# APPLICATION OF THE THERMALLY STIMULATED DEPOLARIZATION METHOD FOR STUDYING THE STRUCTURE OF POLYMER COMPOSITES

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The Maxwell–Wagner–Sillars (MWS) losses and the  $\alpha$ -transition in filled polyvinylchloride (PVC) have been investigated making use of the thermally stimulated depolarization (TSD) method. The maximum of the electric MWS losses in such microheterogeneous systems has been found to depend on the time  $t_p$  of the formation of a thermoelectret in the external electrostatic field, the electric field strength E, the time delay of the exposition after the polarization  $t_e$ , and the type and the concentration  $\varphi$  of a superfine filler in PVC. The factors that are responsible for the emergence of the dispersion regions for the kinetic units, which belong to the structural formations in a heterogeneous polymer system (HPS), have been analyzed in the framework of the theory of molecular relaxation. The researches carried out in the framework of the theory of normal modes showed that the activities of PVC fillers, when considering their influence on the character of the TSD spectrum, are ranged as follows: W, Zn, graphite, talc, and corundum.

## 1. Introduction

One of the relatively new methods for researching the molecular relaxation in polymers is the TSD one. The results obtained with its help evidence for the mobility of various sections of macromolecules and the variation of structure formations in a composite under the action of the force and temperature fields [1]. In addition to studying  $\alpha$ - and  $\beta$ -transitions, the TSD method allows the value of the electric losses of the MWS-type to be determined. It is especially important for amorphous flexible chain polymers and heterogeneous systems on their basis, because the study of their structure by "straightforward" methods is complicated [2]. At the same time, it should be

emphasized that searching for active methods, which would allow one to create structure formations in such systems by the directional application of the external electrostatic field, which makes it possible to obtain thermoelectrets as a new type of insulators that are capable to preserve the residual polarization, is in progress [3]. In so doing, the attention of researchers is focused on two aspects. First, the response of the HPS to the action of the external force fields substantially depends on the structural factors and the mobility of molecules. Secondly, the structure of the polymer can be substantially changed during the formation of the thermoelectret, affecting the whole complex of the HPS properties. However, despite the success achieved in the research of these processes, the issues concerning the influence of low-molecular components with various dielectric permittivities  $\varepsilon'$ , the physical and chemical properties of the surface, the field strength E, and the filler concentration  $\varphi$  on the electret properties of the HPSs remain open [4].

The aims of this work were to fabricate thermoelectret composites, to study the behavior of the fillers of various nature in a polymer matrix making use of the TSD method, and to find the interrelation between the properties of the fillers and the binding polymer with the electret properties of the composites concerned. The results of the work were planned to be useful in developing the methods of purposeful control over the thermoelectret effect in the filled amorphous polymer composites and to assist in fabricating materials with a predetermined set of properties.

### 2. Experimental Method

The PVC, a typical representative of linear flexible chain polymers, was selected for investigations. The molecular weight of the reprecipitated PVC was  $1.4 \times 10^5$ . The powders of tungsten, zinc, graphite, talc, and corundum with the average dimension of particles of 7  $\mu$ m were used as fillers. Experimental specimens (29±1) mm in diameter and (0.2±0.02) mm in thickness were fabricated by hot pressing in the T - p regime at a temperature of 403 K and a pressure of 10.0 MPa. In order to provide a reliable electric contact between the electrodes and the specimen, aluminum foil was adpressed to each side of the specimen.

The specimen was polarized in an electric field of a constant strength for 5 min. Afterwards, the specimen was cooled down to room temperature in the electric field with the same strength for 30 min. The measurements of the TSD currents in composites and the calculations of their electric relaxation parameters were carried on following the GOST 25209-82 requirements. The discharge current was registered by a U5-9 electrometric amplifier.

#### 3. Experimental Results

The researches of the TDS current, measured while heating up the initial PVC specimen with a constant rate of 3 K/min, showed (Fig. 1,*a*-*c*) that, if the temperature lies within the temperature interval 20–110 °C, two maxima – at about 40 °C and in the range of the  $\alpha$ relaxation transition – are observed in the depolarization spectra. The specimens were polarized at  $T > T_c = 110$ °C and  $E = 1.5 \times 10^6$  V/m. The polarization of the polymer at a certain temperature and its depolarization under a linear rate of heating testify that only one relaxation time dominates at every temperature, so that the current density obeys the equation [5]

$$j(t) = \frac{dP(t)}{dt} = -\frac{P(T)}{\tau(T)},\tag{1}$$

where P is the polarization of the specimen.

Under the conditions indicated, there are two maxima in the dependence I = f(t) of the depolarization current on time (Fig. 1), which correspond to different relaxation transitions. It is evident from Fig. 1 that a significant deviation of the system towards the equilibrium state is observed as the time interval between the PVC specimen polarization and the depolarization current measurement increases. For example, the value of  $T_c$ , which corresponds to the



Fig. 1. TDS current curves for PVC, measured in 30 min (a), 24 h (b), and 72 h (c) after polarization

 $\alpha$ -transition in the initial PVC, amounted to 79 °C (Fig. 1,*a*), 82 °C (Fig. 1,*b*), and 84 °C (Fig. 1,*c*) if it was measured in 30 min, 24 h, and 72 h, respectively, after the polarization of the specimen. Similar effects were observed while registering the dependence  $(\partial V/\partial T)_t$  [6]. The low-temperature maximum in the I = f(t) dependence is considered [7] as associated with the MWS losses; the latter are stimulated by the microheterogeneity of the structure, which allows, in its turn, the short-chain segments and the lateral groups of PVC to rotate at  $T < T_c$ .

Under condition [5]

$$I(T) = -P_0\omega_0 S \times$$

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$$\times \exp\left(-\frac{E_a}{kT} - \frac{\omega_0}{\beta} \int_{T_0}^T \exp\left(-\frac{E_a}{kT'}\right) dT'\right),\tag{2}$$

where  $I = jS = \frac{dP}{dt}S = \beta \frac{dP}{dT}S$ ,  $\omega_0 = 1/\tau_0$ ,  $\tau = \tau_0 \exp\left(\frac{E_a}{kT}\right)$ ,  $\omega = \omega_0 \exp\left(-\frac{E_a}{kT}\right)$ ,  $E_a$  is the activation energy, and k is the Boltzmann constant, we have

$$\frac{E_a}{kT_m^2} - \frac{\omega_0}{\beta} \exp\left(-\frac{E_a}{kT_m}\right) = 0 \tag{3}$$

in the maximum  $T = T_m$  of dependence (2). According to relation (3), the calculations of  $E_a$  for this relaxation process, carried out in the framework of the Garlick-Gibson method [8], showed that the value of this quantity is equal to 12 kcal/mol. This indicates that the relaxation transition at  $T = 39^{\circ}C$  is caused by the motion of a segment of the freely joined chain, because the values obtained for the activation energy of this process are close enough to theoretically calculated ones and do not depend on the chemical composition of linear flexible chain polymers [9]. However, it is characteristic that the longer the time interval t between the polarization of the system and the registration of the dependence I = f(T), the lower is the maximal value of the depolarization current at 39 °C; at t = 72 h, this maximum disappears completely. In accordance with the theory of normal modes [10], a PVC macromolecule can be approximated by a sequence of Gaussian subchains, which are forced to execute independent vibration-like motions under the action of friction forces exerted by neighbor molecules. As a result of the dissipative losses of energy by such kinetic elements of the structure, this



Fig. 3. TSD current curve for PVC+0.5 vol.% NaCl

process ceases to run in 72 h after polarization, owing to the fact that the system loses its microheterogeneity. In this case, the first maximum (at 39 °C for the initial PVC) is caused by the bulk charge polarization, and the second one (in the temperature range 79–84°C) by the orientational polarization of the PVC segments.

It is typical that the first maximum of the dependence I = f(T) is inherent not only to the initial PVC, but also to the HPS fabricated on its basis (Fig. 2). The origin of the first maximum (polarization of the bulk charge) is confirmed by Fig. 3, where the TSD current curve for the PVC filled with ionogenic NaCl to  $\varphi = 5.0$  vol.% is depicted. As is seen from Figs. 2 and 3, the charge, which has been induced in PVC under such conditions, is unstable ( $E_a \approx 0.2 \text{ eV}$ ) and "disperses" already at 50 °C and above. The first maximum disappears from the TSD current curves if specimens have been polarized at  $T = T_c$ .

The second maximum lies in the temperature range of the PVC vitrification and is stimulated by the dipolesegment relaxation [11]. The shape of this maximum substantially depends on the strength E of the applied electric field (Fig. 4).

The decreasing of E down to  $5 \times 10^5$  V/m brings about the reduction of the heterocharge magnitude and stability. The growth of E up to  $3 \times 10^6$  V/m increases the surface charge of the PVC electret and, to some extent, makes its stability worse ( $E_a \approx 1.80$  eV at  $E = 3 \times 10^6$  V/m, whereas  $E_a \approx 2.25$  eV at E = $1.5 \times 10^6$  V/m). The TSD current curves for PVC filled with fillers of various physical and chemical origins are shown in Fig. 5. Since  $T \approx T_0$  at the initial interval of the heating of PVC systems, relation (2), after taking its logarithm, acquires the form

$$\ln |I(T)| = \ln (P_0 \omega_0 S) - \frac{E_a}{kT},$$
(4)

which can be used for finding the value of the quantity  $E_a/kT$  as the slope angle tangent for dependence (4) and for calculating the frequency factor  $\omega_0 = 1/\tau_0$ . The minimal time of charge relaxation in the electret under operational conditions were determined from the equation [2]

$$\lg \tau_e = \lg \tau_{\rm M} + 0,4343 \frac{E_a}{R} \left( \frac{1}{T_e} - \frac{1}{T_{\rm M}} \right),\tag{5}$$

where  $T_e = 293$  K is the operating temperature of the material under investigation, and  $E_a$  is the minimal activation energy of charge relaxation expressed in J/mole units. The residual charge  $Q_{\rm res}$  and its surface density  $\sigma_{\rm res} = Q_{\rm res}/S$  in the electret were determined by integrating the TSD current dependence I(T). The results of calculations of the electric relaxation parameters for thermoelectrets belonging to the PVC system, which were carried out on the basis of the relations considered above, are summarized in the table.

#### 4. Discussion of the Results

The comparison between the calculated and experimental data (Figs. 1-5) demonstrates that the temperature dependence I = f(T) of the TSD current is governed by the structural factors of composites.

For example, in the case of PVC filled with a filler of organic nature, there exists a weak adhesive interaction at the phase interface, which results in the appearance of a loosened boundary layer (BL) there [12]. Under the action of the external polarizing electric field, the segments of PVC macromolecules acquire the orientation capability and, thus, a significant initial heterocharge. However, such a charge is unstable, and, owing to the disorientation action of the external temperature field, its value quickly decreases. If the PVC fillers are of the metallic origin (W, Zn), the emerging oxide films were found strong and possessing insignificant thickness, 1-2% of metal ions can participate in the ion-dipole interaction [12]. The possibility of a chemical interaction between PVC and metals has been repeatedly pointed by a number of authors [1]. All this allows one to consider the formation of the PVC+0.5 vol.% Zn or PVC+0.5 vol.% W composite as a process where the active filler is engaged,

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Fig. 4. TSD current curves for PVC subjected to various polarizations:  $E = 3 \times 10^6$  (a),  $1.5 \times 10^6$  (b), and  $5 \times 10^5$  V/m (c)

and the mass transfer of PVC macromolecules is directed towards its surface, which favors the significant interaction of components at the PVC-metal interface. If an electric field is applied to such composites, the charge of a certain magnitude and a sign is generated on the surface of metallic fillers [13]. The composites acquire an electret charge, which remains stable after the external

Parameters of electric relaxation in PVC systems

Specimen composition	$\begin{array}{c} \sigma \times 10^{-4}, \\ \mathrm{nC/m^2} \end{array}$	$E_a, eV$	$ au_e,  ext{s}$	
PVC without fillers	22.94	1.96	$10^{8}$	$10^{25}$
PVC+0.5 vol.% W	45.39	1.74	$10^{7,4}$	$10^{22}$
PVC+0.5 vol.% Zn	43.13	1.66	$10^{7}$	$10^{21}$
PVC+0.5 vol.% C	135.61	0.65	$10^{4}$	$10^{6}$
PVC+0.5 vol.% talc	38.22	1.13	$10^{5,5}$	$10^{14}$
$\rm PVC{+}0.5$ vol.% corundum	40.35	1.08	$10^{5}$	$10^{13}$



Fig. 5. TSD current curves for PVC filled with fillers of various physical and chemical nature: PVC without fillers (1), PVC+0.5 vol.% W (2), PVC+0.5 vol.% graphite (3), and PVC+0.5 vol.% talc (4)

electric field having been removed, because the mobility of the polymer segments in the BL is limited not only by steric but also by energy effects.

In the case of dielectric fillers, it has been found that their surface contains structurally bound hydroxyl groups and the layer of adsorbed moisture [10]. At  $T > T_c$ , when the composite starts to form, polar PVC macromolecules, owing to ion-dipole bonds, uniformly surround the talc or corundum surface. Dielectric fillers, in contrast to electroconductive ones, do not strengthen the electric field inside the composite. After an external electric field has been applied to such systems (at  $T = T_c$ ), the dipoles, whose electric dipole moments are oriented in the opposite direction to **E**, will be disoriented. Accordingly, the acquired heterocharge will be disorientated at E =0 by the filler's surface, and its lifetime will be insignificant.

#### 5. Conclusions

1. It has been shown that the TSD method is an effective tool for studying the structure features of polymer composites.

2. The maximum of electric losses of the MWS type, in addition to the  $\alpha$ -transition, has been found to emerge in such microheterogeneous systems, in particular, three-phase ones (polymer (PVC) – BL – superfine filler). The value of the maximum depends on the thermoelectret formation time in an external

electrostatic field, the field strength, the time delay of the exposition after the composite polarization, and the type and the concentration of a superfine filler in the composite.

3. The activities of superfine fillers in PVC, with respect to their influence on the character of the TSD spectrum, are ranged (at  $\varphi = 0.5$  vol.%) as follows: W, Zn, graphite, talc, and corundum.

4. The existence or the formation of the additional microheterogeneity in the systems based on linear flexible chain polymers, making use of superfine fillers, opens an opportunity to carry out the stable directional control with high temporal and power parameters over their thermoelectret properties.

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#### ЗАСТОСУВАННЯ МЕТОДУ ТЕРМІЧНО СТИМУЛЬОВАНОЇ ДЕПОЛЯРИЗАЦІЇ ДЛЯ ВИВЧЕННЯ СТРУКТУРИ ПОЛІМЕРНИХ КОМПОЗИТІВ

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Резюме

Методом термічно стимульованої деполяризації (ТСД) крім  $\alpha$ -переходів досліджено втрати максвелл-вагнер-сілларсівського типу (MBC) у наповненому полівінілхлориді (ПВХ). Встановлено, що в таких мікрогетерогенних системах величина максимуму електричних втрат MBC-типу залежить від часу  $t_p$ формування термоелектрету у зовнішньому електростатичному полі, напруженості поля E, часу  $t_e$  експозиції після поляризації, типу і вмісту  $\varphi$  високодисперсного наповнювача у ПВХ. Згідно з теорією молекулярної релаксації проаналізовано джерела утворення областей дисперсії кінетичних одиниць структуроутворень гетерогенної полімерної системи. Дослідження, проведені з використанням теорії нормальних мод, показали, що активність високодисперсних наповнювачів у ПВХ стосовно впливу на характер спектра ТСД розподіляється в ряду: W, Zn, C, тальк, корунд при  $\varphi = 0,5$  об. %.