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Dielectrical relaxation dynamics and thermally stimulated depolarization current in polymers

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The dynamics of dielectrical relaxation of polymer materials has been studied. Concept for depolarization process simulation based on the primitive charge transport model was proposed for the reason of relaxation mechanisms investigation in polymer structure. Depolarization current in polymer exposed by homogeneous electric field suddenly switched-out in a certain instant of time was calculated on the basis of the model and the model parameters was discussed to achieve consistent results with dielectric relaxation experiments. The aim of our work is to recognize if the dielectrical relaxation and depolarization are connected with the same process of spatial rearrangement of fixed charge carriers of dielectric system. In this paper the investigation of polymer relaxation dynamics by simulations based on the proposed primitive charge carriers transport model is suggested and teoretical principles of thermally stimulated depolarization currents (TSDC) are analysed in term of the model. Experimental results of TSDC measurements in polymethyl-metacrylate (PMMA) and polyethylene-terephthalate (PET) are presented and exploitation of the measured data in polymeric materials research is discussed.

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1. Introduction

Dielectrical relaxation is a process of establishing equilibrium state of the fixed charges in dielectric structure. The time scale of this process is determined by dielectric relaxation time τ. The dielectric relaxation time is the characteristic time for charge fluctuations to decay under the influence of the field that they produce. The fixed charges system that is examined a time much longer than the relaxation time τ is seen to be in equilibrium. On the contrary, when the observation time is shorter then relaxation time τ we see a snap shot of frozen in nonequilibrium system. The dielectric relaxation time is related to the electrical conductivity of dielectric materials, in the case of high charge carriers mobility the relaxation time τ can be very small. We recognized whether it is possible to think of depolarization as a relaxation process of dielectric structure. If so then the dynamics of both depolarization and dielectrical relaxation process can be controlled by the same relaxation time τ and data correlation obtained from the measurements of both TSDC and electrical conductivity can be investigated.

The main goal of the present work is to better understand the dielectrical relaxation of polymers and consequently to offer the alternative basis for theoretical analysis of TSDC experimental technique. Many polymers build up of continuous network. Several relaxation mechanisms of the polymer chain have been proposed, such as reptation [1], tube length fluctuation [1], and thermal [2] and convective [3] constraint release [3].

We have proposed the simple model of dielectrical relaxation mechanism based on fixed charges transport approximation. We assume that the classical description of drift motion of the large charge clusters bounded in the polymer chains is possible and proposed model is usable for polymer materials. The spatial rearrangement of the charge carriers coupled in the polymer structure was described on the basis of the model and problems of relaxation time and thermally stimulated depolarization current were discussed.

2. Theory

2.1 Depolarization process and thermally stimulated depolarization current

One way, in the time domain, to investigate the depolarization process for a dielectric material is to measure depolarization current. Depolarization current density i_{dep} is determined by the time-change of the amount of the material polarization P:

$$i_{dep} = -\frac{dP}{dt} \ . \tag{1}$$

If we assume Debay model of relaxation with a unique relaxation mechanism the equation for the decay of polarization is:

$$\frac{dP}{dt} = -\frac{P}{\tau} \ , \tag{2}$$

where τ is dielectric relaxation time.

The solution of the eq. (2) determines the time dependence of the dielectrical structure polarization $P(t)$

that can be written in the form:

$$P(t) = P_0\, e^{-\frac{t}{\tau}}\ , \tag{3}$$

where P_0 is the initial amount of the system polarization. As it can be seen from eq.(3) the dielectric relaxation time τ is a amount of time it would take for an polarization of system to decay by e^{-1} in the absence of additional forcing.

The depolarization current density can be found easyly find by substitution of solution (3) to the eq.(1):

$$i_{dep} = \frac{P_0}{\tau} e^{-\frac{t}{\tau}}\ . \tag{4}$$

The solution (4) could be acceptable in simple cases of dielectrical relaxation with a single relaxation time if τ is time independent. Mentioned condition $\tau = const$ is usually satisfied at constant temperature of material T. If the temperature of dielectric material changes the temperature dependence of relaxation time must be considered in equation (2) and different solution can be obtained. Consequently we can easy eliminate time t from mentioned solution if we consider:

$$\frac{d\tau}{dt} = \left(\frac{d\tau}{dT}\right)\beta, \tag{5}$$

where:

$$\beta = \frac{dT}{dt} \tag{6}$$

and depolarization current density is just temperature dependent in that case. If relaxation time obeys Arrhenius-type equation the depolarization current density can be written as [4]:

$$i_{dep}(T) = \frac{P_0}{\tau_0} e^{-\frac{E_a}{kT}} exp\left(-\frac{1}{\beta\,\tau_0}\int_{\tau_)}^{\tau} e^{-\frac{E_a}{kT}}\right) \tag{7}$$

Mentioned expression (7) describes thermally stimulated depolarization current. However, the fixed charge carriers drift mobility in material structure has not been fully elucidated in the frame of mentioned phenomenological approach. A good description of depolarization process and analysis of TSDC technique requires some understanding of charges dynamics in material structure.

2.2 Process of dielectrical relaxation

Let's discuss the dielectrical relaxation process. To see the importance of respecting the limitations related to the dielectric relaxation time, imagine to have a polarized dielectric system under the influence of constant homogeneous electric field.

Every charge carrier coupled in the polarized material structure is exposed to the electric field with strength E_0. Consider the electric field oriented along y direction. This carrier is deflected from equilibrium by electric force and we assume that carrier`s equilibrium is y = 0. Let the electric field is switched-out in t = 0 (see Fig.1a). The charge carriers are returned to equilibrium and relaxation is in progress inside the system. There can be considered an equilibrium restoring counter force that is proportional to y for small deviations. Suppose, for the sake of simplicity, that friction is proportional to the carriers velocity $v(t)$. Therefore, the following equation has to be solved for the time evolution of charge carrier deviation $y(t)$ determining:

$$\frac{d^2y}{dt^2} + 2b\frac{dy}{dt} + \varepsilon^2 y = 0\,, \tag{8}$$

$$\text{where}\quad b = \frac{k_b}{2m}\ ,\quad \varepsilon = \sqrt{\frac{k}{m}}\ . \tag{9}$$

m is mass of the charge carrier, k is the spring constant of linear oscillator, k_b is the friction coefficient. The single carrier velocity is defined as:

$$v(t) = \frac{dy(t)}{dt} \tag{10}$$

and following formula can be written for the relaxation electrical current density i_{rel} by means of the simplest classical model of conductivity:

$$i_{rel} = n\,q\,v(t)\,. \tag{11}$$

n is charge carriers number per unit volume and q is electrical charge of the carrier.
Using the simple boundary conditions:

$$ky(t=0) = -qE\ ,\ \ i_{rel}(t=0) = 0\,, \tag{12}$$

we can easy find following relation for the current density i_{rel}:

$$i_{rel}(t) = \sigma_0 \frac{2b}{\alpha} E_0 e^{-bt} sinh(\alpha t), \tag{13}$$

where:

$$\sigma_0 = \frac{nq^2}{k_b}\quad ,\alpha = \sqrt{b^2 - \frac{k}{m}}\ . \tag{14}$$

As it can be easyly found the time dependency of i_{rel} determined by (13) shows a maximum in time t_m that can be written by:

$$t_m = \frac{1}{2\alpha} ln\left(\frac{b+\alpha}{b-\alpha}\right) \tag{15}$$

Relaxation time τ is the most important parameter for description of the dielectric relaxation process. As it can be shown, the molecular relaxation time depends upon macroscopic viscosity of materials. Mentioned fact implies

that dielectric relaxation involves mainly molecular drift motion considered above and not just rotation of single molecules. This argument [5] seemed to be confirmed experimentally by Schallamach [6].

But it is clear that the current density i_{rel} determined by eq.(13) disagrees with solution (4). Fig. 1b shows the time evolution of both the depolarization current density i_{dep} and the calculated current density i_{rel} flowing during the process of dielectrical relaxation. Whereas the depolarization current density i_{dep} should have to show exponential decrease (see eq.4), i_{rel} shows maximum in $t = t_m$. From mentioned results it is not evident if the dielectrical relaxation and depolarization are really connected with same process of spatial rearrangement of charges fixed in material structure. We suggest that the deviation i_{rel} from the exponential decay is a consequence of the fact that charges move slow compared to changes in the electric field.

We shall now examine the possible mutual relation between i_{dep} and i_{rel} calculated above. Total amount of the material polarization P is determined by:

$$P(t) = nqy(t). \tag{16}$$

Taking account of (2), (8) and (16) the following formula for τ can be derived:

$$\tau = \frac{m}{k}\{\alpha ctgh(\alpha t) + b\}. \tag{17}$$

The charge carriers drift motion velocity $v(t)$ cannot change abruptly as a consequence of carriers inertia. Hence we did not find uniform time independent value for τ in (17).

To search a possible coincidence of results (4) and (13) let us determine the τ values (17) for the time $t >> t_m$. As it can be easy seen from (17) in the case if $t \to \infty$ the relaxation time τ comes into the form:

$$\lim_{t\to\infty} \tau = \frac{1}{b-\alpha} \tag{18}$$

The constant value (18) represents relaxation time that characterize the dielectric relaxation process in the time $t >> t_m$. Apparently the relation (13) takes the form (4) for $t \to \infty$. It is evident directly from fig.1b that the depolarization process and process of dielectrical relaxation can be controlled by the same relaxation time in $t >> t_m$. That means the $i_{rel}(t)$ and $i_{dep}(t)$ will be identical for $t_{max} \to 0$ and dielectric relaxation time τ can be estimated the model parameters α and b in that case.

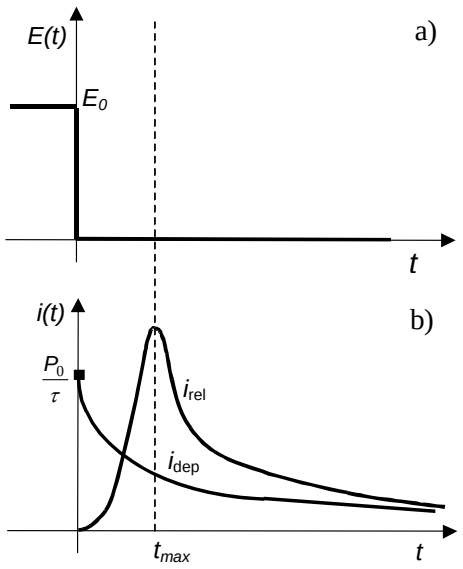

Fig. 1.

Dielectric relaxation time depends upon temperature. Generally, the relaxation time for non-cooperative motion follows an Arhenius law behaviour:

$$\tau(T) = \tau_0 e^{-\frac{E_a}{kT}}, \tag{19}$$

where the apparent activation energy, E_a, could be in the range of real energy barrier, k_B is the Boltzmann constant, T the absolute temperature and τ_0 the pre-exponential factor. If the relaxation is determined by "free volume effect" [7] the relaxation time follows the Vogel equation:

$$\tau(T) = \tau_\infty e^{\frac{1}{C(T-T_\infty)}}, \tag{20}$$

where τ_∞ is preexponential factor, C is average thermal expansion coefficient of free volume, T_∞ is critical temperature at which the relaxation time becomes infinite. This equation is equivalent, after parameters transformation to WLF (Williams-Landel-Ferry) equation [8].

On the other hand, movements of polymer chain segments can involve cooperative motions. The probability of success for cooperative motions is P^Z, where:

$$P \approx \frac{1}{\tau} \tag{21}$$

is the probability of single elementary movement. The Z exponent can be considered as the number of elementary movements [9,10].

If the relaxation cannot be described by a single Debye relaxation, the distribution of relaxation times is

needed in relation (2) and depolarization current density can be different from (4).

Generally, the process of drift motion of charges coupled in the polymer chain can be considerably complicated. However, considering the superposition principle the total amount of current density i_{rel} can be calculated by:

$$i_{rel}(t) = \left\{ \sum_{i=1}^{Z} \sigma_{0i} \frac{b_i}{\alpha_i} \left(1 - e^{-2\alpha_i t}\right) e^{-(b_i - \alpha_i)t} \right\} E_0 \quad (22)$$

where σ_{0i}, b_i and α_i are model parameters mentioned above for i-th type of charge carriers fixed in the polymeric chains. Index i alter from one up to Z, where Z is equal to the total number of distinguishable types of charge carriers conjugated in the polymer structure. The temperature dependence of current density i_{rel} in (22) is determined by temperature dependences of model parameters $\sigma_{0i}(T)$, $b_i(T)$ and $\alpha_i(T)$. Generally, it can lead to non Arhenius-type of relaxation time.

3. Experimental

TSDC method is based on the measurement of electrical current overflowing across the sample in consequence of depolarization process resulting in the sample during the sample controlled heating. First of all the sample is exposed by strong electrical field and charge carriers fixed in material structure are deflected from equilibrium by electric force. Oriented dipoles are created in the sample volume for that reason. During consistent sample cooling there is a increasing of relaxation time what is related with preservation of created dipoles orientation after electrical field disconnection. Relaxation time is shortened during the increasing of the sample temperature and depolarization current can be observed in a consequence of increased drift mobility of charge carriers.

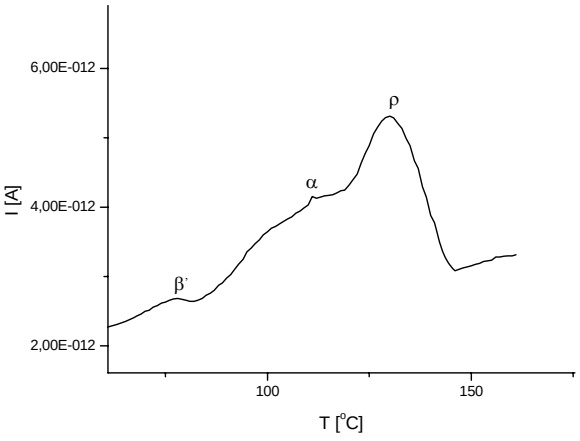

Fig.2. TSDC spectra of PMMA sample at higher temperatures. Polarization parameters: T_P = 120 °C, t_P = 3600 s, E_0 = 500 V.mm^{-1}. Heating rate: v_o = 3 °C.min^{-1}.

TSDC measurements have been performed in samples from polymethyl-metacrylate (PMMA) and polyethylene-terephthalate (PET). Electrodes based on the argentum were deposited on the surfaces of flat shape samples with dimensions 10x10-1mm. The polarization temperature was 120 °C in the case of PMMA and 140°C in the case of PET and electrical field strength E_0 was 500 V.mm^{-1} (PMMA) and 1000 V.mm^{-1} (PET). Investigated samples were polarized during the time period t_P from 3600 sec. up to 7200 sec. and linear heating rate varied between 2°C.min^{-1} and 10°C.min^{-1}. In all cases the samples were cooled until the temperature -195°C. The results of experimental measurements are shown in Fig.2 and Fig. 3.

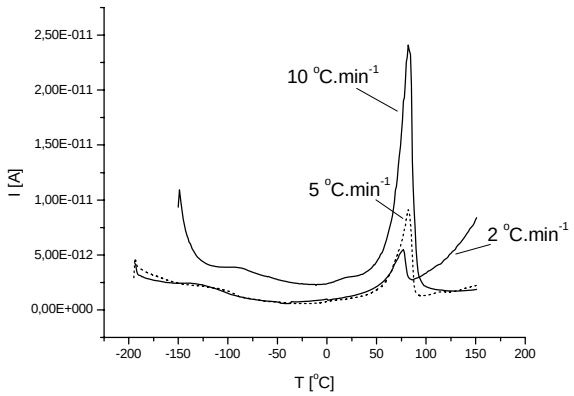

Fig. 3. TSDC spectra of PET sample with various heating rates. Polarization parameters: T_P = 80 °C, t_P = 120 s, E_0 = 1000 V.mm^{-1}.

4. Discussion

There is possible to distinguish a few of sharper peaks in behaviour of TSDC measured on PMMA sample (see Fig.2). Three sharp maxima are evidenced. The mentioned maximums can be attributed to β` (78°C), α (111°C) and ρ (130°C) relaxations. β` relaxation is connected with dipoles orientation, α relaxation is a combination of polar mechanism and glass transition mechanism and at last ρ is space charge relaxation [11,12].

TSDC results measured on PET sample show two good distinguishable relaxation maximums that can be considered a α and β relaxations. Depending upon the measurement conditions the β relaxation maximum occurs at the temperature interval from -137°C up to - 90°C. Sharper α relaxation shows a maximum in the temperature interval from 77°C up to 82°C (see Fig. 3). α and β maximums spacing changes by the measurement conditions variation. TSDC data measured at heating rate 2°C.min^{-1} and 10°C.min^{-1} are almost identical. Decreasing of mentioned α and β peaks spacing was observed at the increasing of heating rate up to 10°C.min^{-1}. Relaxation maximums height increase with the heating rate increasing.

It is clear from performed theoretical analysis the time

dependence of the current density caused by the dielectrical relaxation process is determined by (13). As it can be easy by shown the decrease of depolarization current density does not occur in extreme case:

$$\alpha \approx b\,. \tag{23}$$

If we consider (23) in equation (18) we get:

$$\tau \to \infty\,. \tag{24}$$

We pesume that condition (23) is identical to event:

$$T \to T_{\infty} \tag{25}$$

in equation (20). We expect that temperature dependences of parameters $\alpha(T)$ and $b(T)$ has to be such that condition (23) occurs at temperature determined by (25). Consequently as it results from (13) the time dependence of depolarization current density will take the following form:

$$i_{dep} \approx \sigma_0 E_0 \left(1 - e^{-2\alpha t}\right) \tag{26}$$

in the case determined by (23). Depolarization current should have permanently flow across the sample in that case. If we neglect the transient phase of the process i.e. at time $t \to \infty$ we get:

$$i_{dep} \approx \sigma_0 E_0\,, \tag{27}$$

where E_0 is strength of applied electric field and σ_0 is electrical conductivity of material that is temperature dependent:
$\sigma_0 = \sigma_0(T)$.

Afterwards the depolarization current determined by (27) is thermally stimulated (TSDC). If the approach presented in theoretical part is correct the TSDC phenomena in polymers is possible elucidate by means of dielectrical relaxation dynamics. In that case it is possible to look for a correlation between temperature dependence of electrical conductivity $\sigma_0(T)$ and TSDC spectra [13,14].

5. Conclusions

Amorphous polymers such as PMMA and PET exhibit dielectrical and mechanical relaxation processes identified as α and β relaxations. α relaxation is mechanical or dielectrical response of "dynamical glass transition". β relaxation is a response of macromolecular chain movement [12]. Mentioned relaxations are distinguishable very well on measured TSDC data. Mentioned measurement enables to evaluate quantitatively and qualitatively the occurrence of both of mentioned relaxation in PMMA and PET. ρ relaxation was observed too in the case of PMMA sample.

On the basis of the model presented in the contribution it can be expected that if the model parameters difference $b(T) - \alpha(T)$ approachs to zero value at temperatures $T \to T_{\infty}$ the time dependence of depolarization current determined by equation (13) will be attenuated. Temperature dependence of depolarization current $i_{dep}(T)$ will be dominating in that case and the depolarization current can allowed to be „thermally stimulated“. The results show that correlation between temperature dependence of electrical conductivity and TSDC spectra can be expected.

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