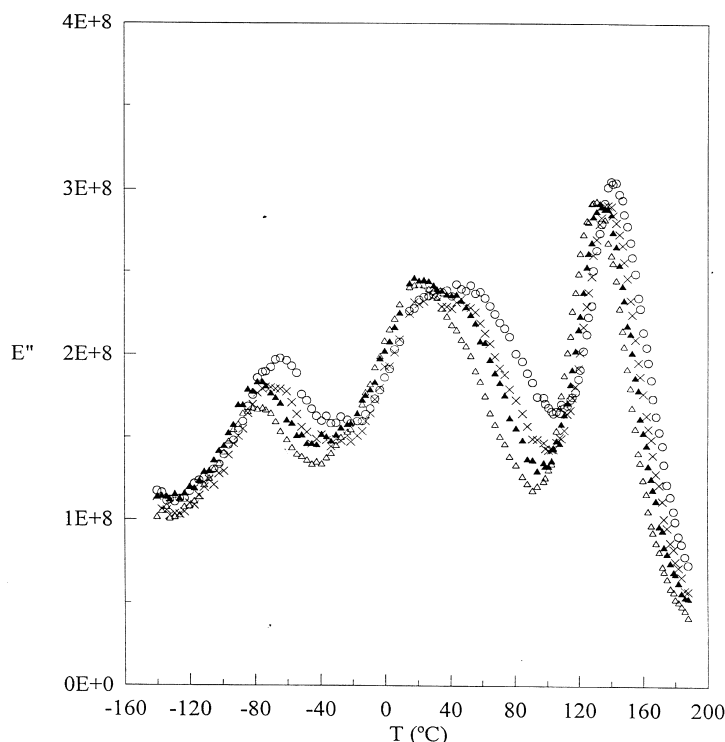


Fig. 2. Viscoelastic loss modulus E'' of as-received PEN at 0.3 (Δ), 1 (\blacktriangle), 3 (\times) and 10 (\circ) Hz as a function of temperature.

at 270°C. The scan corresponding to the as-received sample shows no crystallization peak, which indicates a high degree of crystallinity in the material. The main endothermic peak, located at 270°C, corresponds to the fusion of the crystalline phase, and is preceded by a small endothermic peak probably associated with a solid state transition in the material. According to the extrapolated heat of fusion for a pure PEN crystal ($\Delta H = 103.3 \text{ J g}^{-1}$) and the total heat flow involved in the endothermic peaks, a crystallinity degree of about 33% is estimated for the as-received material.

3.2. Mechanical results

Fig. 2 shows the loss modulus E'' of a dried sample of PEN (24 h at 80°C in vacuum) at frequencies of 0.3, 1, 3 and 10 Hz. We can observe three different relaxation peaks labelled β , β^* and α in the figure. The β relaxation is centred around -70°C at 1 Hz, the β^* relaxation presents two peaks centred around 25 and 40°C at 1 Hz, and the α relaxation peak centred around 135°C at 1 Hz, which is related to the dynamic glass transition.

3.3. Dielectric results

Fig. 3(a) and Fig. 3(b) show respectively the plot of the dielectric permittivity and the dielectric $\tan \delta$ as a function of temperature for PEN at several frequencies. Three main relaxation processes β , β^* and α are detectable by this technique in the temperature range investigated, in good

agreement with the d.m.a. results. The β peak maximum, which appears at approximately -70°C , shifts to higher temperatures with increasing frequency. The β^* peak maximum, located at approximately 60°C, also shifts to higher temperature with increasing frequency, and eventually disappears as it overlaps with the α relaxation. In the case of the lower frequencies analysed the value of the maximum dielectric loss of the α process increases considerably due to the overlapping with the conductive processes.

3.4. T.s.d.c. results

Fig. 4 shows the t.s.d.c. spectra of conventionally polarized PEN samples at $T_p = 130$ and 170°C . In these experiments the electric field is applied at the temperatures indicated for the polarization time t_p , and kept during the cooling of the sample to the initial temperature of the t.s.d.c. measurements (conventional polarization). We can see in this figure three relaxations, labelled in increasing temperature order, β^* , α and ρ . The temperatures corresponding to the maxima of each relaxation are $T_m(\beta^*) \approx 65^\circ\text{C}$, $T_m(\alpha) \approx 130^\circ\text{C}$ and $T_m(\rho) \approx 170^\circ\text{C}$, the α relaxation being related to the glass transition of this material detected by d.s.c. at 125°C .

Further characterization of these relaxations has been undertaken by t.s.d.c. measurements of samples polarized by means of the window polarization method [3], presented below. In the window polarization method the electric field is applied for a time t_p at the polarization temperature T_p , and removed when the cooling of the sample starts or after

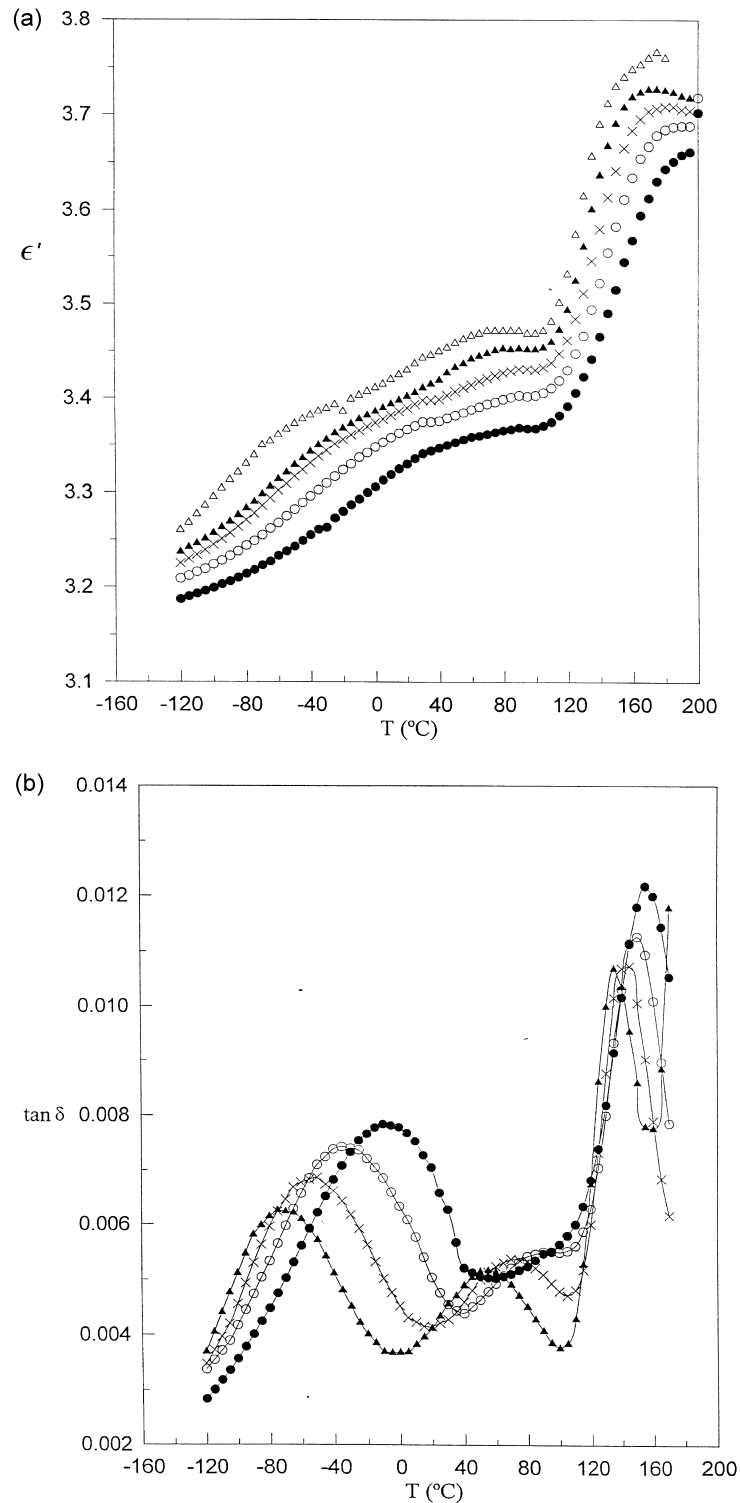


Fig. 3. (a) Dielectric permittivity ϵ' of as-received PEN at 10^{-1} (Δ), 1 (\blacktriangle), 10 (\times), 10^2 (\circ) and 10^3 (\bullet) Hz as a function of temperature. (b) Dielectric loss tangent of as-received PEN at 1 (\blacktriangle), 10 (\times), 10^2 (\circ) and 10^3 (\bullet) Hz as a function of temperature.

the sample temperature has decreased only a few degrees (window polarization width). By using this method the sample is only polarized over a narrow temperature range, and 'quasi-non-distributed' discharge peaks are obtained which are more likely to follow a single Debye process.

In our case the electric field is applied only at T_p , which is the window polarization width of 0°C .

The t.s.d.c. spectra of electrets polarized by window polarization in the temperature range corresponding to the β^* relaxation are presented in Fig. 5. We can see in this

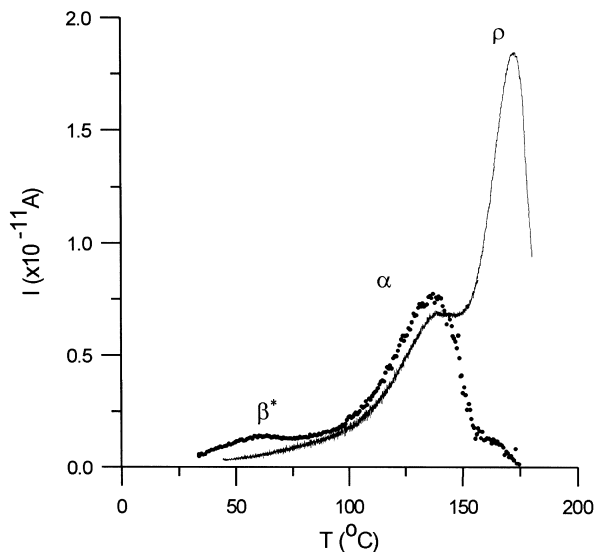


Fig. 4. T.s.d.c. scans of PEN conventionally polarized at $T_p = 130^\circ\text{C}$ (dotted curve) and $T_p = 170^\circ\text{C}$ (continuous line). Other parameters used in both cases are: $V_p = 500\text{ V}$, $t_p = 30\text{ min}$.

figure that for $T_p = 67^\circ\text{C}$, both the peak area and intensity maxima take their highest values, this temperature corresponding to the optimal polarization temperature, T_{po} . Similar measurements in the temperature ranges associated with the α and ρ relaxations are presented in Fig. 6 and Fig. 7. The same behaviour can be seen, with optimal polarization temperatures of $T_{po} = 120^\circ\text{C}$ and $T_{po} = 150^\circ\text{C}$ for the α and ρ relaxations respectively.

4. Discussion

Four relaxations have been detected for PEN by the different techniques used, in the temperature range from -140

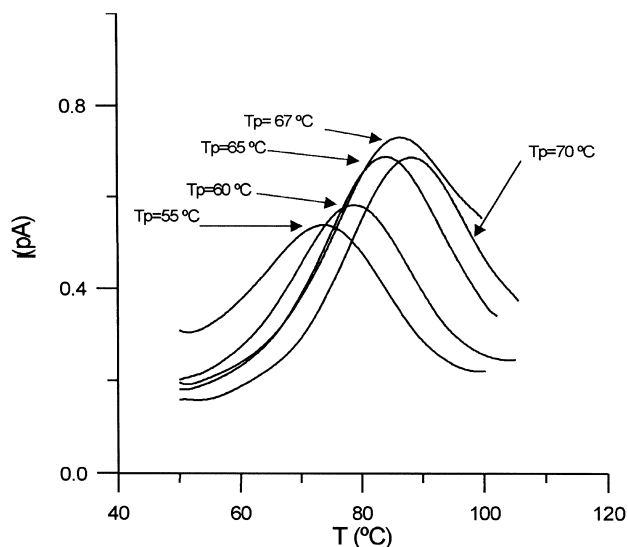


Fig. 5. β^* relaxation spectrum resolved by window polarization. Polarization parameters: $V_p = 1000\text{ V}$, $t_p = 15\text{ min}$, window width 0°C , T_p indicated in the figure.

Table 1

The values of m and ω_{\max} for different temperatures

T ($^\circ\text{C}$)	m	ω_{\max}
-55	0.159	1578
-60	0.145	1117
-65	0.141	658
-70	0.130	353
-75	0.126	125

to 150°C , labelled β , β^* , α and ρ in the different figures (the last one is only observed by t.s.d.c.). The sub-glass β relaxation, detected by mechanical [8] and dielectric [9] measurements, is located around -70°C at 10 Hz (Fig. 8) and it is known to reflect the motion of the $-\text{COO}-$ side groups. As usual, dielectric data can be fitted to different empirical equations. In the present study, we have fitted the dielectric experimental data obtained to the Fuoss–Kirkwood (F–K) [10] equation given by

$$\varepsilon''(f) = \varepsilon''_{\max} \operatorname{sech} \left(m \ln \frac{f_{\max}}{f} \right) \quad (1)$$

where f_{\max} is the frequency at the maximum peak and m is an empirical parameter that increases as the broadening of the relaxation decreases.

By plotting $\cosh^{-1}(\varepsilon''_{\max}/\varepsilon'')$ versus $\ln f$, the values of m at different temperatures were obtained. Fig. 9 shows, as an example, the experimental data of ε'' versus $\log \omega$ ($\omega = 2\pi f$) at -60°C and the fit to the F–K model ($m = 0.145$). The values obtained at other temperatures are summarized in Table 1.

The second sub-glass relaxation β^* is detected by all the techniques used in this work. This relaxation, whose maximum is located around 60°C at 10 Hz in dielectric and t.s.d.c. measurements, shows two peaks centred around 25 and 40°C at 1 Hz in the mechanical loss curve. The fact that this relaxation is not present in PET suggests that this relaxation is probably due to the relative motion of the two naphthalene rings present in the polymer chain. The double peak observed for the β^* process in these mechanical measurements can be related to the two possible conformations in PEN, *trans* and *cis*, of the naphthalene and the two ester links [11].

The α relaxation, located around 130°C in the experimental data obtained by all the techniques, corresponds to the transition detected by d.s.c.. This relaxation is thus associated with the glass transition of the material, involving long-range cooperative segmental motions.

Finally, above the glass transition, the α dipolar relaxation seems to overlap at low frequencies with conductive processes. In these conditions, this process can be conveniently studied by t.s.d.c. In Fig. 4 we can see that this peak, labelled ρ , whose maximum is located at 170°C , should be related to free charge detrapping in the material. To verify this point we have carried out several measurements, polarizing the sample in the window polarization method at

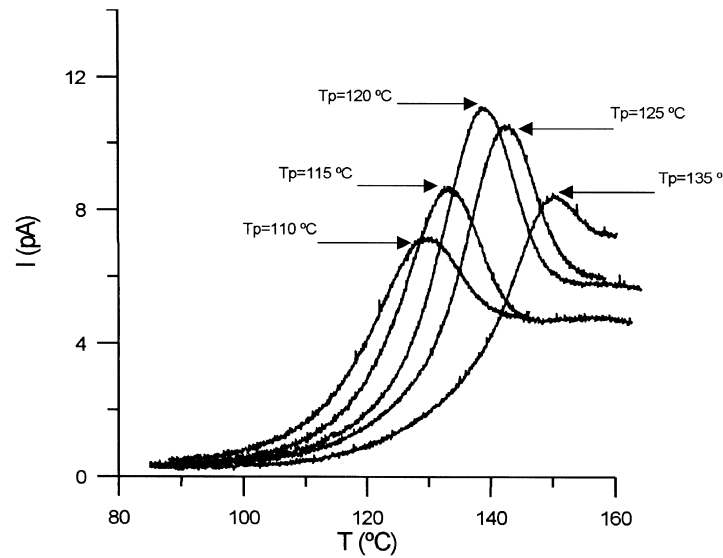


Fig. 6. α relaxation spectrum resolved by window polarization. Polarization parameters: $V_p = 1000$ V, $t_p = 15$ min, window width 0°C , T_p indicated in the figure.

150°C with different applied fields. These curves, presented in Fig. 10, show clearly that there is no linear dependence between the applied field and the peak area which confirms the aforementioned assumption.

4.1. Activation energies

The plot of the logarithm of the observed f_{\max} (frequency

at the maximum of dielectric loss) values as a function of the inverse temperature for each relaxation process (Fig. 11) allow us to evaluate the activation energies from the dielectric results. In the case of sub-glass relaxation processes β and β^* , the temperature dependence of the frequency usually fulfils the Arrhenius equation:

$$\ln f = \ln f_0 - \frac{E_a}{RT} \quad (2)$$

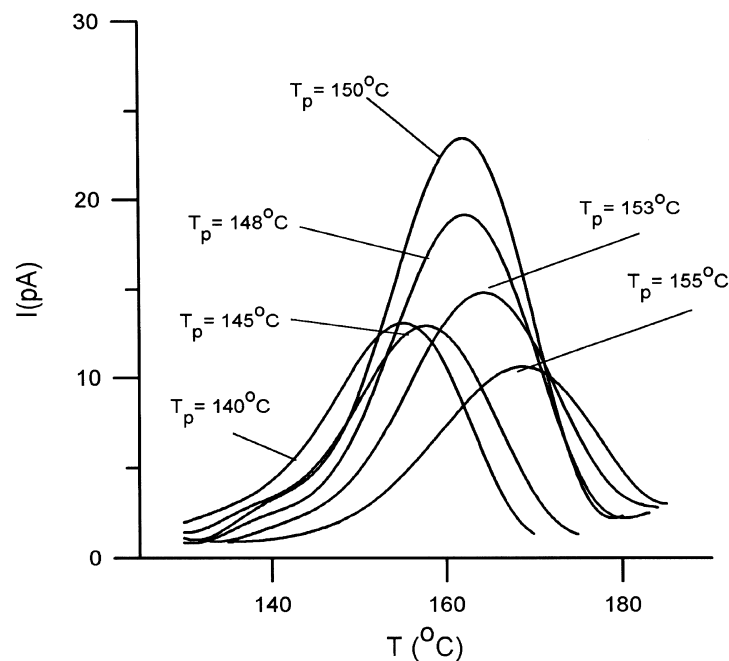


Fig. 7. ρ relaxation spectrum resolved by window polarization. Polarization parameters: $V_p = 1000$ V, $t_p = 15$ min, window width 0°C , T_p indicated in the figure.

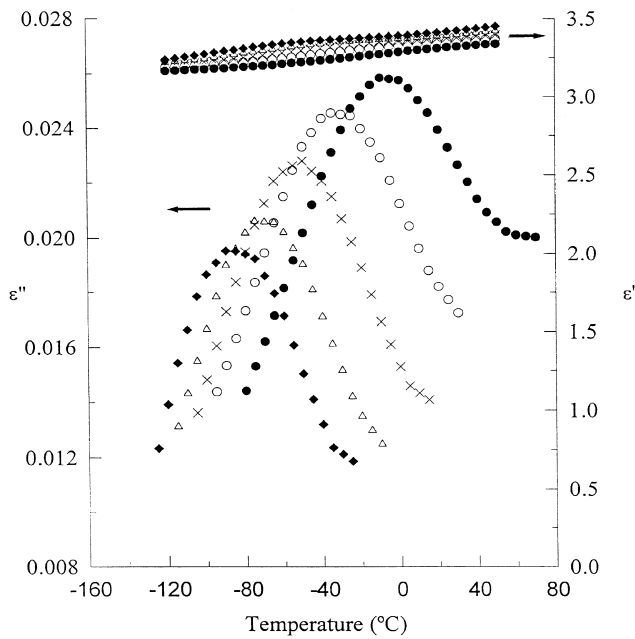


Fig. 8. Dielectric permittivity and loss for β relaxation of PEN as a function of temperature at 1 (\blacklozenge), 10 (Δ), 10^2 (\times), 10^3 (\circ) and 10^4 (\bullet) Hz of PEN.

By fitting straight lines to the experimental points representing the β and β^* processes, the activation energies were obtained from the slopes of these lines. The results are represented in Table 2. The data show, within the experimental error, an increase of the values of E_a from 0.50 eV for the β process (in good agreement with the value of the corresponding relaxation of polyethylene terephthalate (PET) [12]) to 1.09 for the β^* relaxation.

In the case of the α process the temperature dependence of the frequency in dielectric measurements usually fulfils the empirical Vogel–Fulcher equation:

$$\ln f_{\max} = A - \frac{B}{T - T_{\infty}} \quad (3)$$

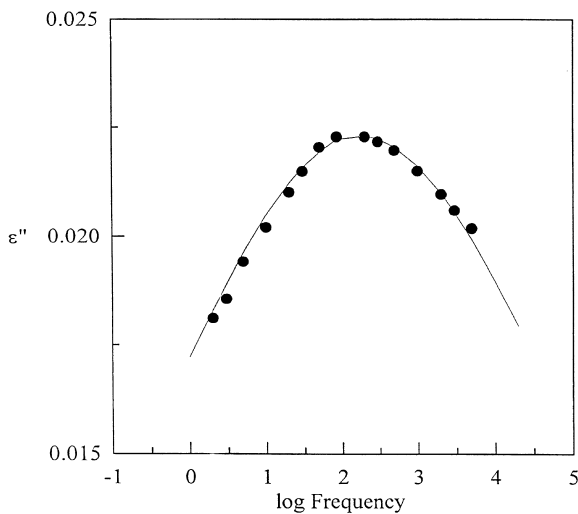


Fig. 9. Dielectric loss for β relaxation at -60°C : (\bullet) experimental, (—) fit to the Fuoss–Kirkwood equation.

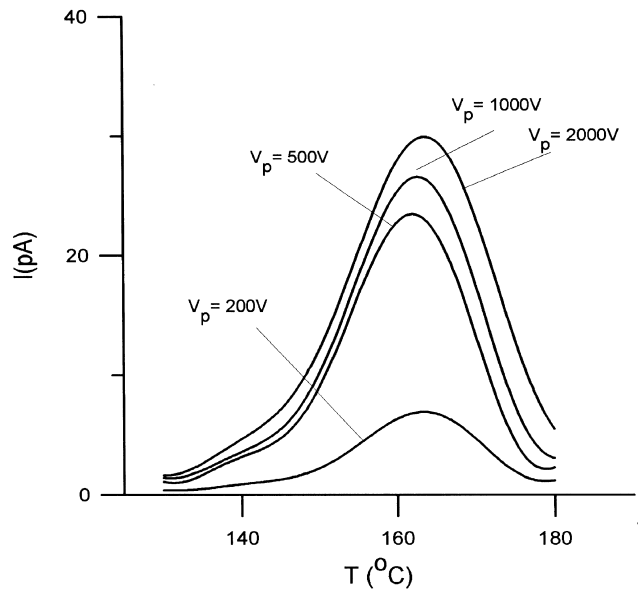


Fig. 10. T.s.d.c. scan of the ρ relaxation obtained with different polarizing fields. Polarization parameters: $T_p = 150^\circ\text{C}$, $t_p = 30$ min, window width 0°C , V_p indicated in the figure.

where A , B and T_{∞} are characteristic constants for the system. T_{∞} must be about 50°C lower than the glass transition temperature T_g . The experimental points corresponding to the α transition in Fig. 11 have been fitted by the Vogel–Fulcher equation. The results are shown as solid lines in Fig. 11. The corresponding parameters A , B and T_{∞} are presented in Table 2.

In order to obtain the activation energies and other kinetic parameters associated with these relaxations from the t.s.d.c. results, we have modelled the discharge processes following conventional theories [13].

For the β and α relaxations a first-order kinetic model, proposed by Bucci and Fieschi [14], has been used to evaluate the intensity of depolarization current given by Eq. (4), where S is the area of the sample and P is the

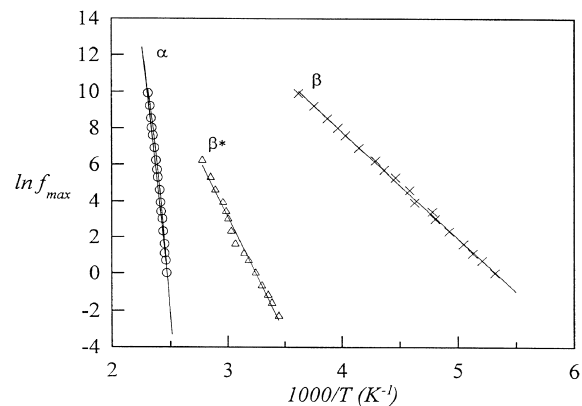


Fig. 11. Arrhenius plot for the dielectric loss maxima: α (\circ), β^* (Δ) and β (\times). The solid line for the α process represents the best fit according to the Vogel–Fulcher equation.

Table 2

Activation energy E_a calculated from the Arrhenius equation for the β and β^* relaxations and fitting parameters corresponding to the Vogel–Fulcher equation for the α relaxation (dielectric measurements)

Relaxation	A_α	B_α	$T_{\infty\alpha}$ (K)	E_a (eV)
β	–	–	–	0.50
β^*	–	–	–	1.09
α	36.64	2500.7	333	–

induced polarization.

$$I(t) = S \frac{dP}{dt} \quad (4)$$

In this model the intensity of the depolarization is obtained assuming for dP/dt a first-order linear dependence on P (see Eq. (5a)) where τ is the relaxation time of the process. For this relaxation time, Arrhenius behaviour is assumed (see (Eq. (5b)) E_a being the activation energy of the relaxation, T the temperature and τ_0 a pre-exponential factor.

$$\frac{dP}{dt} = \frac{P}{\tau} \quad (5a)$$

$$\tau = \tau_0 \exp \frac{E_a}{kT} \quad (5b)$$

The values of E_a and τ_0 were obtained by fitting the experimental t.s.d.c. data to the Bucci and Fieschi equation (Eq. (4)). Fig. 12 shows the calculated discharge (symbols) superimposed on the experimental data (continuous line) for the β^* and α relaxations obtained at $T_p = T_{po}$. There is remarkably good agreement between theory and experiment in both cases. Table 3 and Table 4 summarizes the calculated values obtained for these relaxations on the different

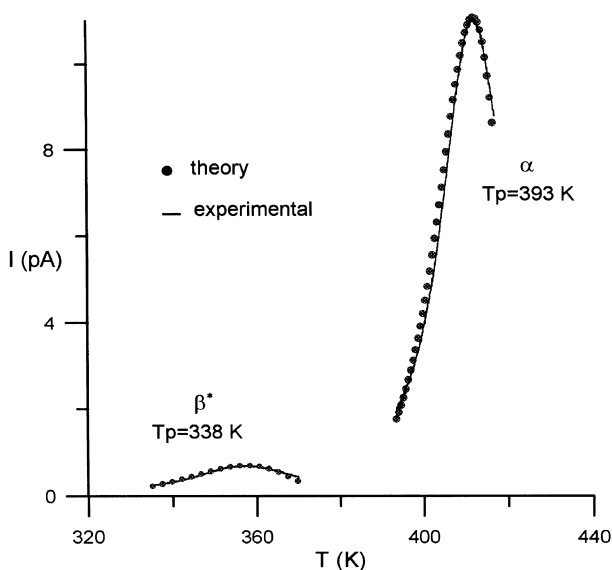


Fig. 12. Calculated (dotted curve) and experimental (continuous line) t.s.d.c. discharge corresponding to the β^* and α relaxations. Polarization parameters: $V_p = 500$ V, $t_p = 30$ min, window width 0°C , T_p indicated in the figure.

Table 3

Calculated parameters for the β^* relaxation

T_p ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	I_m (pA)	E (eV)	τ (s)	Q (pC)
55	72.5	0.559	0.60	7.9×10^{-7}	5.20
60	78.0	0.597	0.63	3.7×10^{-7}	7.74
65	84.0	0.701	0.76	6.7×10^{-9}	8.67
67	86.0	0.742	0.84	5.3×10^{-10}	5.04
70	89.5	0.702	0.92	4.3×10^{-11}	8.11

spectra (see Figs 5 and 6). These results show a slight distribution in the activation energy, increasing in both cases as the polarization temperature increases. Representative values obtained in each case are $E_a = 0.84$ eV and $E_a = 2.06$ eV for the β^* and α relaxations respectively. In spite of the good agreement between the values obtained for the β^* relaxation by t.s.d.c. and those from dielectric measurements, the former are slightly higher than the latter.

The broad range of the values of the pre-exponential factor (τ_0) obtained in each relaxation and the activation energies observed, follow the phenomenological ‘compensation law equation’ [8], according to:

$$\tau = \tau_c \exp \left[\left(\frac{E}{k} \right) \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (6)$$

where two new parameters, T_0 (compensation temperature) and τ_c (compensation time), are introduced. According to this equation in combination with Eq. (5b), the plot of $\ln(\tau_0)$ versus E should correspond to a straight line of slope $1/kT_0$. Fig. 13 reproduces this representation where in fact two straight lines appear.

The ρ relaxation, associated with space charge relaxation within the material as discussed above, can be modelled from the t.s.d.c. results assuming a kinetic phenomenological equation [4]

$$I(t) = - \frac{dn}{dt} = n^b s'_0 \exp \left(\frac{-E}{kT} \right) \quad (7)$$

where n is the trapped charge at this instant, b is the kinetic order of the process, s'_0 is a pre-exponential factor and E_a is the energy of the trapping. Fig. 14 shows the calculated discharge, for the ρ relaxation obtained at $T_p = T_{po}$, superimposed on the experimental data (represented by the continuous plot). There is also remarkably good agreement obtained between the calculated and experimental curves.

Table 5 summarizes the calculated values for this relaxation (ρ relaxation) obtained from the different spectra (see

Table 4

Calculated parameters for the α relaxation

T_p ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	I_m (pA)	E (eV)	τ (s)
110	130.5	7.18	1.59	3.09×10^{-18}
115	133.5	8.71	1.98	5.40×10^{-23}
120	138.5	11.1	2.06	1.13×10^{-23}
125	143.0	10.6	2.25	7.35×10^{-26}
135	150.0	8.50	2.35	1.52×10^{-26}

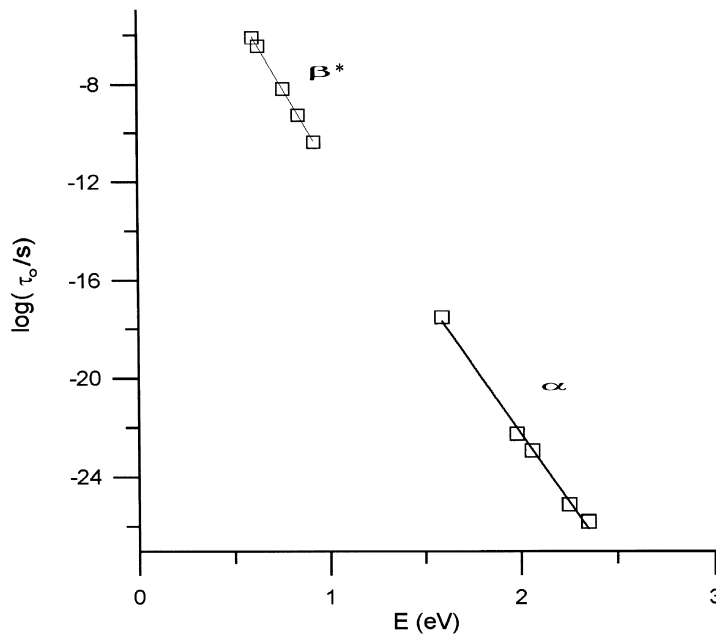


Fig. 13. Representation of $\log(\tau)$ versus E for the calculated values corresponding to the β^* and α relaxations.

Fig. 5). These results show a smooth distribution of the activation energy, with a mean value of $E_a = 2.2$ eV. The initial trapped charge, n_o , shows a maximum at $T_p = T_{po}$ as expected, and the mean value of the b parameter is $b \approx 1.3$ indicating the predominance of a recombination mechanism in this relaxation.

Table 6 reproduces the calculated values obtained in the modelling of the t.s.d.c. curves corresponding to the ρ relaxation obtained with different polarizing fields at $T_p = T_{po}$ (see Fig. 10). Similar values of the kinetic parameters E_a and b are obtained in this case. The value of n_o increases with the applied field as expected.

Table 5
Calculated parameters for the ρ relaxation

T_p (°C)	I_m (pA)	T_m (°C)	n_o (pC)	s_o (Hz)	E (eV)	b
145	12.94	158.5	7149	1.63×10^{20}	1.93	1.1
148	19.84	162.0	10314	7.64×10^{25}	2.43	1.5
150	23.77	163.5	12134	2.17×10^{22}	2.13	1.1
153	15.15	165.0	8424	3.04×10^{23}	2.24	1.4
155	16.42	164.0	9035	3.31×10^{24}	2.32	1.5
158	10.43	169.5	6820	1.00×10^{20}	1.96	1.3

Table 6
Calculated parameters for the ρ relaxation with different polarizing fields

V_p (V)	n_o (pC)	s_o (Hz)	E (eV)	b
200	3561	6.92×10^{27}	2.60	1.5
500	12134	2.17×10^{22}	2.13	1.1
1000	14518	3.73×10^{22}	2.15	1.1
2000	18506	3.78×10^{22}	2.15	1.5

5. Conclusions

Four relaxations $\beta(T_m = -70^\circ\text{C})$, $\beta^*(T_m = 60^\circ\text{C})$, $\alpha(T_m = 130^\circ\text{C})$ and $\rho(T_m = 170^\circ\text{C})$ have been detected in PEN by d.m.a., d.e.a. and t.s.d.c., and the origin of each relaxation has been discussed. Several kinetic parameters have been obtained by fitting the experimental data to conventional models.

For the β relaxation the Fuoss–Kirkwood model has been

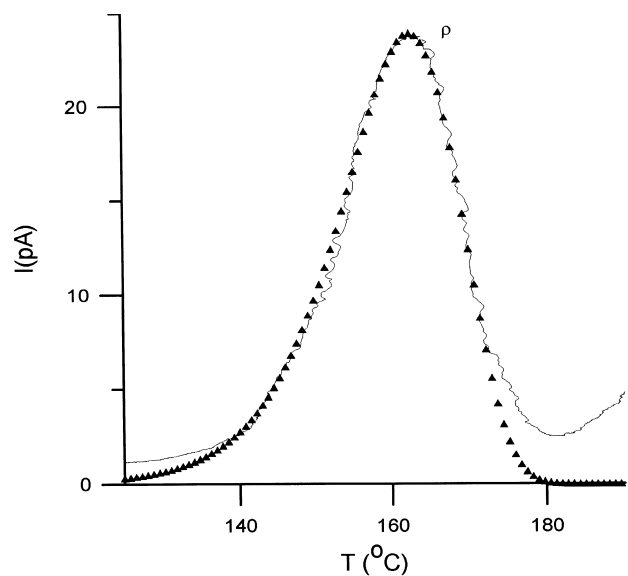


Fig. 14. Calculated (dotted curve) and experimental (continuous line) t.s.d.c. discharge corresponding to the ρ relaxation. Polarization parameters: $V_p = 500$ V, $t_p = 30$ min, window width 0°C , $T_p = 150^\circ\text{C}$.

used to fit experimental data obtained by d.e.a., and the values of the m parameter were obtained at different temperatures.

In the case of the β^* and α relaxations, d.e.a. data have been analysed according to the Arrhenius and Vogel–Fulcher equations respectively. t.s.d.c. data was modelled by the Bucci–Fieschi equation. The results obtained in both cases are in good agreement, with similar activation energies values for the β^* relaxation: $\beta^*(\text{d.e.a.}) = 1.09 \text{ eV}$; $\beta^*(\text{t.s.d.c.}) = 0.92 \text{ eV}$, $T_p = 70^\circ\text{C}$.

The Bucci–Fieschi equation applied to the t.s.d.c. results obtained by window polarization in the range of temperatures of the β^* and α relaxations show that the fit obtained through this theoretical model is reasonably good for the β^* peak. However, the model diverges in the case of the α relaxation for temperatures above the maximum of the peak. This is attributed to the relation between the α peak and the glass transition of the material, as well as to the superposition of the α peak and the ρ peak at high temperatures. The results also show that the value of E_a progressively increases with increasing polarization temperature, from 0.6 to 0.92 eV in the case of β^* and from 1.59 to 2.35 eV in the case of the α relaxation. The maximum of the peaks shift to higher temperature as T_p is increased indicating that the β^* and α relaxations are distributed. These results are shown to follow the compensation law.

The ρ peak associated with the charge trapped in the

material is only detected by the t.s.d.c. technique and the results have been fitted to a general kinetics order model. In this case the value of E_a shows a smooth distribution with a mean value of 2.1 eV.

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