BEHAVIOUR OF SPACE CHARGE DISTRIBUTION IN AIR-AGED SAMPLES OF POLY(METHYL METHACRYLATE)

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ABSTRACT

Polymeric materials are used in various environments in which they are subjected to different stresses. In this setting, samples of poly(methyl methacrylate) were treated in aqueous salt solutions at 100 °C for 20 min. The Thermal Step Method (T S M) and the Thermally Stimulated Discharge Current method (T S D C) were used to characterize the electrical state of these samples.

In order to study the influence of ageing process on polarization and space charge distribution, air-aged samples were left for one year on aluminium paper at room temperature. The TSM and the TSDC measurements were then applied on aged samples.

The comparison between space charge distributions and TSDC currents measured before and after ageing, shows that the ageing process affects the space charge distribution.

INTRODUCTION

Several publications (Crine *et al*., 1991; Zebouchi *et al*., 1995; Kawamura & Nawata, 1998) have shown that electrical properties of insulating materials depend strongly on the space charge accumulation under external constraints like high electric field, mechanical friction, irradiations *etc*. It is important to locate charges within an insulator, and to follow the space charge evolution in these materials.

The poly(methyl methacrylate) (PMMA) is a well-studied polar polymer (Toureille, 1995; Notingher *et al*., 1999; Cerveny *et al*., 1999; Vella *et al*., 1994; Yang & Schruben, 1994). Its polarizability is due to the presence of side ester groups of dipolar moment of about 1.5 Debye (Notingher, 1999). It is shown (Notingher, 1999) that cross-linking by tetra-ethyleneglycoldiacrylate (TEGDA) favours space charge accumulation in PMMA, which is

proportional to cross-linking degree. Other studies (Cerveny *et al.*, 1999; Vella *et al.*, 1994; Yang & Schruben, 1994) investigated several metal filled composites made of PMMA with aluminium and nickel powder. They found that the relaxation temperatures (T_g, T_β) are very sensitive to the filler fraction.

The present work is a contribution to the study of the space charge evolution in this polymer material (PMMA). The space charge distribution was investigated under different external stresses (temperature, medium degree of salinity, electric field). In order to study the ageing influence in space charge distribution, air-aged samples are investigated. Two techniques were used for measuring space charges: the thermal step method (TSM) and the thermally stimulated discharge current (TSDC). The two techniques give complementary information.

METHODS OF MEASUREMENTS

The Thermal Step Method (TSM)

This method has been previously described and validated by various authors (Cherifi *et a*l., 1992; Toureille, 1987; 1991; 1995; Smaoui *et al.*, 2000). The specific details of this method have been described in previous reports (Toureille *et al.*, 1991; Smaoui *et al.*, 2000; Toureille, 1991). It is based on the measurement of a current after applying a negative thermal step $(\Delta T_o = T_o - T_1)$ to one side of the sample which is placed on a thermal diffuser (Fig. 1a).
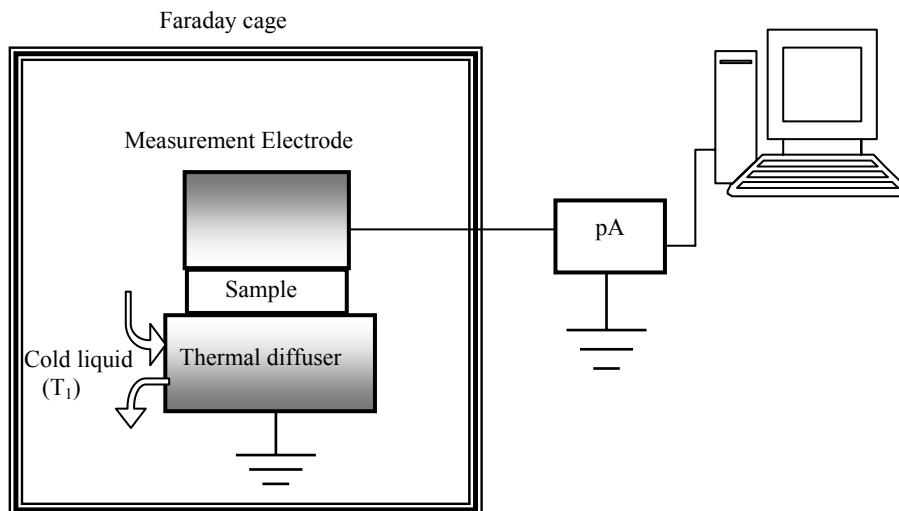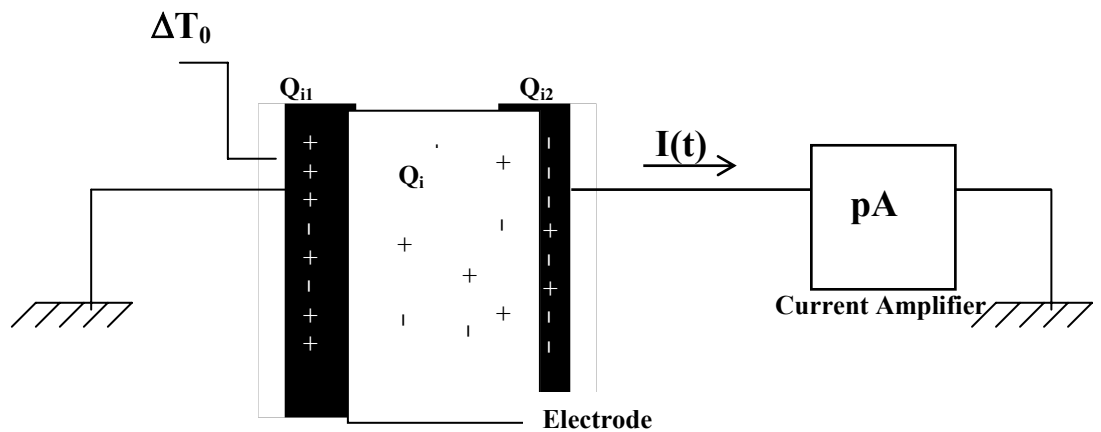

Figure 1a. Measurement cell.

The sample is at room temperature (T_o). The temperature of one side of the sample is then quickly cooled to temperature (T_1) while the other side is kept at room temperature. The propagation of the thermal step through the sample induces a thermal contraction of the successive material layers, which leads instantly to a displacement of the space charges from their initial positions. This displacement will modify the equilibrium of the influence charges on electrodes and consequently create a current in the external circuit joining the two electrodes (Fig 1b). The current is (Vella & Toureille, 1997):

$$I(t) = -\alpha.C \int_0^D E(x).\frac{\partial T}{\partial t}.dx$$

where $\alpha = \alpha_x - \alpha_\varepsilon = -\dfrac{1}{C}\dfrac{\partial C}{\partial T}$, with $\alpha_x = \dfrac{1}{x}\dfrac{\partial x}{\partial T}$: linear expansion coefficient

of the material, and $\alpha_\varepsilon = \dfrac{1}{\varepsilon}\dfrac{\partial \varepsilon}{\partial T}$: thermal dependence of permittivity coefficient.

Q_{i1} and Q_{i2} are the image charges
Q_i : space charge
ΔT_0 : thermal step

Figure 1b: Principle of the thermal step method. Q_{i1} and Q_{i2} are the image charges, Q_i : space charge and ΔT_0 : thermal step.

α is determined by the measurement of the capacitance under different temperatures. T is the temperature. C is the capacitance of the sample, D its thickness, E(x) is the average electric field at distance x through the sample.

The current is amplified and recorded with a computer. The space charge and electric field distributions are calculated from the experimental current by a deconvolution algorithm developed by Toureille *et al*. (1992). The theory and numerical treatment (Fourier series or derivation) have been extensively described in previous papers (Cherifi *et al*., 1992; Toureille, 1987; 1991; Toureille *et al*. 1991).

The Thermally Stimulated Discharge Current (TSDC) Method

The TSDC method (Bucci *et al*., 1966) is based on the depolarisation of the sample by thermal activation. The charged sample is short-circuited through an electrometer in an oven, which is programmed to rise linearly in time.

TSDC method provides information of relaxation processes that occur in polymers.

TSDC spectra present several peaks or bands indicating that several processes are operative. Among these processes, we find the depolarisation of permanent dipoles and the release of charges from traps. These space charges can be intrinsic to the dielectric or injected from electrodes.

For a current due to a dipole reorientation, Bucci and Fieschi (1966) give the following expression :

$$J(T) = A \exp\left[-\frac{E_a}{kT} - \frac{1}{v\tau_0} \int_{T_0}^{T} \exp\left(-\frac{E_a}{kT'} \right) dT' \right]$$

Where the pre-exponential factor A is given by :

$$A = \frac{N\,m}{\tau_0} = \text{constant},$$

and the relaxation time τ at temperature T is given by :

$$\tau = \tau_0 \exp\left(\frac{E_a}{kT} \right)$$

with E_a : activation energy
            k : Boltzmann constant
            T_0 : initial temperature and T : temperature at the time t
            v : rate of heating (degree/sec)
            τ_0 : relaxation time.
            $m = q\,\delta$: dipole moment
            N : volume density of dipoles

In the present study, TSDC measurements are realised with a thermal rate of 2°C/min on a temperature range from 25°C to 150°C.

EXPERIMENTAL PROCEDURE

Preparation of samples

PMMA samples were squares of $(70 \times 70 \times 5)$ mm^3, ($M_w \approx 600\,000$ u) prepared by polymerisation of methyl methacrylate monomers (MMA).

Sample 1 was not treated. The other samples were submitted to two types of treatments:
(a): thermal process, which consists to immerse samples in boiling distilled water during 20min (sample 2).
(b): sample processing in boiling salt solutions (Na^+, Cl^-) (1M), during 20 min (sample 3).
The samples were then slowly cooled to room temperature.

Circular aluminium electrodes (diameter: 30mm) were deposited under vacuum on opposite sides of each samples.

Poling of samples

Preliminary space charge measurements were performed by TSM technique in order to verify that the samples don't contain charges. Samples were then submitted to a thermal and electrical stresses.

In this study, a poling technique under direct high voltage between electrodes has been utilised (Figure 2). First the temperature is linearly raised to a poling temperature $T_c = 90°C$, then the high voltage $V_c = 20kV$ is applied during a time of $\Delta t_c = 30$ min. At the instant t_c, the temperature is lowered to T_0 (room temperature) keeping the voltage applied in order to avoid any relaxation of dipoles and/or charges, then the applied voltage is removed and the sample is short-circuited between aluminium sheets during a time $t_{cc} = 30$ min in order to eliminate surface charges.

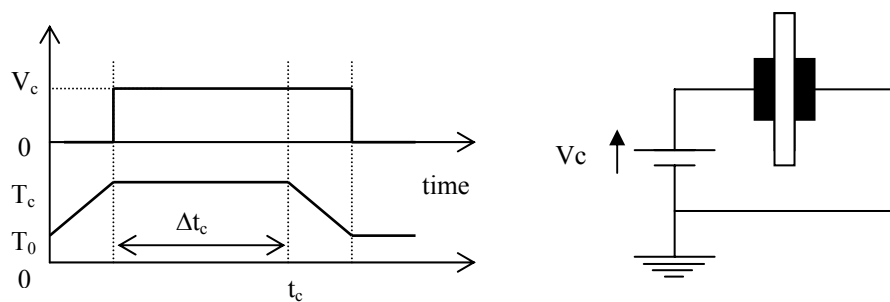The space charges have been then characterized by a TSM measurements followed by TSDC measurements.

Figure 2. Procedure of sample poling.

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RESULTS AND DISCUSSION

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Thermal effect

Figure 3 gives the space charge distributions in samples 1 and 2. They have a profile which is characteristic of polarization phenomenon. An important variation of the polarization ($\frac{dP}{dx} \neq 0$) was observed throughout the samples. This profile indicates that there is an inhomogeneous distribution of dipoles in the bulk of the material. Figure 3 indicates that the polarization variation ($\frac{dP}{dx}$) is bigger in sample 1, which should correspond to a bigger gradient of dipolar orientation. But polarization remains a predominant phenomenon in the two samples. The injected charges are not clearly present. In TSDC measurements (Figure 4), the α peak relaxation which was related to the main chain motion in PMMA was observed. The main chain motion is identified with the glass transition which marks the onset of the long range main chain wriggling motions (Allen, 1978). The location of this peak can be defined as the glass transition temperature Tg. The Tg value obtained in sample 1 (Tg = 105°C) is similar to those generally reported in PMMA (McCrum *et al*., 1991; Papaléo *et al*., 2000; Muzeau *et al*. 1995; Goyanes *et al*., 1997). As it is known, a β relaxation in PMMA appears in lower temperatures. It is associated with the partial rotation of the ester group ($COOCH_3$) about the C-C bond linking it to the main chain (Heijboer, 1978). In Figure 4 this peak is so small that it merged with the large α peak.
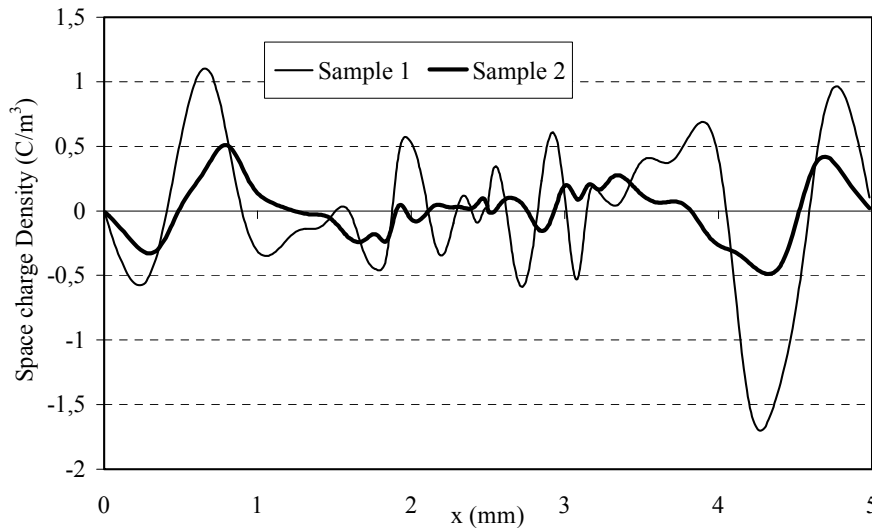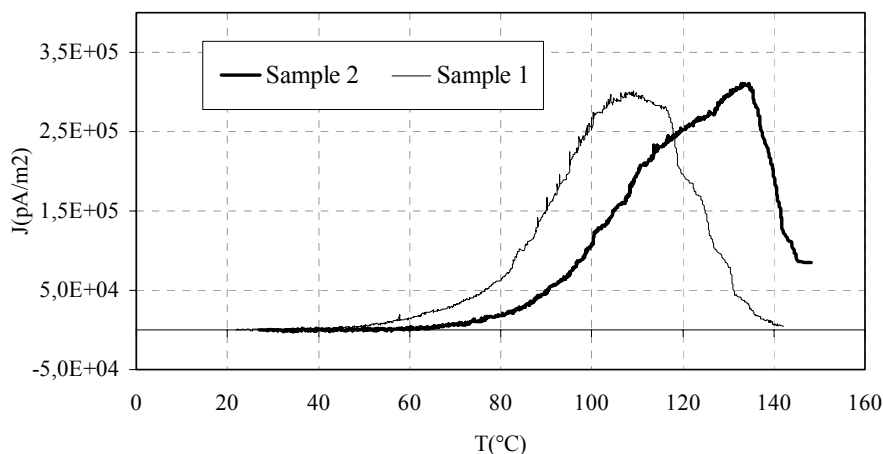

**Figure 3. Space charge distributions throughout the samples 1 and 2 of PMMA.
(Anode at left, Cathode at right).**

Figure 4. TSDC curves in samples 1 and 2 of PMMA.

In sample 2, the presence of another peak at higher temperature which characterized the homocharge relaxation was also noticed. This is the ρ peak , which is overlapped with the α peak. This peak appears when samples were heated to higher temperatures to obtain relaxation of the injected charges, which are trapped deeper. In fact, the activation energies for injected charges are higher than in the case of polarization (Vella *et al*., 1994). According to Vanderschueren (1973; 1994), the injected charge relaxation was characterised by the TSDC peak, which appears at a higher temperature in sample 2 (about 135 °C). While the first peak was attributed to β relaxation of dipoles at glass transition (Tg). Figure 4 shows that thermal treatment of PMMA samples before electrical poling favours charge injection. A difference of space charge injection between the two samples (1 and 2) can also explain the difference of profile observed in Figure 3. The charge injection was observed at the cathode in cross-linked PMMA after poling at 60 °C, 6kV.mm^{-1} (Notingher *et al*., 1999).

The TSDC curves (Figure 4) show also an increase in the Tg value under thermal treatment (in sample 2). This shift was due to an increase in the activation energies of dipoles. An α peak drop which shows a decrease of oriented dipole number caused by the impurities recombination when the sample was heated was also noticed.

The width of TSDC peaks suggests an important distribution of energy levels.

Salt effect

The distribution of charges in the samples 2 (boiling in distilled water) and 3 (boiling in aqueous salt solution 1M) are given in figure 5. While Figure 6 shows the TSDC curves in those samples, Figure 5 shows more charges in sample 3 (1M) than in sample 2 (M = 0). This fact is due to ionic diffusion in the bulk of material. The presence of these ions near the molecular chains, creates new local energy states, which act like charge traps. This result is in broad agreement with those obtained by Notingher *et al*. (1999). The ion diffusion

induces an increase of chain mobility, which is perceptible on the TSDC spectrum by a shift of the peaks to the lower temperatures, due to a decrease of the activation energy of dipoles. On the other hand, we noticed a slight increase in TSDC values indicating an increase in the number of oriented dipoles. As it is known, Na^+ ions have a high mobility so their presence creates new sites of polarization by conduction (charge transport from a site to another). It appears that charges are more deeply trapped in sample 2 than in sample 3.
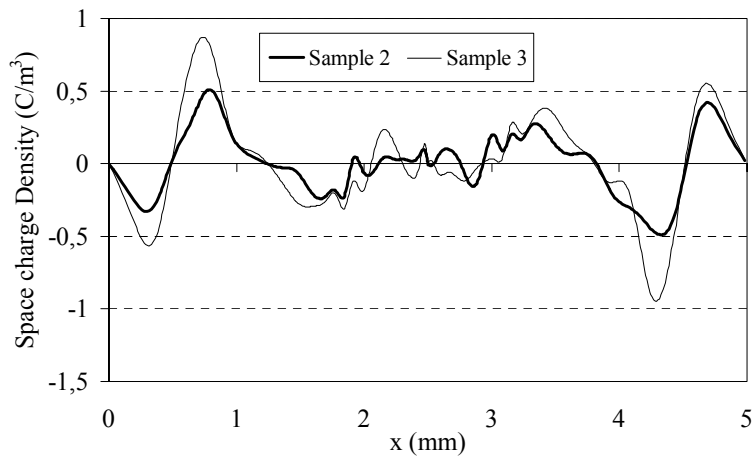
Figure 5. Space charge distributions throughout the samples 2 and 3 of PMMA.
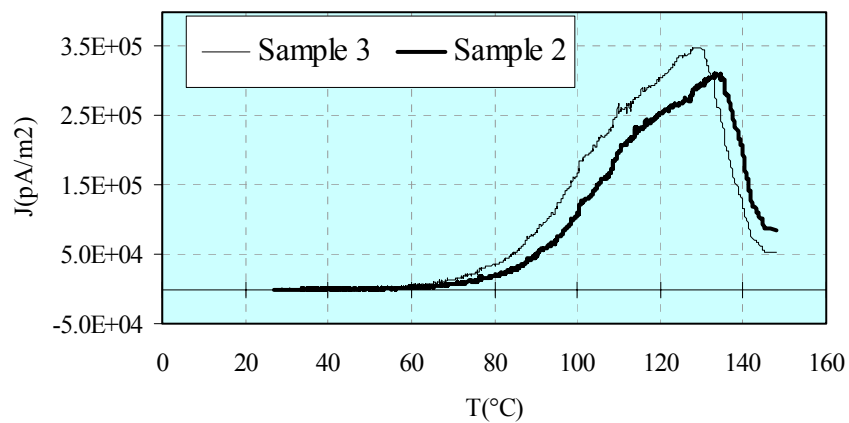
**Figure 6. TSDC curves in samples 2 and 3 of PMMA.**

Ageing effect

The samples 1, 2 and 3 were kept for one year on aluminium paper at room temperature, then they have been submitted again to the same poling conditions (4 kV/mm for 30 minutes at 90°C).

The distribution of charges in each aged sample, are given in Figures 7a, b and c, for comparison with the distributions in unaged samples. A remarkable decrease of the charge density in aged samples was observed, with a shape characteristic of polarization phenomenon.
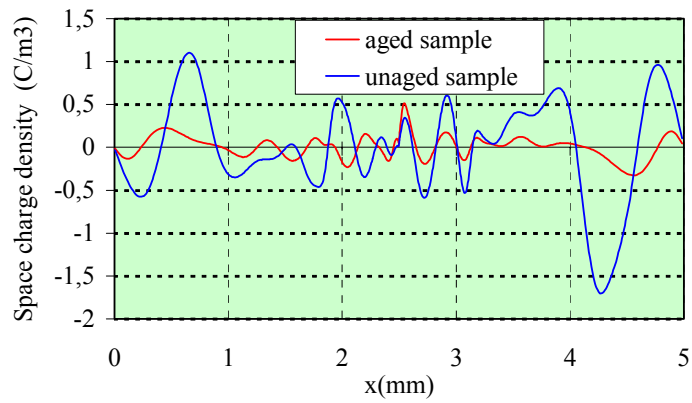
**Figure 7a. Comparison of space charge distributions in aged and unaged samples :
(a) samples 1, (b) samples 2, (c) samples 3.**
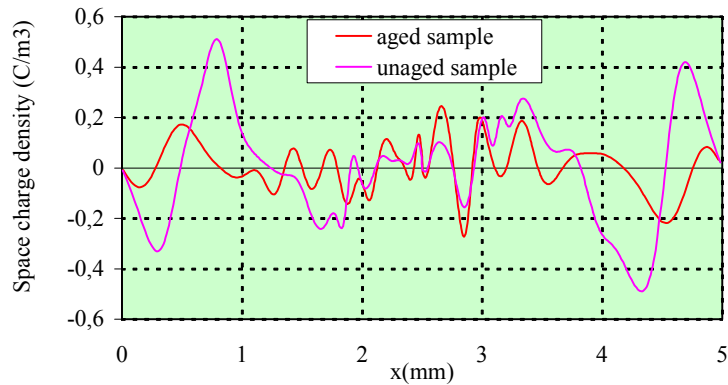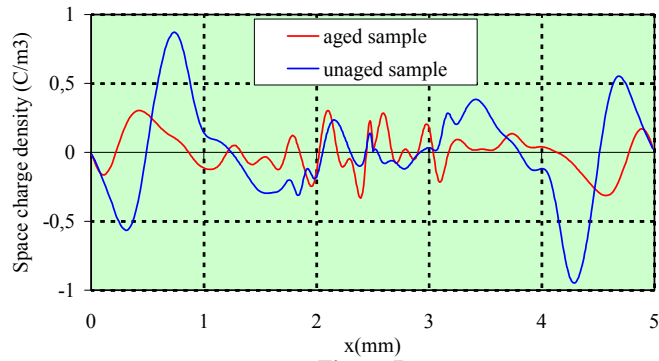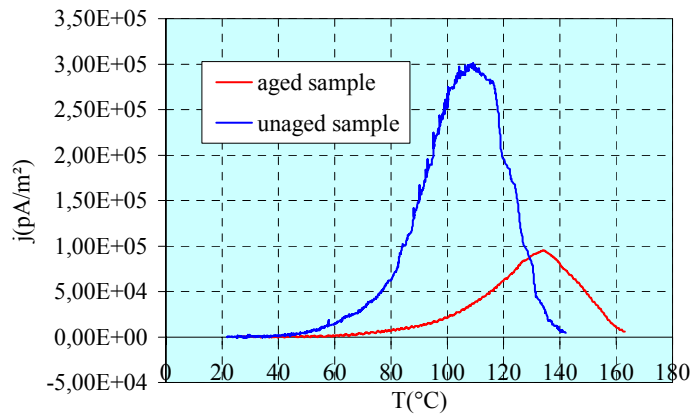

Figure 7b.

Figure 7c.

**Figure 8a. Comparative representation of TSDC currents in aged and unaged samples :
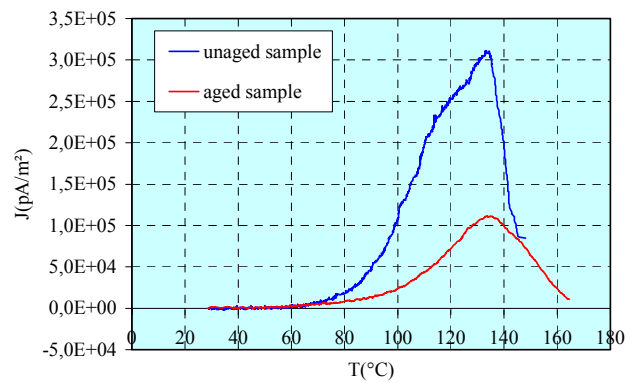(a) samples 1, (b) samples 2, (c) samples 3.**
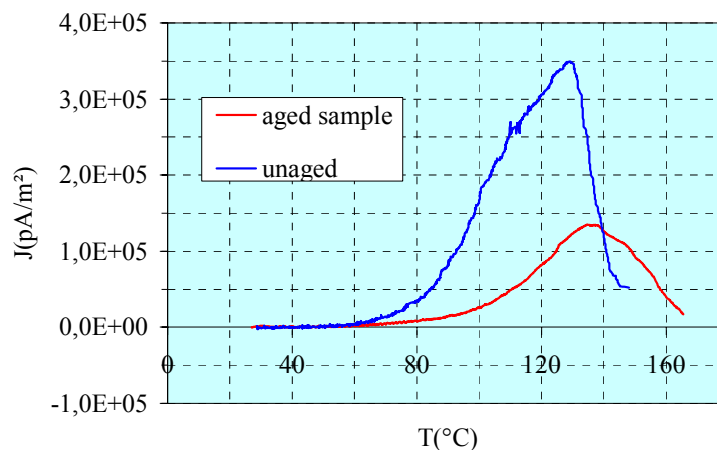

Figure 8b.

Figure 8c.

In order to explain this behaviour, we measured the TSDC current in aged samples was measured. Figures 8 a, b and c give the comparative representation of the TSDC current in aged and unaged samples. Two relevant facts can be noticed: a strong shift to higher temperature in the Tg value, with a strong decrease in the intensity of the α relaxation peak. This indicates that ageing process leads to an increase in activation energy of dipoles and a strong decrease in the number of dipoles which were oriented with the applied electric field. Since chain mobility increased at Tg , this behaviour is attributed to a stabilization of the chains. Thus, the chains are more stiff in aged samples.

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