

Space charge relaxation in high density polyethylene (HD-PE)

J. FRAILE, A. TORRES, J. JIMÉNEZ

Departamento de Física de la Materia Condensada, Facultad de Ciencias, 47011 - Valladolid, Spain

A general order kinetics approach has been used to study the space-charge relaxation in high-density polyethylene (HD-PE). The analysis of the activation energy, E , and the kinetics order, q , allows the determination of two relaxation regions above the glass transition temperature; one between -24 and 16°C , and a second above 16°C . Both relaxations are discussed on the basis of the structural characteristics of polyethylene.

1. Introduction

The investigation of the temperature margins where the dielectric relaxation occurs has received a great deal of attention in order to characterize polymeric materials. The glass transition temperature is clearly observed from the dependence with temperature of a large variety of physico-chemical properties of polymers. The study of secondary relaxations, mainly associated with either dipolar or space-charge relaxation, is much more complicated and strongly depends on the resolution of the experimental technique used. TSDC (thermally stimulated depolarization current) is a widely used technique for the study of the dielectric relaxation in polymers [1]. This technique provides a high resolution together with experimental simplicity. Some additional information is required in order to associate the observed relaxation mechanisms with the molecular structure of the specimen.

This technique was initially used for characterizing alkali halides [2], which are systems with low dipolar concentration. Thus dipolar relaxation can be studied on the basis of a non-interacting relaxation mechanism, which allows a Debye type relaxation time [3] to be used for the process.

Complex systems, such as polymers, are characterized by TSDC peaks, where the shape deviates from that typically observed in alkali halides and other ionic crystals. In fact, the TSDC peaks of such solids undergo a significant broadening on the high temperature side. This is usually explained on the basis of the limitations of the experimental process itself and is analysed by means of distribution functions [4], which describe the elementary Debye peaks (first-order) giving the experimental response. These distribution functions can hardly justify the physics of the relaxation of non-linear systems [5]. We have developed an empirical law for the relaxation time of complex systems, taking all these considerations into account which accounts for the case of cooperative relaxation mechanisms. This has been successfully used for studying crystals with structural dipoles (associated with hydrogen bonds) [5, 7] and some polymers, such as PVDF- α [8], for which we were able to determine the

typical temperatures associated with dipolar relaxations as well as their characteristic parameters.

In the present paper this approximation has been used to study the thermally activated relaxations in polyethylene of high density (HD-PE) at temperatures above the glass transition temperature, T_g , between -24 and 48°C . The experimental peaks, resolved by the thermal sampling technique, are fitted to the mathematical expression of the electrical current deduced from a general order kinetics relaxation equation [9]. The fitting parameters are the activation energy, E , the pre-exponential factor s_0 , and the order of the kinetics q . A classification of these parameters as a function of the temperature provides a valuable analysis for the characterization of the relaxations of PE in the considered temperature margin.

2. Experimental set-up

The experimental procedure of a classical TSDC or TSC (thermally stimulated current) experiment is well known; detailed descriptions can be found in [1, 6, 10]. The elementary peaks we studied were isolated by means of the thermal sampling technique [9], which basically consists of the following stages.

- (1) The sample is biased at high temperature, T_p .
- (2) It is cooled down and then the applied electric field is removed.
- (3) The sample is short circuited and warmed up to a temperature some degrees below T_p . Thereafter it is cooled down again.
- (4) It is heated in short circuit, and the elementary TSDC peak is simultaneously recorded.

This technique permits the electric current associated with the relaxation in a narrow temperature interval (2 K) to be recorded.

High density polyethylene (HDPE) samples, manufactured by Rio Ródano (Miranda de Ebro-Spain) were used for measurements. The weight-average and the number-average molecular weights were 100 000 and 6400 respectively. The specimens were melt pressed at 160°C in an isotropic laminar form. The typical thickness was $200\ \mu\text{m}$, which permitted the application of electric fields over $10^6\ \text{V cm}^{-1}$ to polarize the specimen.

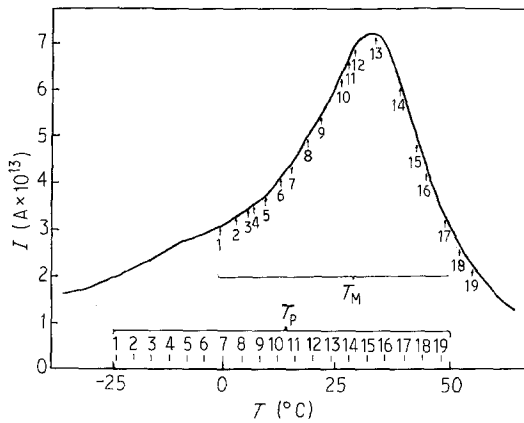


Figure 1 TSDC spectrum obtained after polarization at 46°C with $2 \times 10^6 \text{ V cm}^{-1}$ for 5 min. The arrows indicate the maxima of the elementary peaks obtained by thermal sampling.

Special attention was devoted to the problem of the electric contacts. Different coating metals were used. In agreement with other authors [11, 12] the best signal-noise ratio was obtained for gold plate electrodes pressed on the sample. Other metals tested were not satisfactory and gave a rather poor electric signal. All the experimental results herein reported were obtained with gold. The sample was in vacuum in a small cryostat, which is adequate for performing the thermal sampling technique, and the electrical measurements were made with a Keithley electrometer (model 616).

3. Results and discussion

Fig. 1 shows a typical TSDC spectrum obtained by polarization for 5 min. in an electric field of $2 \times 10^6 \text{ V cm}^{-1}$ at 46°C. The temperature maxima of the elementary peaks resolved by "thermal sampling" are indicated by arrows. Our study will be focused on the analysis of these peaks.

The differential equation accounting for the electrical current associated with the relaxation is the well known general order kinetics equation [10]

$$I = -\frac{dP}{dt} = \frac{P^q}{s} \quad (1)$$

where P is the remaining polarization (or stored

charge) at each instant, which may be considered to a first approximation to be proportional to the area under the peak. s is a proportionality factor which, for the special case of first-order kinetics, takes the form of an Arrhenius-like law, $s = s_0 \exp(E/kT)$ (s_0 is the pre-exponential factor, and E the activation energy), and corresponds to the typical relaxation time of a non-interacting system, for any other kinetics order s does not fit to an Arrhenius law and has no time dimension. Finally, q is the order of the kinetics.

The expression of the electrical current deduced from Equation 1 is

$$I = s^{-1} \left(P_0^{1-q} + (q-1) \int_0^t s^{-1} dt' \right)^{-q/(q-1)} \quad (2)$$

where P_0 is the initial polarization (or stored charge).

Examples of the experimental peak fitting to this equation are shown in Figs 2 and 3. The effective relaxation time, $P/I = sP^{1-q}$, is also represented as a function of $1/T$, showing a linear dependence over the temperature range of the peak. This relaxation time is found to depend on the remaining polarization, P .

The TSDC spectrum herein reported corresponds to a thermal range above the upper glass transition temperature, $T_g(U) = -30^\circ \text{C}$. Therefore the spectrum might be mainly associated with relaxation phenomena related to space charge. On the other hand, the TSDC spectrum is sensitive to both the polarization conditions and the nature of electrodes. It is also found that the area under the curve (stored charge, Q), against V_p plot is clearly non-linear, Fig. 4. All of which suggests that the injected charge plays an important role in the space-charge formation in polyethylene. The TSDC spectrum will be mainly associated with the relaxation of this space-charge. This aspect will be considered later in relation with the discussion of the results.

The analysis of the elementary peaks, obtained by the thermal sampling technique, allows us to assess the activation energy, E , and the q factor. The distribution of both values will lead to the determination of the different relaxation regions [9] in the studied temperature domain. These distributions are represented in Fig. 5 as a function of the polarization temperature, T_p .

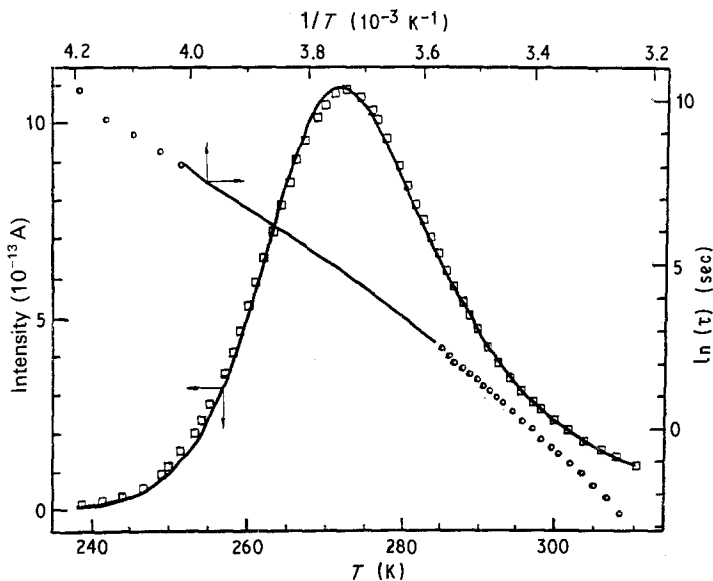


Figure 2 Fitting of the elementary peak ($T_M = 272 \text{ K}$) (—) by Equation 2 ($\square\square\square$). The logarithm of the effective relaxation time, $\tau = sP^{1-q}$, is also represented, showing a linear dependence with $1/T$.

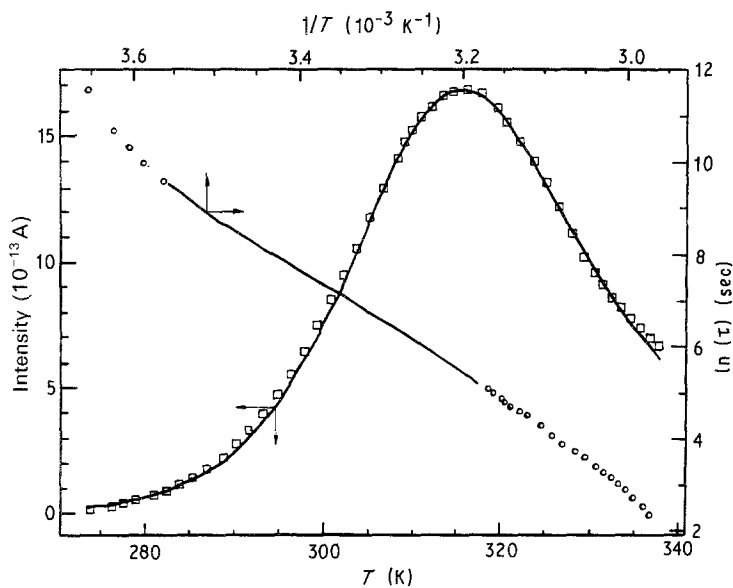


Figure 3 Fitting of the elementary peak ($T_M = 316\text{K}$) (—) by Equation 2 (□□□). As in Fig. 2 the relaxation time is represented.

Two relaxation regions can clearly be deduced from the E and q data. The first region is seen to be between -24 and 16°C , and is characterized by a high value of q , whose average value is $4.27(\pm 0.48)$, and an average activation energy of $1.08(\pm 0.05)\text{eV}$. The second relaxation region is observed above 16°C , and is characterized by a continuous decrease of the q value and the activation energy. The activation energy is $0.89(\pm 0.06)\text{eV}$. On the other hand, q takes a value near unity on the high temperature side ($\approx 50^\circ\text{C}$).

The activation energy of the elementary peaks, as calculated from the initial slope of the low temperature side [13], is also represented in Fig. 5. It should be noted that the above mentioned relaxation regions are observed from this Arrhenius like deduced activation energy. Nevertheless, the energy calculated by this method is slightly higher than that calculated by fitting Equation 2. On the other hand, it is observed that around 20°C the activation energy calculated from the initial slope exhibits an increase. This could be ascribed to the fact that it corresponds to the temperature range between both transitions, and this method only uses the low temperature side of the peak. In this way it should be noted that at this temperature a step in the q value is observed.

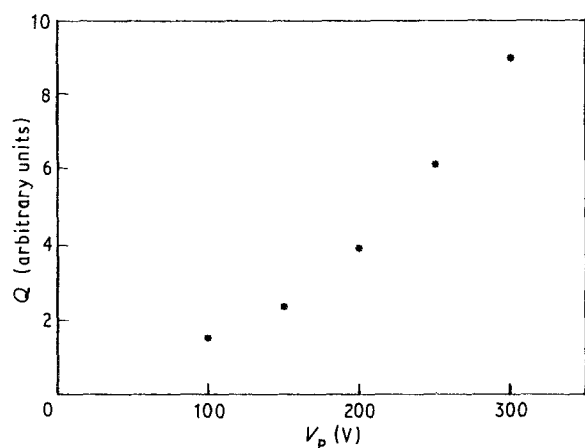


Figure 4 Plot of the area under the curve (Q) against the polarization voltage (V_p). The curve is markedly non-linear. The polarization temperature is 25°C .

The physical description of the space-charge relaxation in polyethylene requires a knowledge of the trapping and detrapping mechanisms accounting for the observed spectrum. The relaxation observed above 16°C seems to be associated with trapping at the crystalline zone of the polyethylene [11, 14], as would be expected from a relaxation in the α region [15]. In fact the α loss dielectric peak is observed in the high temperature side of the relaxation above 16°C . This seems to agree with the fact that, in this relaxation, the q factor takes a value near unity on the high temperature side. All that is also in agreement with the results of charge detrapping reported by other authors in X and gamma irradiated polyethylene [11, 12], for which they observed a TSC (thermally stimulated current) peak, labelled P_5 , which seems to correspond to the high temperature relaxation region reported herein. The trapped carriers are liberated with an activation energy corresponding to that of the carrier in the trap. This energy is provided by the lattice thermal vibrations of the crystalline region.

The low temperature relaxation appears at a temperature intermediate between the β and α transitions, which implies that it might be associated with traps in the grain boundary region between crystalline and amorphous regions, it has been labelled P_4 by other authors [11, 14]. In such a case the detrapping of carriers would be closely related to the molecular chain motions; this seems to agree with the high value of q calculated from our experimental data. Indeed, this relaxation exhibits some similarities with the relaxation mechanism of dipoles, due to the fact that both are associated with molecular motion. In fact, in the dipolar relaxation case a TSDC peak is due to the neutralization of the induced dipole by molecular motion. Space-charge trapped at the boundary regions relaxes as a consequence of the transfer to the trapped carrier of the energy associated with the molecular chain motion. In other words, instead of what happens in the crystalline region, the carriers are liberated with an activation energy characteristic of the molecular chain motion, which is in agreement with the high value of q calculated for this relaxation.

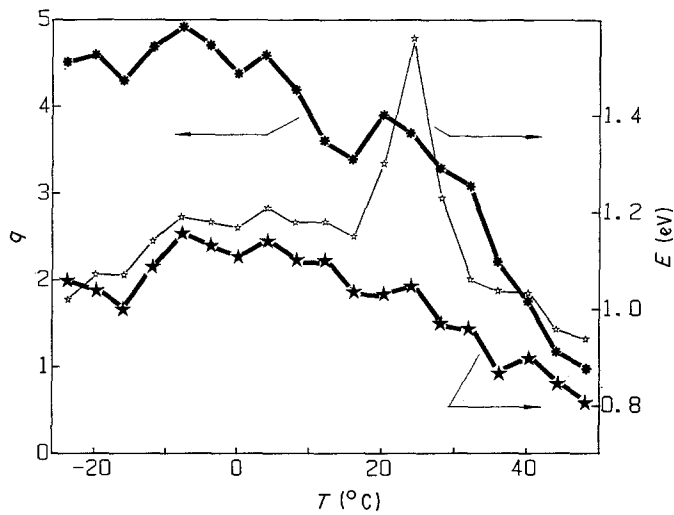


Figure 5 Plot of the activation energy, E (\blacktriangle), and kinetics order, q ($*-*-*$), against the polarization temperature of the elementary peaks as obtained from the fitting Equation 2. The activation energy calculated by the initial slope method is also represented (\triangle). The two relaxation zones are clearly observed below and above 16°C .

In summary, a description of the space-charge relaxation in high density polyethylene (HD-PE) has been carried out on the basis of a general order kinetics approach, which provides a satisfactory method for determining the different relaxation mechanisms of the injected space-charge in high density polyethylene.

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