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Study of poly(methyl methacrylate) relaxations by thermally stimulated depolarization currents and the thermal step method

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Abstract

A combined study of β' and α relaxations in poly(methyl methacrylate) (PMMA) by thermally stimulated depolarization currents and thermal step methods has been made. The use of null width polarization windows to form the electrets allows us to isolate the β' peak. The charge distribution profiles allow us to assign a polar orientational mechanism for the β' relaxation and in the case of the α peak a background polar mechanism over which a temperature-dependent injection and a conduction processes are overlapped. The charge distribution profiles observed by the thermal step method indicate that the increase of the conductivity observed in this material at temperatures just below the glass transition is mainly due to the positive carriers. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Thermal step; Thermally stimulated currents; Space charge

1. Introduction

The study of the charge of an electret which is produced during the polarization process may be carried out from two points of view: the energy distribution of the polarization mechanisms involved and the spatial distribution of the activated charge. A widely used technique to study the distribution in energies is the thermally stimulated depolarization current (TSDC) method [1–3]. Despite the experimental simplicity of the TSDC technique, the interpretation of the resulting spectra is not easy mainly because of two reasons.

One reason is that the charge produced during the polarization may be due to several microscopic processes (induced dipolar polarization, alignment of permanent dipoles, migration of ions or ionic vacancies and subsequent trapping, drift of electrons or holes and their trapping and charge injection from electrodes) [4]. The other reason is that the relaxation processes involved are not elementary as they cannot be generally described by means of a unique relaxation time: in most polymers they have to be described in terms of a distribution of relaxation times or of activation energies. Owing to these reasons two aspects must be considered when a material is studied by TSDC: the origin of the relaxations involved and their kinetic parameters. In order to elucidate the origin of a peak in the TSDC spectrum various methods have been developed. They are mainly related to the behavior of the peak as a function of the polarization parameters [5] and the nature of the electrode [6]. To resolve the structure of a distributed relaxation, the windowing polarization method (WP) can be applied. The WP method allows one to form electrets with an activated charge that is associated with a temperature range determined by the polarization temperature and polarization window width. This fact results in an easier interpretation of the TSDC peaks, as the relaxation processes are quasi non-distributed [7–12]. The differences between the conventional and the windowing polarization methods will be described in the experimental section.

In order to study the spatial distribution of the charge produced, several techniques have been developed [13–18]. Among them, the thermal step method (TS) must be pointed out because of its experimental simplicity and the measurement is non-destructive [15,19]. The charge distribution profile is obtained by means of the following process. The electret is short circuited through an ammeter and a sudden temperature variation is applied to one of its electrodes. The propagation of the thermal step through the sample induces a thermal volume variation which modifies the image charges on the electrodes and, consequently, a

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current is measured. This current is given by:

$$I(t) = -\alpha C \int_0^d E(x) \frac{\delta T}{\delta t} \mathrm{d}x, \tag{1}$$

where C is the sample capacitance, d is the sample thickness, $E(x)$ is the electric field in the sample, and $\alpha = \alpha_x - \alpha_\varepsilon$, with α_x the linear dilatation coefficient of the material and α_ε the temperature coefficient of permittivity.

Recently most interest in the electrical properties of poly(methyl methacrylate) (PMMA) has arisen because of the use of this material as host polymer in guest–host polymeric systems in non-linear optics [20,21]. The TSDC spectrum of PMMA electrets show three relaxations at temperatures above room temperature [22,23]. Only two of them which appear at higher temperature show well defined peaks. In the sense of increasing temperatures they are named β', which has also been observed by a.c. measurements and by dilatometric measurements [24] and has been associated with the presence of heterotactic sequences in conventional PMMA [23]; α, which is related to the glass transition, and ρ. The mechanisms that cause the two lower temperature relaxations have been related to uniform mechanisms, and specifically the α relaxation to microscopic displacements of ions which are eventually trapped [22]. The mechanism of the ρ peak is related to space charge polarization [22,25–27]. The influence of the tacticity of PMMA on TSDC spectra was studied by Sauer and Kim [28]. They showed that atactic PMMA samples had a higher glass transition temperature and that the presence of isotactic sequences contributed to the broad glass transition, extending almost 90°C below the main glass transition, in atactic PMMA. In a recent article [29] a combination of the TSDC and the probe techniques has been used to determine the potential distribution below the glass transition. This potential distribution is used to determine the current–voltage characteristics, which results to show a sub-ohmic character ($J = gV^n$, where $n < 1$ and $g =$ constant).

In the temperature range considered in this article, the proposed relaxation mechanisms are uniform, and may be due to dipole relaxation or to migration of ionic charge carriers. If a non-distributed relaxation process is assumed, both relaxation processes can be described by similar equations for the depolarization current density. The equation, which was introduced by Bucci et al. [30,31] who called their method ionic thermocurrent (ITC), is:

$$J(T) = A\exp\left(\frac{-E_\mathrm{a}}{\mathrm{k}T}\right)\exp\left(\frac{-B}{v}\int_{T_0}^{T}\exp\left(\frac{-E_\mathrm{a}}{\mathrm{k}T'}\right)\mathrm{d}T'\right), \tag{2}$$

where E_a is the activation energy, k the Boltzmann constant, v the heating rate (which is supposed constant), T the absolute temperature and T_0 the initial temperature of the TSDC discharge. In the case of the dipole relaxation the constants A and B are:

$$A = \frac{P_0}{\tau_0} = \frac{N\mu^2 E_\mathrm{p}}{3\mathrm{k}T_\mathrm{p}\tau_0}, \tag{3}$$

$$B = \tau_0^{-1}, \tag{4}$$

where τ_0 is the pre-exponential factor in an Arrhenius type relaxation time and P_0 is the total polarization achieved, which can be expressed in terms of the dipole number per volume unit N, their dipolar moment μ, the applied field E_p and the polarization temperature T_p by means of the Langevin law with the approximation $\mu E_\mathrm{p} \ll \mathrm{k}T$. In the case of ionic charge relaxation these constants are:

$$A = \frac{\sigma_0 Q_0}{\varepsilon_\mathrm{r}\varepsilon_0}, \tag{5}$$

$$B = \frac{\sigma_0}{\varepsilon_\mathrm{r}\varepsilon_0}, \tag{6}$$

where Q_0 is the image charge induced on the sample electrode, σ_0 is the pre-exponential factor in an Arrhenius type conductivity, and ε_0 and ε_r are the vacuum and relative permittivities respectively.

The aim of this article are to show how the high resolution possibilities of TSDC combined with the WP technique allows one to isolate the β' and α relaxations in order to study their kinetic parameters and in contrast, to show how the combined study by TSDC and TS methods can help to determine the origin of these two relaxations and to obtain a better knowledge of the electrical properties of PMMA at temperatures below the glass transition.

2. Experimental

2.1. Material

Measurements were carried out on samples of commercial PMMA (Altuglas®), which were cut from sheets of 1.5 mm thickness. DSC measurements resulted in a glass transition temperature $T_\mathrm{g} \approx 120$°C. It can be inferred from the relatively high glass transition temperature that the material used was atactic PMMA [24,28]. The samples were provided with aluminum electrodes of 3 and 4 cm diameter on both sides by vaporization in vacuum.

2.2. TSDC measurements

The experimental set up is composed of a Heraeus air forced oven, controlled by an Eurotherm model 818 temperature programmer. The current was measured by a Keithley 616 digital electrometer. Temperature and current data were collected by an A/D converter card in a computer and they were processed afterwards.

The polarization of the samples was carried out by conventional polarization and windowing polarization methods. The conventional method consists of applying an electric field E_p at a temperature T_p (polarization temperature), for a time t_p (isothermal polarization time), and the sample is then cooled down to a temperature T_f while the electric field remains applied. The sample is stored

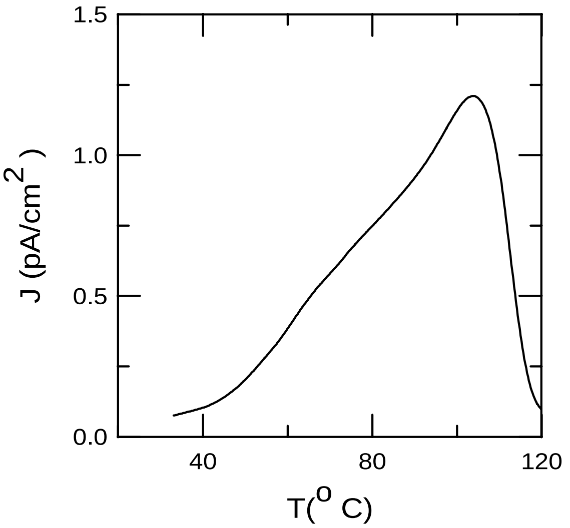

Fig. 1. TSDC of a conventionally polarized PMMA electret. Polarization parameters: $T_p = 100$°C, $t_p = 2$ min, $V_p = 2$ kV.

for a time t_d and then depolarized during heating while it is short circuited through an ammeter, and the current is recorded as a function of temperature. In the WP method the polarizing field is applied during the isothermal step and at the beginning of cooling step. The temperature range between T_p and T_{off}, the temperature at which the polarizing field is switched off, determines the polarization window width. In our case the polarization window width values chosen were zero and 10°C.

The data collected was fitted to Eq. (2). The fitting processes were performed by multidimensional χ^2 function minimization, with P_0 (or Q_0 for ionic peaks), τ_0 (or $\varepsilon_0\varepsilon_r/\sigma_0$ for ionic peaks), and E_a as variable parameters, using software developed in our laboratory, which is based on routines described by other authors [32]. As the formal covariance matrix that comes out of a χ^2 minimization has meaning only if the measurement errors actually are normally distributed [32], in our case no meaningful confidence limits can be given for the model parameters estimated. Owing to this, comparisons between calculated and experimental data will be given as an indication of the fitting accuracy.

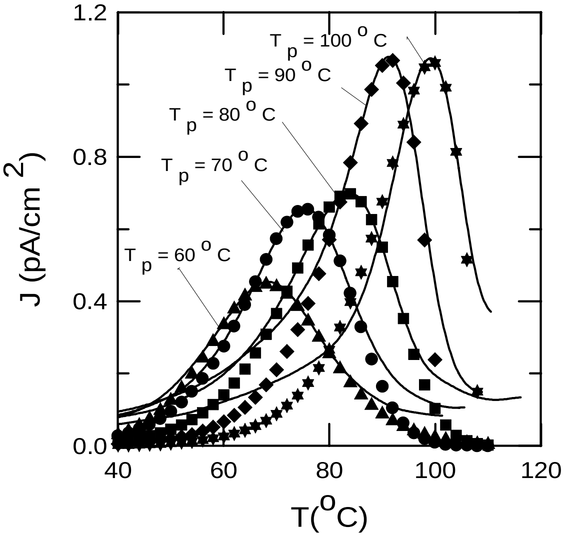

Fig. 2. TSDC of windowing polarized PMMA electrets. Polarization parameters: $t_p = 2$ min, $V_p = 2$ kV, T_p as indicated in the figure, polarization window width 10°C. (Continuous lines: experimental curves; Symbols: calculated values.)

2.3. TS measurements

Previously to the thermally stimulated depolarization of the samples, the charge distribution profile was determined by the thermal step method. The experimental set up has been previously described [15]. The thermal step applied was −40°C. The current was amplified and recorded in a computer as a function of time and the electric field was obtained afterwards by deconvolution of the signal. The numerical treatment has been described in detail in a previous article [33]. Finally, the charge distribution profile was obtained by taking the derivative of the calculated electric field:

$$\rho(x) = \varepsilon_0 \frac{dE(x)}{dx}.$$

3. Results and discussion

The TSDC spectrum for temperatures above room temperature of a conventionally polarized PMMA electret can be seen in Fig. 1. The polarization conditions have been chosen so that only the relaxations β' and α are evident, and both appear overlapped so that β' does not show an apparent peak. This spectrum was resolved by windowing polarization using 10°C width polarization windows and the resulting spectra can be seen in Fig. 2 (continuous line). As these polarization windows are regularly spaced, it can be noted that there is a different behavior between those discharges that correspond to the three lower polarization temperatures and the ones that correspond to the higher polarization temperatures.

Previous to the depolarization, the space charge distribution was studied by the TS method. The resulting charge distribution profiles can be seen in Fig. 3. We see that the resulting distributions are approximately symmetric for polarization temperatures up to 80°C, but above this temperature the asymmetry between the anodic and the cathodic zones increases.

The activation energies of the WP formed electrets have been determined by the initial slope method and by fitting the experimental curve to the Bucci and Fieschi equation. A comparison between the experimental and calculated curves can be seen in Fig. 2. The activation energy values have been plotted as a function of the polarization temperature in Fig. 4. It can be seen that for T_p below 80°C there is an evident difference in value and in trend between the values

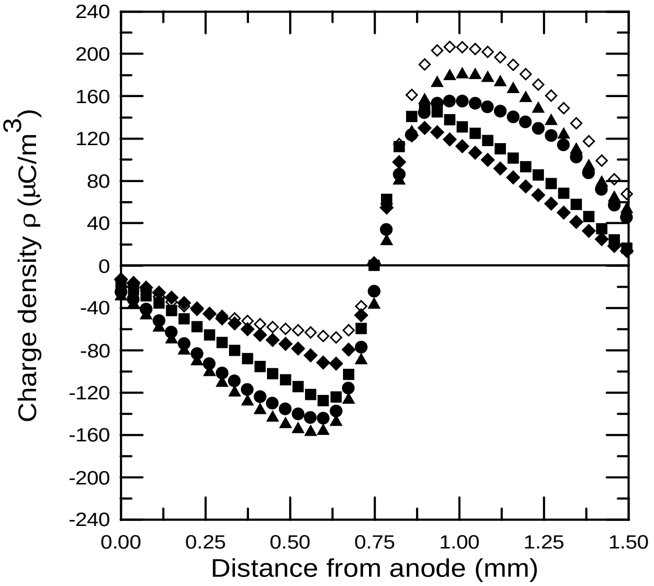

Fig. 3. Space charge distribution profiles of the electrets whose discharges are represented in Fig. 2. They were measured before the stimulated depolarization. Polarization temperatures: ▲ (60°C); ● (70°C; ■ (80°C); ◆ (90°C); ◇ (100°C).

calculated by these methods, but for T_p above this temperature they show a similar trend and eventually they result in similar values for the highest polarization temperature used.

These results are compatible with the existence of two overlapped relaxations in the temperature range studied. The differences in the calculated activation energies can be explained by the different methods used to determine them. In the case of the initial slope method, only the current that corresponds to the low temperature tail of the discharge peak is taken into account, in which the contribution of the β' relaxation which appears at lower temperature is more relevant. In the curve fitting method the whole peak is used so that, if within the peak the response of different mechanisms are overlapped, the values obtained will be affected as they are fitted to a model which assumes an unique relaxation time, and therefore an unique relaxation mechanism. In this sense the behavior may be interpreted as follows: the activation energies obtained by the initial slope method for the lower polarization temperatures are more realistic as they are less affected by the response of the α relaxation in the high temperature portion of the peak. In the case of the highest temperature window, the values obtained by both methods are similar because only the α relaxation mechanism is activated as the polarization temperature range is

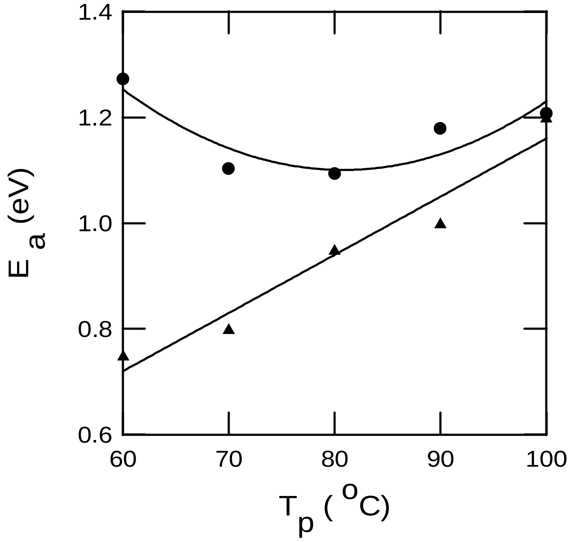

Fig. 4. Activation energies as a function of the polarization temperature. Calculation method: ▲ initial slope; ● curve fitting to the Bucci–Fieschi equation.

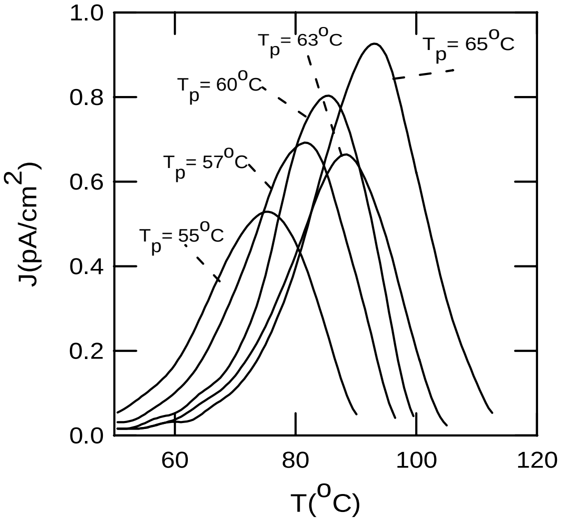

Fig. 5. TSDC of PMMA electrets polarized by a windowing method. Polarization parameters: $t_p = 2$ min, $V_p = 4$ kV, T_p as indicated in the figure, polarization window width 0°C.

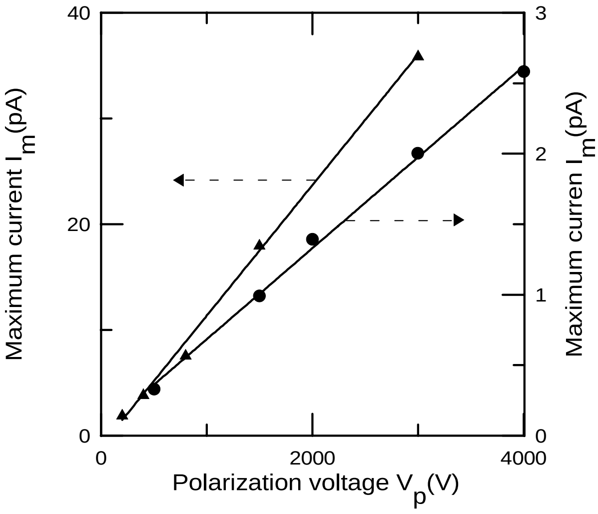

Fig. 6. Maximum current as a function of the applied voltage. Polarization parameters: $t_p = 30$ min; T_p: ● (60°C); ▲ (112°C).

higher than the temperatures for which the β' relaxation is activated in WP electrets.

The effect of the polarization window width can be explained by comparing Fig. 2 and 5. These discharges correspond to electrets formed for 10°C and zero polarization window width, respectively. In the first case only a difference in global behavior is evidenced, as has been previously stated. When a zero window width is used, it can be seen that the height of the maxima increases, it is a maximum for $T_p = 60°C$, then it decreases and finally it rises again, which corresponds to the emergence of α relaxation. This means that there is an optimal polarization temperature T_{po} [5] for which the polarization induced in the sample is maximum for a given polarization mechanism. In our case this temperature corresponds to the temperature at which the mechanism that causes β' is most evident. For higher polarization temperatures, and if the windowing polarization technique is applied, this mechanism is less activated during the polarization and it eventually vanishes, while the contribution of the mechanism that causes α relaxation becomes increasingly important.

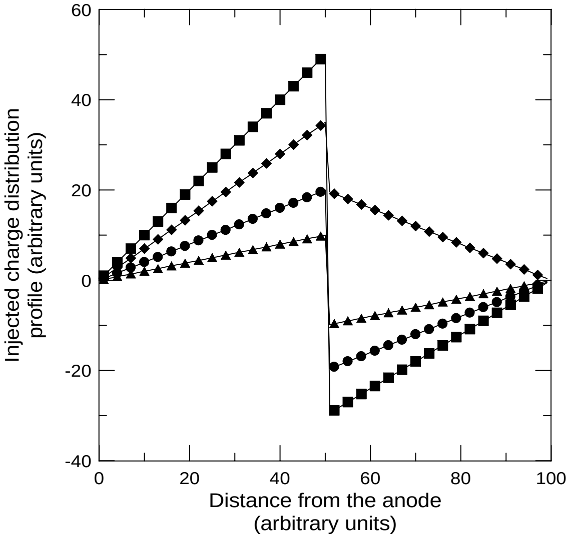

Fig. 7. Idealized profiles of charge injected from electrodes. ▲ (T_1); ● (T_2); ■ (T_3); ◆ (T_4). $T_1 < T_2 < T_3 < T_4$. The profile corresponding to T_4 shows a sharp increase of charge injection from the anode and positive carriers diffusion through the sample.

To explain the origin of these relaxations, the intensities of the maxima have been plotted as a function of the polarizing field for two polarization temperatures: 60°C and 112°C, which correspond to temperatures at which one expects to activate mainly the β' or the α mechanism, respectively (Fig. 6). In both plots a linear correlation is observed so that the mechanisms that gives rise to each relaxation are uniform. Despite this similar behavior observed in the TSDC study, they have to be different in nature because the charge profiles observed by the TS method in the temperature range of each relaxation are quite different: symmetric profiles in the case of β' mechanism and an asymmetric one in the case of α.

This difference can be explained if one assumes that the mechanism that causes β' is due to orientation of the molecular dipoles, so that a symmetric charge distribution profile is expected. In the case of the α relaxation to a combined polar and free charge mechanism. For temperatures above 60°C, charge injection from both electrodes becomes increasingly important. This effect is simulated in Fig. 7 in which we show idealized profiles of injected charge distribution in the material with a larger charge injection for increasing temperatures. In the case of the profile corresponding to the higher temperature, we have assumed that charge injection from the anode becomes much bigger than cathodic injection and also that positive carriers diffuse through the sample resulting in an excess of positive carriers. It can be seen in Fig. 8 that the addition of the idealized injected charge distribution profiles added to a polar symmetric profile results in a behavior that corresponds to our measurements. The temperature at which this effect takes place is approximately 90°C, which is in good agreement with the resistivity of PMMA which exhibits a noticeable decrease above this temperature [34]. Thus, we can say that in PMMA the α peak is due to a background polar relaxation mechanism over which a free charge contribution becomes increasingly important with temperature as a result of the increasing injection from the electrodes and increasing conductivity. Finally, it must be pointed out that in the temperature range just below the glass transition of this material, the increase of the conductivity is associated with the positive carriers.

The evidence of space charge in the charge distributions profiles stands in contradiction to the linearity of the current maxima with the polarization field which has been previously stated. The current maximum is proportional to the value of the initial polarization P_0 of the sample. However, the charge density measured by the thermal step

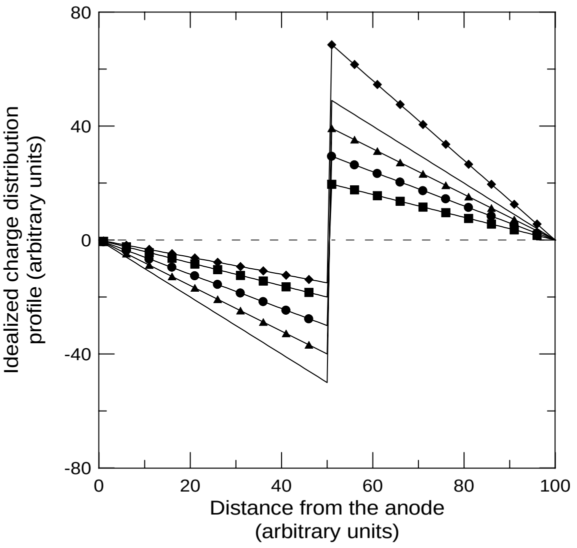

Fig. 8. Profiles resulting from the addition of the idealized profiles of Fig. 7 to a polar symmetric profile (continuous line without symbols). The symbols are as indicated in Fig. 7.

method is the total density (free plus bounded charge density):

$$\rho(x) = \rho_\mathrm{f}(x) + p_\mathrm{b}(x) = p_\mathrm{f}(x) - \frac{\mathrm{d}P(x)}{\mathrm{d}x}. \qquad (7)$$

In the case of a sample with a great value of the polarization, but nearly homogeneous, a small quantity of free charge may become comparable to the derivative of the polarization, but its contribution to the total current should be masked by the large contribution of dipoles to the depolarization current. Therefore, the aforementioned contradiction can be explained if one assumes that the space charge contribution to the total depolarization current is very small compared to the dipole contribution, but the polarization in the sample is very homogeneous (inhomogeneity may be mainly due to differential cooling rates between zones close to the surface and the bulk of the samples).

Measurements of time lags in the impulse voltage breakdown in a PMMA whose T_g is approximately the same as in our case [35] show that there is change in the trend of the field required to attain a 50% probability of breakdown in the temperature range at which we observe a most significant injection from anode. A significant reduction of the breakdown field required is observed for temperatures above 80°C which is attributed to anodic injection [36]. Measurements of charge distribution profile in PMMA by the electrically stimulated acoustic wave method [37] show that also a net charge located in the vicinity of the poling anode is observed in some cases, and it becomes most significant at 90°C. But in this case the charge observed is negative. However, the poling conditions used by Bernstein and Cooke differ from that of ours. In their case the anode was grounded during the polarization whereas in our case that cathode was the grounded electrode. Moreover, their poling process was conventional, i.e. the voltage was applied throughout the thermal transition periods. In our case the windowing polarization method was used, i.e. the electric field was applied during the isothermal polarization step and a short thermal interval (10°C) at the beginning of the cooling. After the field is removed the cooling process follows up to room temperature. In our material also a net negative charge has been observed in the case of a conventional poling of the sample followed by a peak cleaning process to avoid the dipolar response, but it was used a higher polarization temperature (130°C) [19].

4. Conclusions

The combined use of TSDC and TS in the study of electrets results in complementary information on the electret charge distribution: the energetic and spatial distribution of charges. This combined study allows us to explain the mechanism of the polarization in the material. The use of zero width polarization windows enhances the sensitivity of TSDC and enables us to resolve the structure of distributed and overlapped relaxations.

In the case of PMMA these methods combined allow us to assign a dipole orientation mechanism for the β' peak and a background polar mechanism with a free charge contribution overlapped with it in the case of the α peak. The increase of the conductivity in PMMA at temperatures just below the glass transition of this material is mainly due to the positive carriers in the material.

Acknowledgements

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