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Polymer 40 (1999) 2659–2665

polymer

Windowing polarization: considerations for the study of the space charge relaxation in poly(methyl methacrylate) by thermally stimulated depolarization currents

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Received 22 September 1997; revised 9 June 1998; accepted 16 June 1998

Abstract

The windowing polarization technique is an electret formation method which has been widely used to study the structure of polar relaxations in polymers. In this paper we have studied the effect of some polarization parameters to extend the applicability of this method to the explanation of space charge relaxation in poly(methyl methacrylate). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: PMMA; Space charge; Fractional polarization

1. Introduction

Thermally stimulated depolarization currents (TSDC) is an experimental method which has proved to be useful in the study of relaxation phenomena in polymeric materials. It has been used to study molecular motions [1,2] and structural relaxations [3,4]. This method is applied to electrets, which are dielectric materials that after combined thermic and electric treatment retain long lasting polarization. A classical TSDC study of an electret can be described as follows: the electret is formed in a sandwich configuration (electrode–dielectric–electrode), after which it is heated at a constant rate while being short-circuited through an ammeter. The depolarization current is recorded as a function of the temperature, and the relaxation processes can be seen as current peaks in the curve that reflects the TSDC spectrum. The electret formation and subsequent TSDC discharge have been widely described in the literature [5,6]. This method is equivalent to dielectric loss measurements at a very low frequency (approximately 10^{-3} Hz) [7].

Despite the apparent experimental simplicity of the TSDC technique, interpretation of the resulting spectra is not simple for two main reasons. The first is that the charge activated during the polarization can be due to several microscopic processes (induced dipole polarization, alignment of permanent dipoles, ion or ionic vacancy migration and subsequent trapping, drift of electrons or holes and their trapping, excess charge injection from electrodes) [8]. The other reason is that the relaxation processes are not elementary as they can not be generally described by a unique relaxation time, and therefore have to be interpreted by means of a relaxation-time distribution (when an Arrhenius-like dependence on the temperature is assumed, such a distribution can be related to both the pre-exponential factor and the activation energy). Therefore, two aspects must be considered in the study of a dielectric material by TSDC: the physical mechanisms that originate the relaxation processes and the determination of the kinetic parameters of those processes. In order to determine the origin of a peak in the TSDC spectrum, some methods have been developed. They are based on the behavior of the peak as a function of the electrode nature [7,9] and the polarization parameters [10]. Another method is the windowing polarization technique (WP), used to resolve the complex TSDC spectrum into elementary spectra well approximated by a unique relaxation time. This technique has been applied, with some differences, since the 1970s by different authors, which has resulted in different denominations [11–17]. In this paper we have applied the WP technique to activate the space-charge relaxation in a way that, restricted by the experimental bounds, the distribution effects are the least evident as possible. The space-charge response of poly(methyl methacrylate) (PMMA) electrets formed by WP have been fitted to models that consider a unique relaxation time and reasonable results have been obtained in the case of the general order kinetics model [18].

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PII: S0032-3861(98)00505-9

In the general order kinetics model [19], the current intensity is assumed to follow the empirical equation:

$$I = -\frac{dn}{dt} = s_0{}'n^b \exp\left(-\frac{E_a}{kT}\right) \tag{1}$$

where n is the trapped charge at time t, E_a is the activation energy (the depth of the trapping sites in this model), T is the absolute temperature, k is the Boltzmann constant, $s_0{}'$ is a pre-exponential factor of units $C^{(1-b)}s^{-1}$, and b is the kinetic order, an empirically determined parameter. In the case of a constant heating rate β, the solution of this equation (for $b \neq 1$) is:

$$I = s_0 n_0 \exp\left(-\frac{E_a}{kT}\right) \times \left(\frac{(b-1)s_0}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E_a}{kT'}\right)dT' + 1\right)^{\frac{-b}{(b-1)}} \tag{2}$$

where n_0 is the initial trapped charge and $s_0 = s_0{}'n_0^{(b-1)}$ is a frequency factor. Although this equation is not valid for the case $b = 1$, it reduces to the Randall and Wilkins equation [20] in the limit b tending to 1 (first order kinetics, which is valid in the case where recombination is the most likely relaxation process). In the case of $b = 2$, this equation reduces to the Garlick and Gibson equation [21] (second order kinetics, which is valid in the case of a strong retrapping probability). In spite of cases of b different to 1 or 2 not having correspondence with physical reality, this equation can describe a wider variety of kinetic phenomena, and the activation energy calculated using this model is very close to its true value [22]. In this paper we have made a study of the effect of parameters that determine the electret formation by WP, such as the polarization window width and the cooling rate, in order to extend the applicability of this technique to the study of relaxation of the space charge in PMMA. The relaxation kinetic parameters have been studied by means of fitting the resulting depolarization current to the general order kinetics model.

2. Experimental procedure

2.1. Material

Samples were cut from commercial PMMA sheets (ALTUGLASS®) of 1.5 mm thickness. Circular aluminium electrodes of 2 cm diameter were vaporized in vacuum on both sides of all samples.

2.2. Experimental apparatus

The experimental set-up consists of a measuring cell placed in an air-forced Selecta oven, modified to be controlled by an Eurotherm model 818 temperature programmer. Current was measured by a Keithley 610C electrometer. Current and temperature data were collected in a computer by a PCLAB 814B A/D converter card and later computer processed.

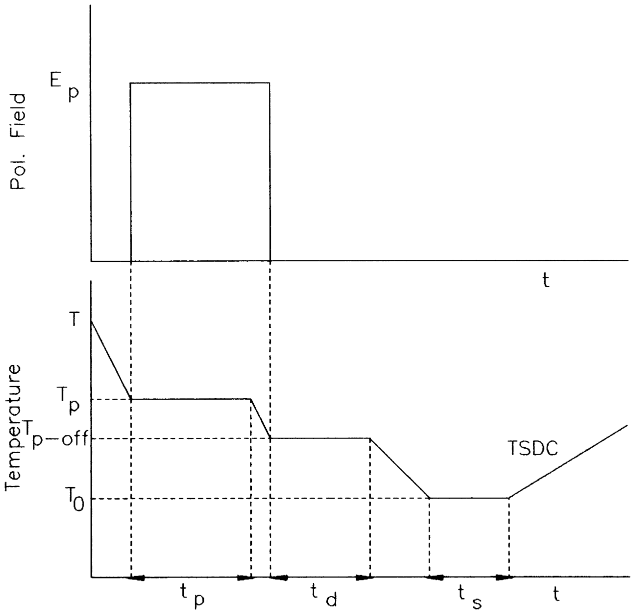

Fig. 1. Thermic and electric treatments to form electrets by windowing polarization.

2.3. Polarization technique

The WP technique was used to polarize the samples. The differences between the conventional polarization method and the WP technique can be explained by means of Fig. 1. In the case of the conventional polarization process, the polarizing field is applied during the isothermal polarization and during the whole cooling process (non-isothermal polarization), which does not produce the step shown in the figure and consists of a monotonous temperature decrease down to T_0. It is obvious that the charge activated by this process is related to a wide temperature range. In the case of a WP process (shown in Fig. 1) the field is applied during the isothermal polarization time t_p and only over a short temperature range $\Delta T_w = T_p - T_{p\text{-off}}$ during the cooling time. This temperature range determines the window width, usually less than 10°C. Some authors keep the sample stored at the temperature $T_{p\text{-off}}$ for a time t_d. Then the sample is cooled down to the temperature T_0 and stored at this temperature for a time t_s before the TSDC discharge. Windowing polarization has proved to be useful for studying the structure of complex TSDC peaks and also for separating partially overlapping relaxations in some cases [23].

In our case, several window widths were used ($0 \leq T_p - T_{p\text{-off}} \leq 20$°C), and no intermediate storage time was applied ($t_d = 0$). Heating and cooling processes were performed at a rate of 2.5°C/min unless another value is specified.

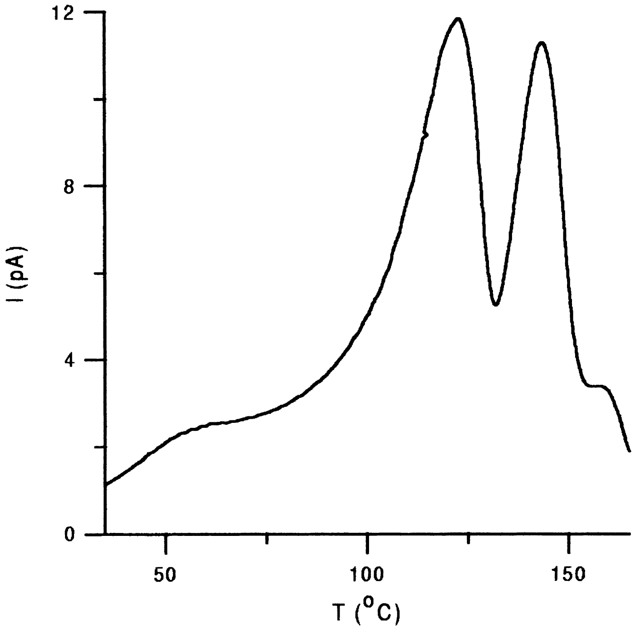

Fig. 2. TSDC discharge of a conventionally polarized PMMA electret. Polarization parameters: $T_p = 135°C$, $V_p = 500$ V, $t_p = 45$ min, $T_0 = 30°C$, $t_s = 5$ min.

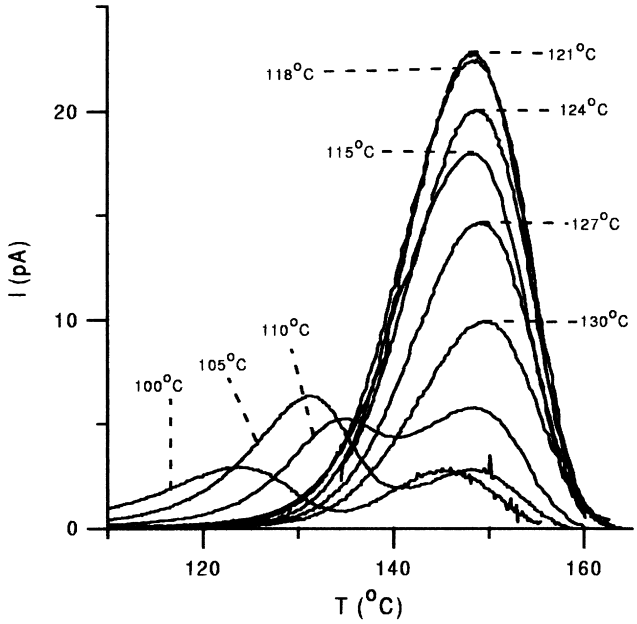

Fig. 3. TSDC discharges of windowing polarized PMMA electrets. Polarization parameters: T_p as indicated in the figure, $V_p = 5000$ V, $t_p = 15$ min, $T_0 = 80°C$, $t_s = 2$ min, $\beta = 5°C/min$, window width $\Delta T_w = 0$.

2.4. Data modelling

Collected data (current versus temperature) were fitted to the general order kinetics equation. The fitting processes were performed by multidimensional χ^2 function minimization with n_0, s_0, E_a and b as variable parameters, and using software developed in our laboratory, based on routines described by other authors [24]. As the formal covariance matrix produced by a χ^2 minimization has meaning only if the measurement errors are normally distributed [24], no meaningful confidence limits on the estimated model parameters can be given in our case. Because of this, some comparison examples between calculated and experimental data will be given as examples of the fitting accuracy.

3. Results

The discharge by TSDC of a conventionally polarized PMMA electret for temperatures above room temperature is shown in Fig. 2. In this figure, four peaks can be noted. At approximately 60°C appears β' peak, which has also been detected by AC and dilatometric measurements and has been associated with the presence of heterotactic sequences in conventional PMMA [25,26]; at about 120°C appears α peak, which is related to the glass transition in the material [27]; at approximately 140°C appears ρ peak, which is related to the relaxation of space charge in the material [28,29], and, finally, at approximately 160°C can be seen a peak which is related to a liquid–liquid transition [16].

Discharges of electrets polarized by WP at several polarization temperatures in the range over which ρ relaxation is evident are shown in Fig. 3. It can be seen that for polarization temperatures up to 110°C the mechanisms responsible for α and ρ peaks are activated. For polarization temperatures above this temperature, α peak is successively less activated and finally (for $T_p \geq 115°C$) only ρ peak is evident. It can be also noted that the maximum current of the peaks reaches a maximum value for $T_p \approx 121°C$, which is the optimal polarization temperature, T_{po}. The presence of optimal polarization temperatures has been studied in other materials [10]. In the case of space charge relaxation in PMMA, it has been related to the distribution of trapping levels [18]. The temperature at which the maximum appears, T_m, shifts to slightly higher values with T_p.

The effect of the polarization window width on the space charge peak can be seen in Figs 4 and 5. In the case of Fig. 4, the polarization temperature was $T_p = 125°C$ and it can be seen that the increase of the window width results in a slight increase in the peak area and also in its maximum height. When the window width is 10°C or larger, then the presence of α relaxation is quite evident. On the other hand, when the polarization temperature was 135°C (Fig. 5), the changes in the shape of ρ peak with the window width are more evident: a large increase in the height and area can be noted, and only for the largest value of the window width used ($\Delta T_w = 20°C$), α peak is observed as a shoulder in the rise of ρ peak. In both figures it can be noted that the most significant differences occur on the lower temperature tail of the peak.

The effect of the cooling rate was studied in the case of electrets polarized using null window width and cooled at rates of 1, 2.5 and 5°C/min (Fig. 6). We can observe that when the cooling rate is increased there is a significant

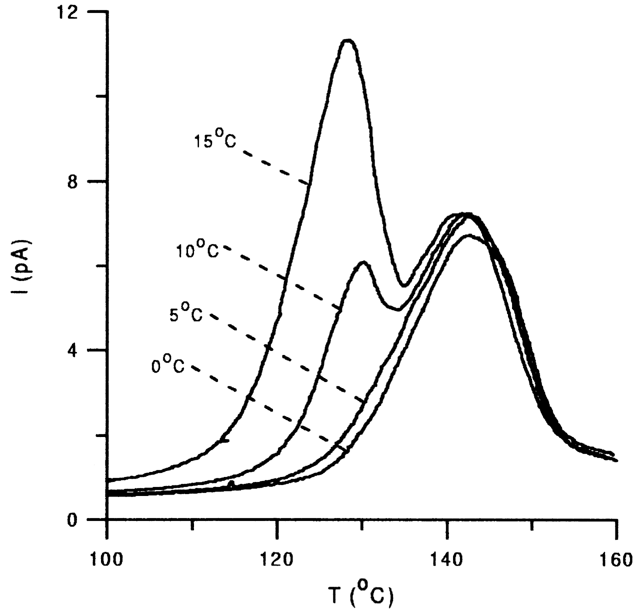

Fig. 4. Effect of the polarization window width on the TSDC discharge of PMMA electrets formed by WP. Polarization parameters: $T_p = 125°C$, $V_p = 1000$ V, $t_p = 40$ min, $T_0 = 100°C$, $t_s = 5$ min, $\beta = 2.5°C/min$, window width ΔT_w as indicated in the the figure.

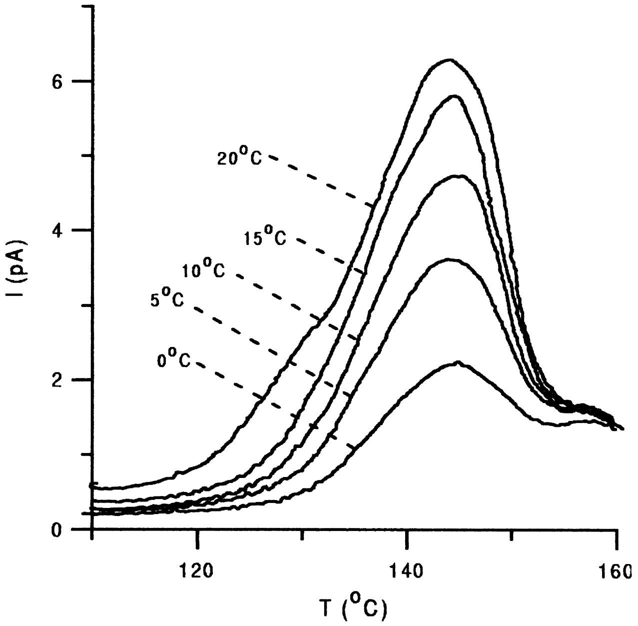

Fig. 5. Effect of the polarization window width on the TSDC discharge of PMMA electrets formed by WP. Polarization parameters: $T_p = 135°C$, $V_p = 1000$ V, $t_p = 40$ min, $T_0 = 110°C$, $t_s = 5$ min, $\beta = 2.5°C/min$, window width ΔT_w as indicated in the figure.

increase in the peak area and height. This can be explained by relaxation of charge during cooling. Since a relaxation time characterizes the carrier detrapping process and this time decreases with temperature, there are a significant number of carriers which become detrapped during cooling if a low rate is used. This fact is due to the longer time that the sample is subjected to temperatures close to the polarization temperature, that is, temperatures for which the involved polarization–depolarization processes have similar relaxation times.

The application of the windowing polarization technique results in quasi-non distributed peaks, so that interpretation of the resulting spectra is easier than the depolarization discharge which is obtained from a conventionally polarized electret [18,23]. We have fitted the discharges resulting from several polarization window widths in the case of $T_p = 135°C$ (Fig. 5) to the general order kinetics model. The effect of the window width on the kinetic parameters can be seen in Table 1. Two comparisons between the experimental and calculated data are shown in Fig. 7.

It can be noted that the initial trapped charge, n_0, increases with the window width, which is consequent on the behavior explained above, as the area of the peak is proportional to the total released charge. In the case of the activation energy, we can see that there is a decrease in its value as ΔT_w increases, but for $\Delta T_w = 15°C$ it increases again. For this value it can be seen in Fig. 7 that the calculated values only fit well on a short interval around the peak maximum. We can say that the fitting process is not accurate in this case because the fitted curve does not correspond to a non-distributed peak (the polarization window is wide and the distribution effects become evident). We think that this last value must not be considered correct, as a non-distributed relaxation cannot be assumed in the case of a wide polarization window and the calculated value of the activation energy resulting from the proposed model is not precise. If the activation energy value corresponding to $\Delta T_w = 15°C$ is neglected for the aforementioned reason, one observes a decrease in the value of the activation energy with increasing ΔT_w.

The behavior of the TSDC space charge relaxation in PMMA can be explained by the existence in the material of trapping sites distributed in depth with a maximum number of trapping sites at a certain depth (Fig. 8). When the

Table 1
Kinetic parameters obtained by fitting TSDC curves shown in Fig. 5 to the general kinetic-order model as a function of the window width (ΔT_w)

ΔT_w (°C)	n_0 (nC)	E_a (eV)	s_0 (s^{-1})	b
0	1.08	2.52	1.69×10^{28}	1.54
5	1.68	2.43	1.84×10^{27}	1.31
10	2.09	2.10	1.62×10^{23}	0.89
15	2.22	2.41	9.93×10^{26}	0.90

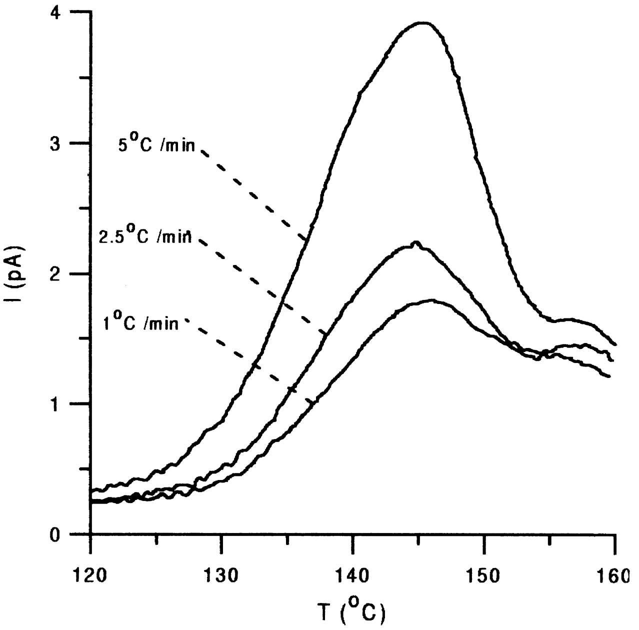

Fig. 6. Effect of the cooling rate on the TSDC discharge of PMMA electrets formed by WP. Polarization parameters: $T_p = 135°C$, $V_p = 1000$ V, $t_p = 40$ min, $T_0 = 110°C$, $t_s = 5$ min, $\Delta T_w = 0$, heating rate $\beta = 2.5°C/min$, cooling rate as indicated in the figure.

windowing polarization technique is used to form the electrets, only the fraction corresponding to the range of trapping depths ΔE_a is filled with carriers which are not in thermic equilibrium due to the effect of the electric field during the polarization process. This fraction is dependent on the polarization temperature and the window width. These carriers, not in equilibrium, are the ones that originate the depolarization current when they are thermally stimulated

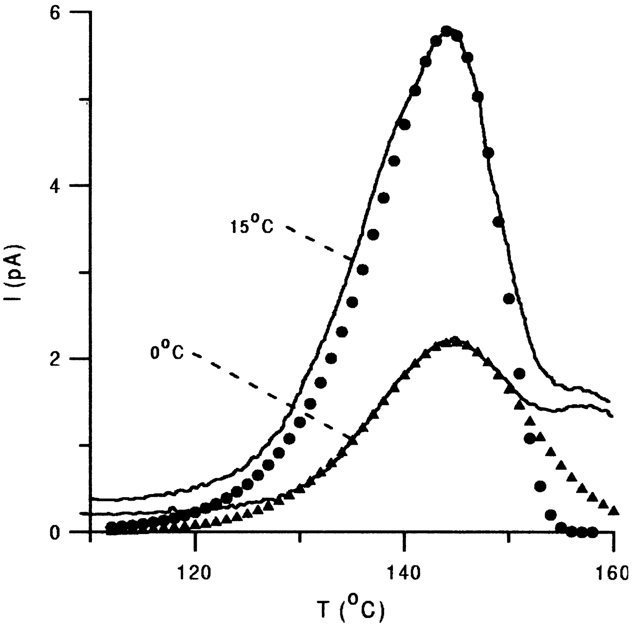

Fig. 7. Examples of curves fitted to discharges plotted in Fig. 5.

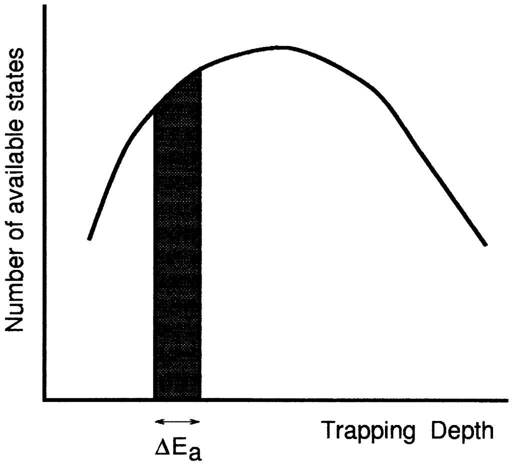

Fig. 8. Sketch of the trapping levels distribution proposed.

to relax to the equilibrium state, which corresponds to a depolarized sample. In the case of a null-width polarization window, the range of trapping depths ΔE_a is centered at increasingly deeper trapping levels when the polarization temperature is increased. This is due to the increase in the carrier mobility with T_p, which allows the emptying of shallower levels and the occupation of deeper ones and, therefore, the mean depth increases with T_p. This is evidenced by an increase of the temperature at which the peak maxima takes place. In a previous work on space charge in PET [30], it was observed that the temperature of the maximum shifted to higher temperatures with the storage time, t_d. In this case the intensity of the maximum decreased sharply with t_d, indicating that the range ΔE_a is not as sharply defined as is represented by the idealized plot shown in Fig. 8, but sharply decreasing tails may be considered on both boundaries. Discharges obtained by means of this process, for polarization temperatures in the range for which the ρ relaxation is activated, are related to increasingly deeper traps with T_p. Therefore the distribution of trapping levels can be scanned by windowing polarization in the thermal range for which the space charge distribution is activated. The assumed distribution easily explains the existence of an optimal polarization temperature, for this temperature corresponds to the temperature at which the carriers are trapped at a depth at which the distribution shows its maximum, i.e. a depth at which there is the maximum number of available states.

The assumed distribution also explains the changes in the peak shape when the window width is increased. When the electret was polarized at 125°C, the polarization temperature was slightly higher than the T_{po}. Since when we apply the polarizing field during cooling we are ‘freezing’ the charge whose activation takes place at temperatures corresponding to the thermal interval of the polarization window, during the discharge we get the response of the polarization that we have achieved not only during the isothermal step, but also the polarization achieved during cooling, the effect of which appears at a lower temperature. From this point of view, our experience has been that if at $T_p = 125°C$ (slightly above T_{po}) the window width was increased (Fig. 4), we obtained an evident change close to the maximum of the peak for $\Delta T_w = 5°C$ if compared to the peak obtained for $\Delta T_w = 0°C$. For this width, the polarization window enclosed T_{po}, therefore for wider polarization windows, we were activating carriers that were trapped at levels with successively lower numbers of available traps (levels which are related to $T \leq T_{po}$). Because of this, the changes in the peak shape were less evident for polarization windows wider than 5°C. These changes can be observed close to the maximum of the peak. The contribution of the emerging α peak to the total discharge is responsible for the change in the peak shape.

In the case of $T_p = 135°C$ (Fig. 5), the polarization temperature was above the optimal polarization temperature, so that, when the polarization window width was increased, one expected the addition of a contribution which was increasingly important until the optimal polarization temperature was included in the thermal range of the polarization window (the charge was trapped at levels with increasing numbers of available sites up to this temperature). It can be noticed in this figure that, although the window width increase between the curves is constant, the differences observed between the curves obtained for $\Delta T_w = 15°C$ and $\Delta T_w = 20°C$ are less evident than between any other pair of consecutive curves. This difference in behavior is due to the fact that the optimal polarization temperature is reached in the case of $\Delta T_w = 15°C$, and, for $\Delta T_w = 20°C$, the additional trapped carriers are localized at levels with decreasing numbers of available sites. In the case of $\Delta T_w = 20°C$, there is an evident contribution of α relaxation in the low temperature tail of the peak.

The values of the calculated frequency factor (Table 1) are several orders of magnitude greater than the Debye frequency (10^{12}–10^{13} Hz). These values have also been found in the case of α relaxation and they have been explained by means of the cooperative nature of chain segment motions. We think that the high values found in the case of the space charge relaxation are related to the importance of the polymer chain motions in the relaxation mechanism of the space charge. The behavior of the frequency factor s_0 is similar to that previously discussed for the activation energy. If the value corresponding to $\Delta T_w = 15°C$ is neglected again, it can be said that s_0 decreases with the polarization window width. If an influence of chain segment motions on the space charge relaxation process is assumed, the decrease of the calculated frequency factor can be explained by means of the decrease in the frequency of chain segment motions at lower temperatures. The charge trapped during the cooling step is related to sites that are activated at lower temperatures, i.e., to temperatures at which the frequencies of the chain segment motions are lower. Because of this, one expects a decrease in the pre-exponential factor with decrease in polarization window width.

The kinetic order, b, of the discharge tends to decrease with the window width (Table 1). This parameter may be interpreted as a balance between first- (fast recombination, negligible retrapping) and second-order kinetics (retrapping dominates the relaxation mechanism). The decrease in the kinetic order is thus related to a change in the most probable relaxation mechanism of the space charge. It can be explained as follows: the charge trapped during cooling is related to increasingly shallower sites as the polarization window width is increased. When carriers trapped in shallow sites are thermally stimulated, they can reach the conduction band, where they move with a higher mobility, until they are eventually captured in a recombination center. In contrast, carriers trapped in deep levels do not, initially, get enough energy to reach the conduction band, and so move by hopping between localized states and can therefore be retrapped and subsequently detrapped again until finally reaching a recombination center. Because of this, for these carriers, retrapping is the most likely relaxation mechanism.

4. Conclusions

Windowing polarization, a technique which has been widely used to study dipolar relaxations in polymeric materials, is also a useful way to study space charge relaxation in these materials. Using this technique, electrets can be formed whose discharge reflects only the presence of ρ peaks, enabling this relaxation can be studied separately from other contributions.

The study of the polarization window width effect shows that if, as is usually the case, the window is made about 10°C in width, the distributed nature of the relaxation and also the overlapped response of a close relaxation can become evident. The use of null-width polarization windows is therefore better because greater resolution can be achieved in the case of distributed relaxations and overlapping relaxations.

It has been observed that the cooling rate is also a determinant parameter of peak shapes. For higher cooling rates one gets larger areas (i.e. more polarization), explained by carrier detrapping during cooling.

A change in the kinetic order of the relaxation when the window width is increased has been observed. In the general order kinetics model, this change is related to a change in the predominant relaxation mechanism. This fact allows one to conclude that the use of null width polarization windows in the study of space charge relaxation is convenient in order to avoid changes in the relaxation mechanism, as such changes are associated with the distribution in trapping depths of the charge activated during the cooling step in a WP process with $\Delta T_w \neq 0$.

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