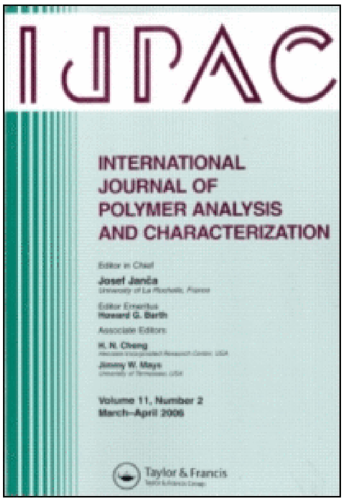

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Berdous, S. , Saidi-Amroun, N. , Saidi, M. and Bendaoud, M.(2008) 'Influence of External Stress on Dielectric Behavior of PEN', International Journal of Polymer Analysis and Characterization, 13: 6, 428 — 440
To link to this Article: DOI: 10.1080/10236660802401170
URL: http://dx.doi.org/10.1080/10236660802401170

International Journal of Polymer Anal. Charact., 13: 428–440, 2008
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ISSN: 1023-666X print
DOI: 10.1080/10236660802401170

Influence of External Stress on Dielectric Behavior of PEN

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Abstract: Polymers find an important field of application in the electrical industry because of their utilization as insulators and dielectrics. The presence of polarizable units in materials may be an advantage or a drawback. Thus, it is important to know the mechanism of loss and its evolution as a function of different types of stress. An experimental investigation has been carried out on poly(ethylene naphthalene-2,6-dicarboxylate) (PEN), which is increasingly replacing some dielectrics such as polypropylene and polyethylene terephthalate, to determine the changes in dielectric properties as a function of temperature and electric field. Dielectric loss values have been determined in the 10^{-5} to 10^{0} Hz frequency range.

Keywords: Dielectric loss; Electrical conduction; Frequency response; PEN film

INTRODUCTION

Poly(ethylenenaphthalene-2,6-dicarboxylate) (PEN) is a polymer obtained by polycondensation of naphthalene-2,6-dicarboxylic acid and ethylene glycol.[1]

The new family of polycondensates containing naphthalene groups in the repeat structure shows good promise to fill the need for higher

Submitted 17 July 2008; accepted 11 August 2008.
Du Pont de Nemours is thanked for providing us with PEN samples.

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thermal and mechanical performance. This class of polymers includes polyethylene terephthalate (PET), poly(p-phenylene sulfide), poly(ether ether ketone), and poly(ether ketone). Because of the stiffness of the polymer backbone this class of polymers, which includes PEN, they can be formed into amorphous glasses by rapid quenching from the melt and can be crystallized by stress or thermal effects or combination of both.

In the domain of electronics and electrical engineering, PEN is a new aromatic polyester of the same chemicals as PET, from which it differs only by its double aromatic naphthalate ring, instead of the single phenyl group in PET. PEN has been developed as a dielectric material in film form because of its better thermal characteristics[2,3] and ability to withstand radiation, compared to PET and other polymeric dielectrics used in dielectric film fabrication, e.g., polypropylene (PP), as well as the possibility of obtaining films as thin as $<0,9\,\mathrm{mm}$,[4] thereby giving a response to the very demanding requirements of electrical engineering like the thermal stress in surface-mounted technology,[5] the demand for longer lifetime for electrical devices, and finally the miniaturization of capacitors. The same high-temperature properties allow the use of PEN for a variety of applications like flexible printed circuit boards where it is subjected to high temperature during soldering operations.

The reliability of this equipment is strongly related to the morphological characteristics of materials used and the stresses applied. The aim of this work is to present some dielectric properties obtained for PEN film from measurements of charging and discharging currents.

It is generally observed that the charging current flowing through a polymer film by application of a step voltage decays with time until a steady state is achieved, and it follows approximately the empirical law, $I_{ch}(t) \alpha\, t^{-1}$, where l is a constant characteristic of the material, often observed to be close to unity; this is the well-known Curie-Von Schweidler relationship (referred to later as the Curie law, for simplicity). A reverse transient discharging current (or resorption current) is also observed after the removal of the field and obeys the Curie law t^{-n}, where n is similar to l. There are numerous interpretations of these currents in the literature. However, the most important mechanisms that have been proposed are dipolar relaxation (with distribution of relaxation times), charge injection forming trapped space charge, tunneling, hopping of charge carriers, and electrode polarization.[6–11]

PRELIMINARY DISCUSSION

The permittivity ε_r or relative permittivity of a material is defined as the ratio of the capacitance of a capacitor whose reinforcements are separated by the dielectric and the capacity with vacuum from the same condenser. The reason is that the dielectric contains polar units that already exist in the material or that are likely to be created under the action of an electric field. If the electric field is alternating, the permittivity will not be the same one according to whether the polarizable units have or do not have a time to be directed in the direction of the field. Indeed, when the frequency of the field increases, we note around certain particular values of frequency f_{mi} the reductions in ε_r' owing to the fact that the polarizable units of a certain type cannot follow the electric field any more.

For these frequencies there is a phenomenon of resonance, and the frequency of the field is equal to the natural frequency of vibration of the polarizable units of the type in question. It follows from there a maximum exchange of energy between the electric field and the medium, the effect of which is to cause a heating of material when the dielectric loss is important. This is represented by the imaginary part of the complex permittivity, or factor of loss ε_r'', which presents the maximum at the frequencies considered.

If the response to a voltage is linear, we can pass to the frequential response by applying the Hamon approximation[12] to the resorption (discharging) current:

$$\varepsilon_r''(\omega) - \frac{\sigma}{\omega\varepsilon_0} = \frac{I(t)}{C_0 V_0 \omega} \tag{1}$$

with

$$t = \frac{0{,}63}{\omega} = \frac{0{,}1}{f}$$

where $\varepsilon_r''(\omega)$ is the loss factor, σ is the conductivity, ω is the pulsation of the applied field, ε_0 is the permittivity of the vacuum, C_0 is the capacity of the air between electrodes, V_0 is the applied voltage, and $I(t)$ is the resorption current.

EXPERIMENTAL PROCEDURE

The semicrystalline PEN sample, 25×10^{-6} m thick, was provided by DuPont de Nemours (Luxembourg). The film was obtained by biaxial orientation and prepared with aluminium evaporated electrodes, 1 cm in diameter, on both sides of the sample. The experimental apparatus used in our work and the measurement procedure are described elsewhere.[13,14] The PEN was examined over the temperature range 100°–180°C in electric field from 24×10^6 V/m to 72×10^6 V/m. The discharging current was measured for period of up 1×10^4 s.

RESULTS AND DISCUSSION

Discharging Current Transients

Figure 1 shows the resorption currents as a function of temperature, below and above glass transition temperature $T_g = 128°C$, obtained by measuring the short circuit current after DC voltage removal.

In the temperature range of 100°–130°C, the current decreases monotonously with time over several orders of magnitude following the Curie law, while at temperatures of 140°–180°C, the current decreases but can be divided in two domains with different exponents of the Curie law. This dependence of discharging currents is observed for different values of electric field. For instance, Figure 2 shows the resorption currents at 64×10^6 V/m.

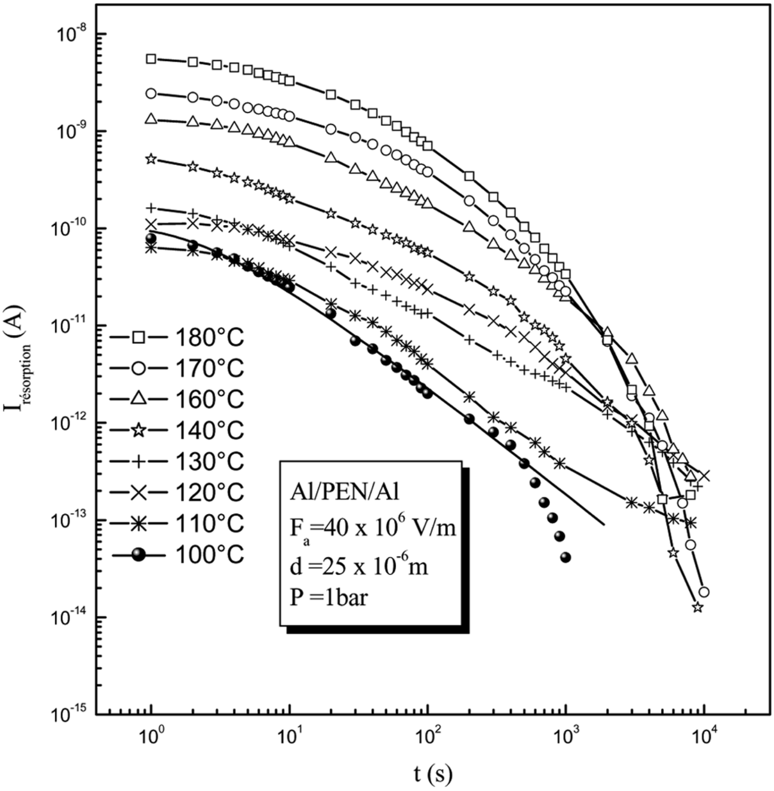

Figure 1. Time dependence of resorption currents in PEN, at $F_a = 40 \times 10^6$ V/m.

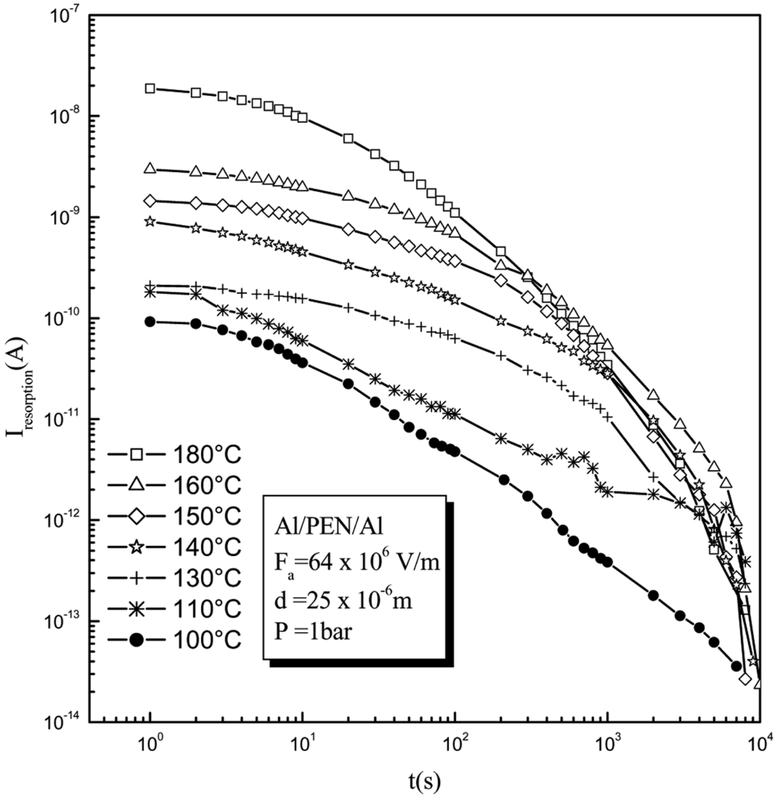

Figure 2. Time dependence of resorption currents in PEN, at $F_a = 64 \times 10^6$ V/m.

The time localization t_c of the change of n at different temperatures, extracted from discharging currents curves in Figure 2, are shown in Table I. This time decreases when the temperature was increased. It can be presented as an Arrhenius plot to give an activation energy of 2,33 eV.

The existence in PEN of localized states acting as traps for charge carriers has been demonstrated by the use of thermally stimulated conductivity (TSC) measurements;[15,16] hopping of charge carriers is not expected to be the dominant mechanism. In fact, systems dominated,

Table I. Parameter t_c as a function of temperature

Temperature (°C)	130	140	150	160	180
t_c (s)	6865	1332	162	34	5

at low temperature, by hopping of ionic or electronic charge carriers generally show a transient decay of the discharging current divided in two successive domains characterized by $n = 1$ and n approaching 0, respectively.[17]

The change observed between 100° and 130°C was attributed to the internal change associated with the glass transition.[13]

From these experimental results and those given by other authors,[18] the change observed in transients discharging evolution is an indication of the onset of an additional relaxation phenomenon.

The characteristic observed experimentally is that the relaxations are thermally activated, so that from Wintle,[19] double logarithmic current-time plots are translated along a direction with the slope – 1 as the temperature changes.

Obviously, it has to be borne in mind that, as a general rule, dipolar processes involved in polymers are characterized by a distribution in relaxation times and that overlapping of several processes are likely to be observed.[20] This also implies that the Curie law can be considered only as a more or less rough approximation of the real time dependence and can depict the transient phenomena only over short periods of time. Keeping this in mind, some interesting points can raised from our experimental data.

Dielectric Loss

The discharging currents were transformed into the frequency domain using the Hamon transform to give the dielectric loss as a function of frequency (Figure 3).

The existence in PEN of three main dipolar relaxations was demonstrated years ago by the use of thermomechanical stimulation and dielectrical measurements.[21,22] The first relaxation, localized around −50°C and labeled the β process, has been attributed to noncooperative molecular motions of some parts of the principal PEN chain. This relaxation phenomenon is comparable to the one known as molecular orientation (or dipolar), related to the polarizable groups of the molecule. It is characterized by a broad distribution in relaxation times. Since our measurements are carried out at high temperatures, it can be expected that the dipoles involved in this β process orient within a very short period of time at the moment of the removal of the electric field and thus do not contribute significantly to the observed transient current. The same relaxation appears in PET, which could imply that it is inherent to the ester groups (O−C=O).[16,23]

The second dipolar process, namely β^* process, centered around 65°C, is associated, according to the studies of Blundell et al.,[24] on liquid

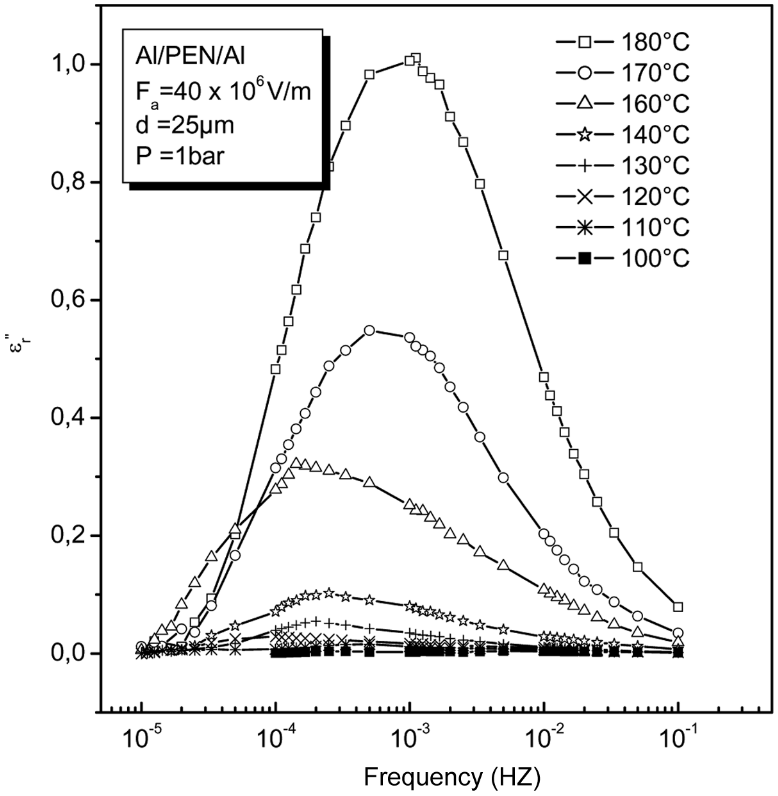

Figure 3. Frequency dependence of dielectric loss in PEN, at $F_a = 40 \times 10^6$ V/m.

crystal polyesters containing 2,6 naphtyl groups, with the motion of the naphthalene rings and neighboring carbonyl groups both constituting a total entity rotating about the main polymer axis. This relaxation process is not mentioned by the authors who have investigated PET, in consequence of which it was suggested that β^* was related to the relative motion of the two naphthalene rings present only in PEN chains.[25] However, Menegotto et al.,[26] investigating dielectric spectrometry and thermally stimulated currents, have shown the resolution of two peaks, β_1 and β_2. The first (β_1), probably equivalent to β^*, is thought to be due to the phenyl rings; the second (β_2) corresponding to β, is assigned to the carbonyl groups. We will see below that the associated mechanisms with this relaxation process are more complex and depend upon the measurement frequency.

Previous works[27–29] on amorphous and bi-xially stretched PEN samples of different morphologies have lead to the identification of the two sub-T_g relaxations, β and β^*, associated to local motions of ester groups (like for PET) and to partially cooperative movements of naphthalene aggregates, respectively.

The third dipolar process, namely the α process, results in micro-Brownian and cooperative motions of chain segments by a configuration rearrangement of the entire chain,[15,27–29] involving long chain segments and reflecting the mean relaxation of the amorphous PEN structure.[30] This process is located around 130°C. Thus, it seems likely that the dipolar α relaxation process could be responsible for the transient discharging current. It also should be noticed that this relaxation is characterized by mean relaxation times τ_0 of nearly 10^2–10^4 s, which are compatible with the condition mentioned by Wintle[19] to observe dipolar transient current $\frac{t}{\tau_0} \ll 1$, where t is the electrification time. Moreover, our results lead us to conclude in favor of a homogeneous distribution of dipoles within the thickness of the sample.

Figure 4 shows that, at a constant electric field, there is a loss peak whose position moves to lower frequencies as the temperature is between

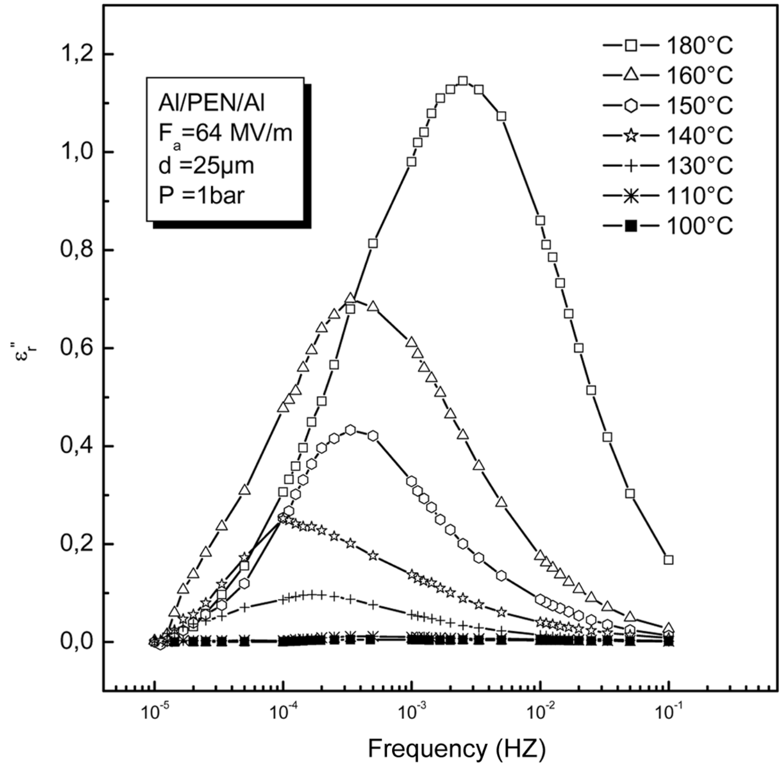

Figure 4. Frequency dependence of dielectric loss in PEN, at $F_a = 64 \times 10^6$ V/m.

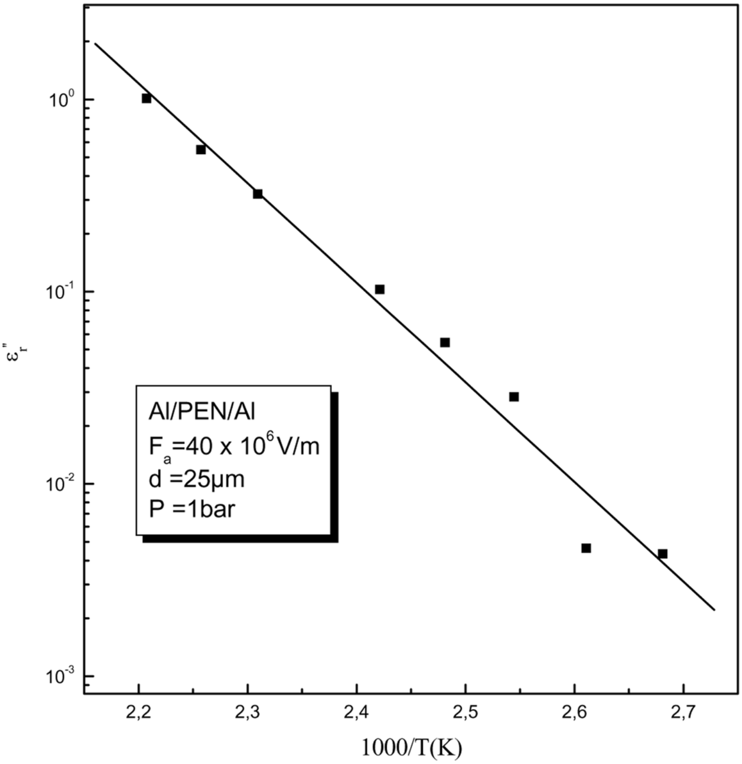

Figure 5. Temperature dependence of the loss maximum at $F_a = 40 \times 10^6$ V/m.

100° and 150°C and to higher frequencies above 150°C. In addition, it can be seen that the magnitude of the peak increases with temperature. Similar variation is observed at 64×10^6 V/m (Figure 5).

The temperature dependence of the relaxation maximum, at 40×10^6 V/m, is shown in Figure 5 by plotting the logarithm of the maximum loss as a function of the reciprocal temperature.

This plot assumes the Arrhenius law:

$$\varepsilon''_r \approx \exp\left(\frac{-E_a}{kT}\right) \tag{2}$$

where k is the Boltzmann constant and T the absolute temperature. The apparent activation energy E_a was evaluated as 1,03 eV.

Figure 6 shows the Arrhenius plot, at 72×10^6 V/m, using the maximum frequency as a parameter.

It should be noted that the evolution of this experimental curve exhibits a slight change in the slope, showing a breakpoint at $T \approx 146{,}65$°C.

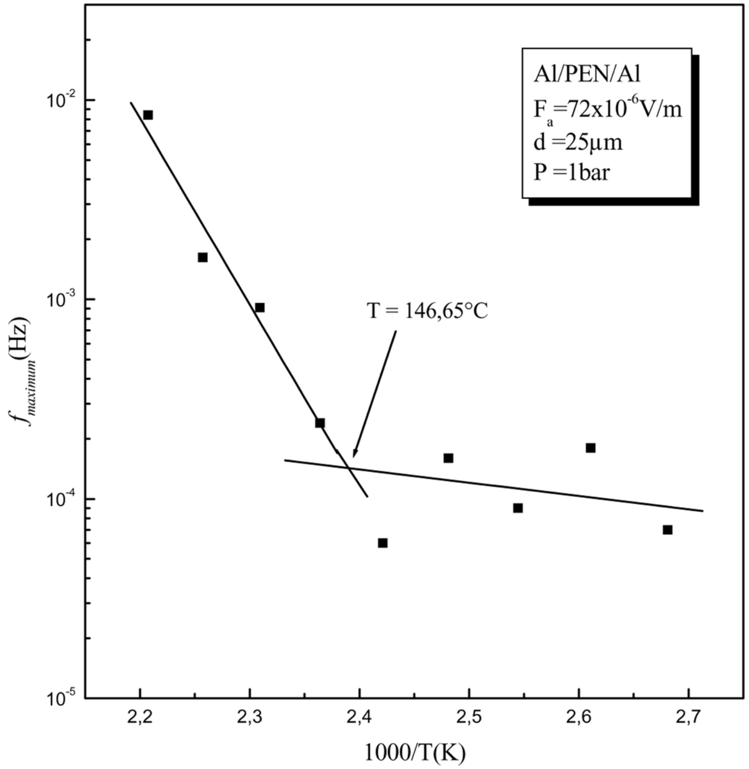

Figure 6. Temperature dependence of the frequency maximum at $F_a = 72 \times 10^6$ V/m.

This defines two values of the average apparent activation energy E_a: $E_a = 0{,}13$ eV at $T < 146{,}65$°C and $E_a = 1{,}85$ eV at $T > 146{,}65$°C. Mackersie et al.[18] have studied the low frequency response of PEN over the range 130°–150°C in 20×10^6 V/m; the activation energy value was 2,31 eV.

Figure 7 gives the dielectric loss on PEN as a function of frequency for different values of electric field. It can be seen that there is a loss peak whose magnitude increases with electric field. This figure also shows a modification in dielectric behavior of PEN film. Indeed, at 140°C (temperatures less then 150°C), the peak position moves to lower frequencies. At 150°C, for different values of the field, the loss peak appears at the same frequency. When the temperature increases beyond 150°C (at 170°C), loss position displaces to higher frequencies. These results allow defining a critical temperature localized around 150°C,

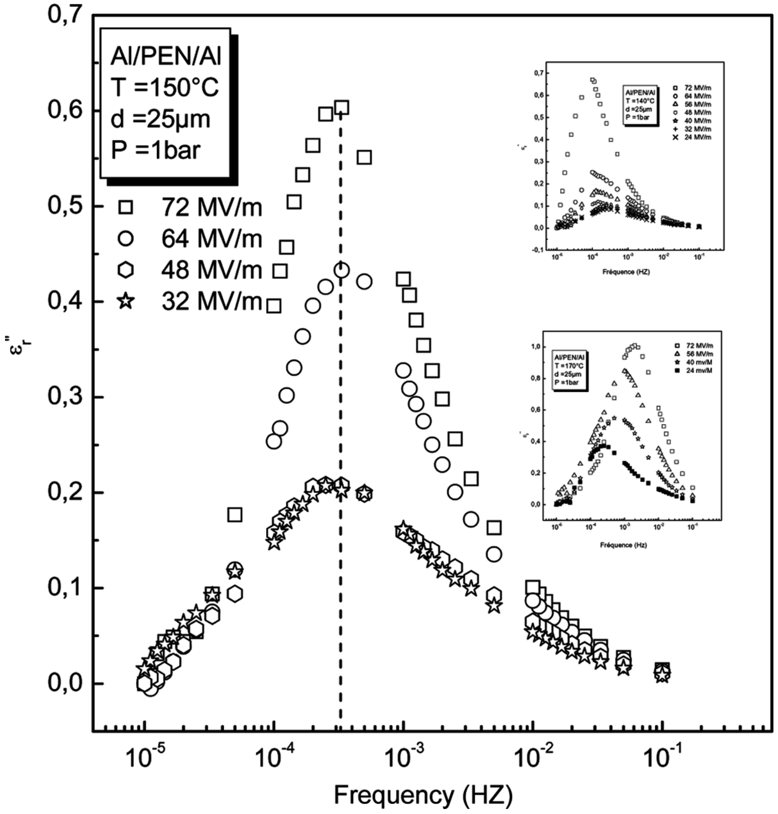

Figure 7. Frequency dependence of dielectric loss in PEN.

since it is near the first crystallization temperature of the polymer (160°C).[22]

CONCLUSION

The change observed in the discharging current behavior, at the vicinity of the glass transition temperature, after removal voltages to thin PEN in a wide range of temperatures, indicates a modification in the relaxation mechanism. This change was observed in low-frequency dielectric loss as well as in an increase of the frequency maximum with temperature, which shows a break in the region between 140° and 150°C, given two activation energies, and in the form of moves in the position of a loss peak beyond a temperature of 150°C, which we consider a critical temperature.

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