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Temperature Effect on Transient Charge and Discharge Currents in Poly(Ethylene Naphthalene-2,6-dicarboxylate)

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Abstract: Poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) and poly(ethylene terephthalate) (PET) are of particular interest in electrical applications. A presence of aromatic cycle confers on these polymers good electrical and mechanical properties and high thermal and chemical stabilities. The main objective of the present work is to analyze the effect of temperature on electrical conduction in PEN, in comparison with previous work on PET. Charging and discharging current were measured with electrical fields ranging from 24×10^6 to 72×10^6 V/m and temperatures between 100 and 180°C. Peaks in the charging current were observed to be dependent on temperature and field. Current characteristic versus field gives information about the conduction mechanism.

Keywords: PEN; Electrical conduction; Anomalous current; Glass-transition temperature

INTRODUCTION

Polymers are currently used as dielectrics in a wide range of electro-technological applications. Since the poly(ethylene naphthalene-2,

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6-dicarboxylate) (PEN) polymer gives high performance films with physical, thermal, and chemical characteristics better than those of poly(ethylene terephthalate) (PET), it is used as a substitute for the latter in a large number of applications, particularly in film capacitors. The aim of this article is to present some electrical characteristics obtained for PEN films from measurements of charging and discharging currents.

It is generally observed that the charging current after DC voltage application in most cases decreases monotonously with time until a steady current is achieved. Removing the external voltage causes a discharging current flow in the opposite direction, usually equal in magnitude to the absorption current (charging current reduced by the steady-state current). The time-dependent current density $J(t)$ (current divided by electrode area) usually follows the empirical law^[1], $J(t) \propto t^{-n}$, t being the elapsed time and n a constant with a value near unity. A number of mechanisms have been proposed^[1] to explain the origin of transient currents; the most important are dipolar polarization, hopping of charge carriers from one localized state to another, interfacial bulk polarization (amorphous boundaries, etc.), and electrode polarization. These processes are influenced by various parameters such as field strength, electrode material, sample thickness, water content, and temperature.

Several authors reported the effect of different parameters, on PEN properties.^[2–12] On electrical properties, some studies have been published. Chavez et al.^[7] have investigated the effect of crystallinity on electrical conductivity at high field and ambient temperature. Guastavino et al.^[8] have analyzed electroluminescence and conductivity measurements at high field and ambient temperature. Ishiharada et al.^[9] have investigated electrical conductivity in the temperature range 45–141°C. Kojima et al.^[10] have studied electrode effect on electrical conductivity at high field and temperatures below 30°C. Thielen et al.^[11] have measured transient current at low field and temperature $T = 23^\circ\text{C}$. The study of temperature effect on transient current in PEN films has rarely been done in previous investigations.^[12]

In this article, the temperature dependence of the transient current in PEN has been explored at high electrical field ($72 \times 10^6 \text{ V/m}$) and in a wide range of temperatures (80–180°C), including a glass transition temperature $T_g = 128^\circ$.

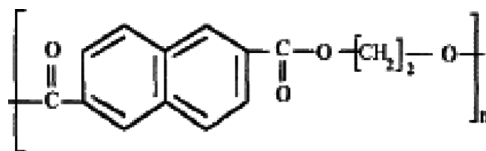


Figure 1. Chemical structure of PEN.

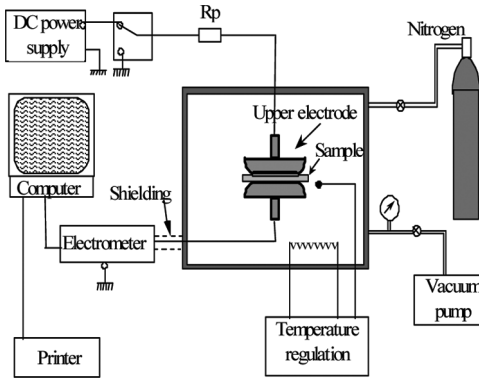


Figure 2. Schematic view of the experimental setup.

MATERIALS AND EXPERIMENTAL SETUP

The PEN film of 25 μm thickness 40% crystallinity, and 1.36 g/cm^3 density was provided by Dupont de Nemours Luxembourg. The chemical structure of polyethylene naphthalate is reported in Figure 1. The PEN sample was prepared with aluminium evaporated electrodes, 2 cm in diameter, on both sides of the sample. A DC voltage was applied to a sample at a certain temperature, and the charging current was measured for three hours. The voltage was then removed and the discharging current of the short-circuited sample was also recorded for three hours according to the experimental setup shown in Figure 2. The experimental cell is connected to a vacuum pump and a gas cylinder. This allows controlling the nature of the gas inside the cell and removing the moisture from the sample. A temperature controller connected to the heating element located inside the cell sets the temperature. The DC voltage is obtained from a Hewlett Packard stabilized power supply, which delivers voltages up to 4000 V. The current is measured by a Keithley 617 programmable electrometer driven by a microcomputer. A high-voltage relay switches from polarization when the sample is subjected to the voltage and to depolarization when the sample is grounded.

RESULTS AND DISCUSSION

Transient Current

Figure 3 shows typical charging current density $J(t)$ characteristics for an applied field, $F_a = 72 \times 10^6 \text{ V}/\text{m}$. It can be seen that the magnitude of the

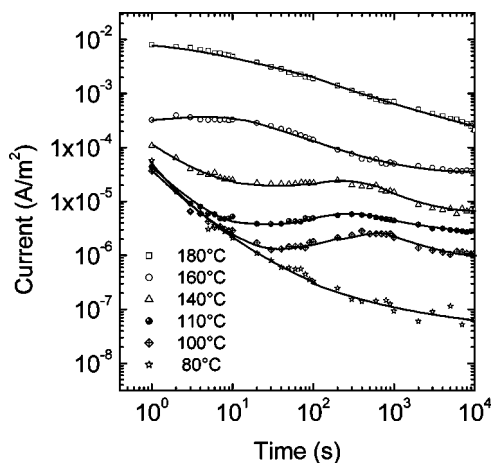


Figure 3. Time dependence of charging currents in PEN, at $F_a = 72 \times 10^6$ V/m.

current increases with temperature. For instance at $t = 10^4$ s, the current passes from 2×10^{-12} A at 80°C to 8.6×10^{-9} A at 180°C . In addition, it can be seen that, at 80°C , the current decreases monotonically up to the steady state. But from 100°C , the charging current deviates from this dependence: the current at first decreases then increases with time before finally decreasing until it reaches a steady-state value, showing a peak. This current is a so-called “anomalous charge current.” The peak shifts to shorter times as the temperature is increased and disappears completely at 180°C . These results allow us to define a critical temperature localized between 80° and 100°C , above which the current does not again exhibit normal behavior. Several works have reported the existence of these peaks with different polymers, like polyethylene (PE),^[13–17] polyethylene terephthalate (PET),^[18] and polypropylene (PP).^[19] For PEN very few references cited this behavior: Mackersie et al.^[12] have observed similar peaks in PEN films between 130° and 150°C .

To compare the present results with those already obtained in PET films,^[20] charge current-time characteristics $J(t)$, are shown in Figure 4, at different temperatures. From these curves, it can be seen that at temperatures 40° , 60° , and 80°C (below T_g) no peak was observed, while at 100°C (above T_g) a peak exists. This implies that a critical temperature, localized between 80° and 100°C , was associated with glass transition temperature T_g . In PEN film the critical temperature is much lower than $T_g = 128^\circ\text{C}$ and is associated with β^* relaxation. Indeed, in recent studies of dielectric and mechanical relaxation in PEN, Hardy et al.^[4] found a β^* relaxation at $T = 80^\circ\text{C}$. This temperature is associated with molecular fluctuations of aggregate of naphthalene ring.

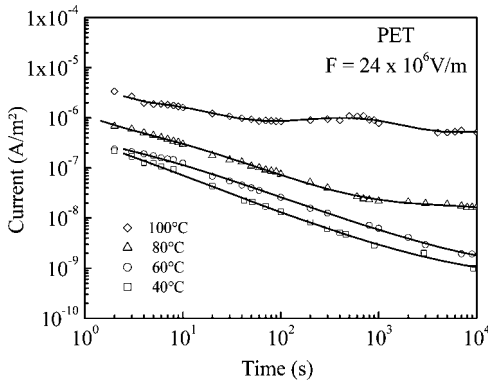


Figure 4. Time dependence of charging currents in PET at various temperatures.

The charging current peak in Figure 3 is similar to that given by Many and Rakavy^[21] relating to transient SCLC (space charge limited current). This peak appears at time t_p :

$$t_p = 0.786 \frac{d}{\mu F_a} \tag{1}$$

and a steady-state current J_∞ , at infinite time t , was:

$$J_\infty = \frac{9}{8} \varepsilon \mu \frac{F_a^2}{d} \tag{2}$$

where F_a is the applied field, d the sample thickness, μ the carrier mobility, and ε the permittivity of the sample. This time was related to the transit time of a space charge between electrodes. In our case, at high field (72×10^6 V/m), the presence of a peak was explained by an increasing space charge limited current, which was added to decreasing dipolar current^[20]. The time localization t_p of the peaks at different temperatures, extracted from $J(t)$ curves in Figure 3, are shown in Table I. This time decreased when the temperature was increased. It can be presented as an Arrhenius plot to give an activation energy of 1 eV. It was seen that the peak at 150°C didn't follow the same evolution. The shift of the peak to lower time under higher temperature was also observed in low-density polyethylene (LDPE).^[13] In addition, it was shown in this article that the peak shifts in the same direction under electrical and mechanical strength (hydrostatic pressure).

Figure 5 shows typical discharging current measurement subsequent to the charging current displayed in Figure 3. It can be seen that for the temperatures 100° and 110°C, the discharging current can be fitted to

Table 1. Parameters t_p , l , and λ as a function of temperature

Parameter	$T(K)$					
	373	383	413	423	433	453
t_p (s)	498	275	197	475	4	1
l	3.0	2.8	1.2	1.1	1.2	2.0
λ (Å)	44	41	23	20	31	37

straight lines in a log-log scale, suggesting a dependence on time given by the Curie-von Schweidler law:^[1]

$$J = At^{-m} \quad (3)$$

with $m = 0.5$, while for temperatures above 130°C , the curves describe two separate intervals where the slope m passes from 0.1 at shorter times to 1.5 at higher times. The change observed between 110° and 140°C was associated with internal change, associated with the glass transition, localized in this material at $T_g = 128^\circ\text{C}$. On the other hand, it should be noted that the absorption current is not the mirror image of the discharging current. This suggests that in transient regime, the dipolar mechanism was not the predominant process in this case. Mechanisms of dipolar origin are generally predominant at low field.^[1]

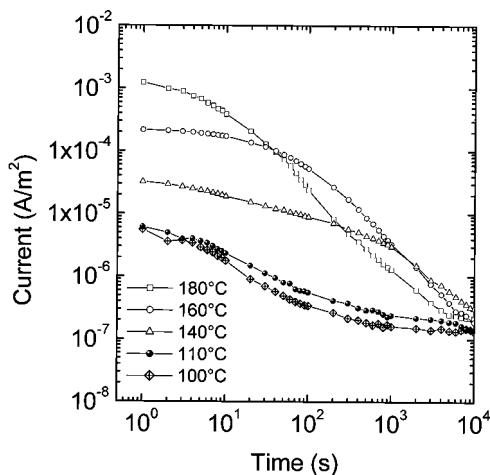


Figure 5. Time dependence of discharging currents in PEN at various temperatures.

Steady-State Conductivity-Temperature Effect

Figure 6 shows $\log(J) - (1000/T)$ plot assuming Arrhenius law:

$$J = J_0 \exp\left(\frac{-E_a}{kT}\right) \tag{4}$$

where k is the Boltzmann constant and T the absolute temperature. The average apparent activation energy E_a of the current was evaluated as 0.94 eV. It should be noted that the evolution of this experimental plot presents as light change in the slope at the region between 130° and 140°C, showing a break point at $T = 135^\circ\text{C}$. This defines two values: $E_a = 0.6\text{ eV}$ at $T < 135^\circ\text{C}$ and $E_a = 1.4\text{ eV}$ at $T > 135^\circ\text{C}$. Ishiharada et al.^[9] have observed this break point at temperatures around 108°C (their PEN films have $T_g = 113^\circ\text{C}$). Their activation energy values were 0.8 and 3.7 eV. The break point at the temperature 135°C corresponds to the glass transition temperature of PEN (128°C). This finding implies that the carriers contributing to the electrical conduction are ionic impurities in the region crossing the glass transition temperature. Therefore, the conduction process in the temperature above 80°C was governed by the carriers (ionic impurities) and influenced by the molecular motion in PEN around the glass transition.^[4] However, carrier species below 80°C are assumed to be electronic.^[9] Recently, several authors^[4,6,10] reported on the PEN structure/property relationships by investigating the relaxational processes and the resistivity of samples with different degrees of crystallinity. Semicrystalline morphology is less conductive and more resistant to the development of high mobility carriers. This fact probably shows

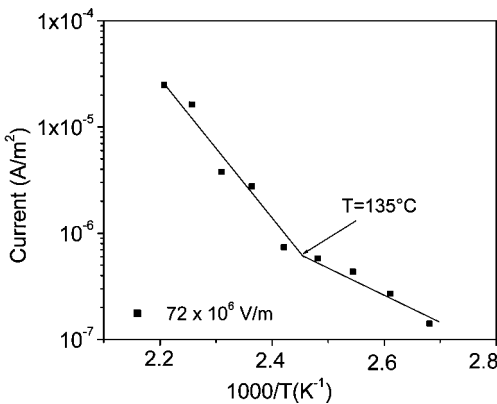


Figure 6. Temperature dependence of the current in PEN at $F_a = 72 \times 10^6 \text{ V/m}$.

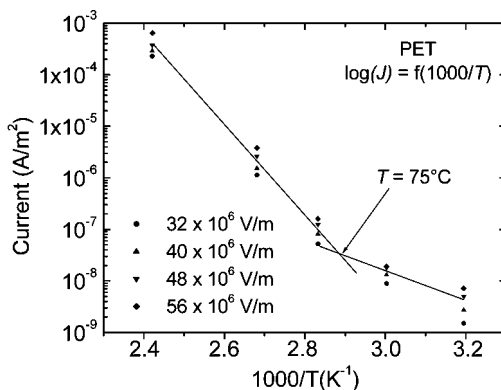


Figure 7. Temperature dependence of the current in PET at various fields.

dependence of bulk conductivity, which is limited in some way by the crystallinity. The increase in the crystallinity favors a decrease of free volume, so the movement of charges is restricted especially by the species of large sizes (ions).

For temperature effect on PET conductivity, Figure 7 shows $\log(J) - (1000/T)$ plot. The break point was observed at $T = 75^\circ\text{C}$, which defines two activation energies: $E_a = 0.6\text{ eV}$ at $T < 75^\circ\text{C}$ and $E_a = 1.7\text{ eV}$ at $T > 75^\circ\text{C}$. So, in each polymer, the break point was observed and associated to T_g . However the importance of this change in PET is greater than in PEN. On the other hand, as expected, PEN films are more electrically resistant than those of PET.

Conduction Mechanism

The dependence of steady-state currents with applied field was characterized by a power law:

$$J(F) \propto F^l \quad (5)$$

The values of l at different temperatures, calculated from $\log(J) - \log(F_a)$ characteristics, are reported in Table I. Three features can be seen: first, l decays from 3 at 100°C to 1.2 at 140°C , then it passes through a minimum at 150°C , and finally it increases up to 2 at 180°C . This suggests ohmic conduction in the region $140^\circ\text{C} - 160^\circ\text{C}$, where l closes to 1. The same result was procured by Guastavino et al.^[8] in similar PEN films, but the values of l obtained were higher than the values given above because they studied PEN behavior at higher electrical fields (from 80×10^6 to $260 \times 10^6\text{ V/m}$).

The electrical field dependence of current shows a “hopping” plot. In the ionic hopping model, the current density is given by:^[22]

$$J(F_a) = K \exp \left[-\frac{\phi_o - eF_a\lambda}{2kT} \right] \quad (6)$$

where F is the electrical field (V/m), K is the preexponential factor, ϕ_o is the barrier height, and λ is the hopping distance. The hopping plot gives values of λ summarized in Table I. For temperatures between 100° and 120°C the value of λ was about 40 Å, for temperatures between 140° and 160°C, λ was equal to 20 Å, and from 160° to 180°C, λ was greater than 30 Å. The sharp decrease of λ was observed at a temperature located in the glass transition region. This implies that, in this region, the movement of ionic carriers became easier with lower hopping distance λ . Indeed, it is well known that glass transition is associated with chain segment cooperative motions induced by diffusive rearrangement of main chain portions.^[4]

CONCLUSION

The application and removal of DC voltages to thin PEN film in a wide range of temperatures, including a glass transition temperature $T_g = 128^\circ\text{C}$, resulted in changes in the steady-state and transient current behavior.

These changes were observed in an increase of the steady-state current with temperature, which shows a break in the region between 130° and 140°C in the neighborhood of T_g , giving two activation energies: 0.6 eV and 1.4 eV. These results are confirmed by the change in discharge current behavior between 110° and 140°C. The study of temperature effect on electrical conductivity, assuming ionic model, shows a sharp decrease of hopping distance λ (40 to 20 Å) at temperatures around T_g (120°–140°C). Indeed, above T_g , there is an important increase of free volume that facilitates the migration of ions. This finding implies that the carriers contributing to the electrical conduction are ionic impurities. The conduction process is influenced by the molecular motion. The comparison between PEN and PET shows that both of the polymers exhibit a break point at T_g .

In the study of transient charge current, the appearance of peaks (anomalous current) was observed from a critical temperature localized between 80° and 100°C. This temperature is associated with the β^* relaxation, which is related to molecular fluctuations of aggregate of naphthalene ring. The presence of a critical temperature, between 80° and 100°C, was also observed in PET films, but in this case, it was associated with glass transition temperature.

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