ELECTRET PROPERTIES OF ZrO₂ NANOPARTICLES – POLYPROPYLENE COMPOSITES

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Polypropylene samples with the additive of ZrO_2 nanoparticles at concentration of 3 vol.%, at which the highest electret properties are observed, have been studied by the thermally stimulated depolarization (TSD) current method at different intensities ($5 \cdot 10^6$ V/m, 10^7 V/m and $1.5 \cdot 10^7$ V/m) of pre-applied electrostatic field. The measurement of TSD currents revealed the presence of two main peaks in the spectra of the nanocomposite at 25-35°C and 120-140°C. They appear as a result of destruction of one or another category of traps of injected charges. Calculations have shown that there is a monomolecular mechanism of charge recombination in these nanocomposites. It is shown that increasing the applied electric field leads to an increase in the intensity of the termograms, reaching a maximum at 10^7 V/m and then decreasing at $1.5 \cdot 10^7$ V/m. The activation energy, the total accumulated charge and the relaxation time behave similarly.

Keywords: polypropylene; zirconium dioxide; nanocomposite; charge recombination; thermally stimulated depolarization curren; monomolecular and bimolecular mechanism
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INTRODUCTION

In recent years, there has been an increased interest in obtaining polymer electrets with the highest charge storage capability and stability. The range of use of electrets extends from household appliances to special-purpose equipment. The possibility of regulating the electret properties of polymers by adding fillers to the initial polymer matrix is of sufficient interest [1, 2, 3]. The use of metaloxide nanoparticles for modification of polymers makes it possible to significantly improve a number of properties of polymer compositions, in particular, deformation and strength, fire resistance, electrical conductivity and thermal conductivity [4, 5]. During operation, devices with elements made of polymer nanocomposites are subjected to prolonged exposure to electric fields [6,7]. The use of external fields and radiation (electric field exposure, corona discharge, electron or ion bombardment, laser and X-ray radiation) contributes to an increase in the electret effect of polymer composites due to the formation of active functional groups in the structure [8, 9]. Earlier we have shown that at a concentration of 3 vol.% ZrO_2 in polypropylene an increase in electret properties is observed [10].

The aim of this work is to establish the mechanism of electric field effect on the electret properties of polypropylene with a concentration of 3 vol.% ZrO_2 nanoparticles.

EXPERIMENTAL

The isotactic polypropylene (PP) granules with dimensions of 5 mm (Dema Import and Export Co. Ltd., China) were used to make the matrix.

Granules were dissolved in toluene at 120°C. The zirconium dioxide particles with sizes of 20-25 nm of the monoclinic phase (Sigma-Aldrich, USA) stabilized by yttrium oxide were added into the mixture and shaken for 1 h using a magnetic mixer. The solution is subjected to thermal treatment for 3-6 hours. To remove free solvents from the solution obtained, it is treated under vacuum conditions. After drying of toluene in fume hood, the composites with zirconium dioxide of 3 vol.% were obtained.

Disc-shaped samples of composites were obtained by hot pressing at temperature of 175°C and pressure of 15 MPa. Pressing time after reaching the selected temperature was 3 min. The diameter and thickness of the obtained films were 4 cm and 80-90 μm, respectively.

The samples were subjected to the electrostatic field with different intensity ($5 \cdot 10^6$ V/m, 10^7 V/m and $1.5 \cdot 10^7$ V/m) at room temperature for 1 h. A high-voltage rectifier (VSM-989, Russia) was used as a voltage source.

The charge states were studied by the method of thermally stimulated depolarization (TSD). In order to measure currents, the samples were placed in the grounded heated cell of the sandwich type with clamping stainless steel electrodes. The electrodes were connected to the electrometric amplifier U5-11 (firm MNIPI, Russia) the output of which was attached to the two-coordinate recorder (Endim 620.02, firm RFT, Germany). The measurements of TSD currents depending on temperature were carried out in the temperature range of 0-230°C with a linear increase in temperature at the rate of 4 degrees/min.

The activation energy was calculated by using initial rise method [11]. The total charge Q is defined as:

$$Q = \frac{1}{\beta} \int_{T_1}^{T_2} I(T)dT, \qquad (1)$$

where T_1 and T_2 are the lower and upper temperature limits for the existence of this charge, β is the rate of linear heating process.

RESULTS AND DISCUSSIONS

Fig. 1 shows the thermograms of depolarisation currents in the temperature range 0°C-200°C of PP+3%ZrO₂ nanocomposites, which were subjected to

the preliminary action of electrostatic field of different intensity at room temperature.

As shown in the figure, the measurement of thermally stimulated depolarization currents revealed the presence of two main peaks in the spectra of the nanocomposite at 25-35°C and at 120 -140°C. It indicates the existence of a complex mechanism of charge transfer and relaxation processes in the considered system. The formation of dominant maxima in the spectra of thermally stimulated currents is caused by the formation and disappearance of structural charged defects that were in potential traps before the thermal activation process. They appear as a result of destruction of one or another category of traps of injected charges. In our nonpolar matrix, the stability of

the electret state is determined by localized states (traps) on the surface. Surface traps are often energetically deeper than bulk traps. As a result, homocharge accumulates on surface traps and is efficiently retained by them. The maximum in the low-temperature region is due to the emptying of traps at the interface between the amorphous and crystalline phases of the matrix. [12]. The release of charge carriers from the traps located at the interface between the matrix and the filler, accompanied by an intense movement of the end groups, double bonds and oxidised fragments of the macromolecules, is registered in the TST spectrum in the form of a high temperature peak. [13]
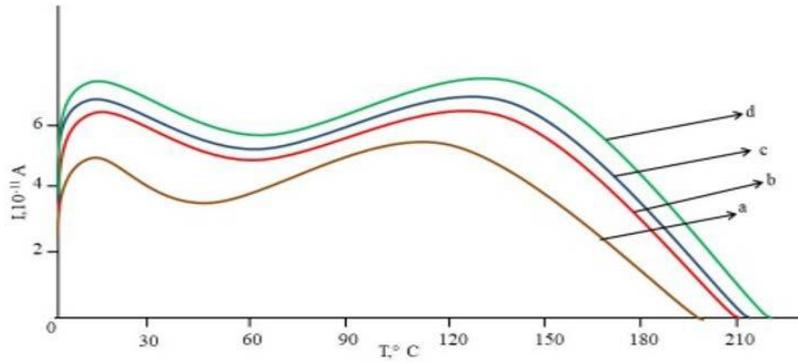

Fig. 1. TSD thermograms for PP+3%ZrO₂ nanocomposites subjected to the preliminary action of electrostatic field of different intensity at room temperature: (a) 0; (b) $5 \cdot 10^6$ V/m; (c)10^7 V/m; (d) $1.5 \cdot 10^7$ V/m.

The mechanism influencing the charge capture and release processes in nanocomposites is defined as follows. The criterion for determining the mechanism of charge recombination is the relation [14]:

$$\delta = \frac{T_2 - T_m}{T_2 - T_1} \qquad (2)$$

where T_m is the temperature corresponding to the maximum of the depolarization current, T_1 and T_2 are absolute temperatures at which the TSD peak has half the magnitude of the peak maximum on the low and high temperature sides, respectively.

To satisfy the monomolecular recombination mechanism, the following relationship must be fulfilled:

$$\delta \leq \frac{1}{e}\left[1 + \frac{2KT}{E}\right] \qquad (3)$$

While the opposite applies to the bimolecular mechanism, namely:

$$\delta \geq \frac{1}{e}\left[1 + \frac{2kT}{E}\right] \qquad (4)$$

where e is base of natural logarithm, k is Boltzmann constant; E is activation Calculations have shown that there is a monomolecular mechanism of charge recombination in these nanocomposites.
Electrical treatment has a noticeable effect on the thermograms. Increasing the applied electric field leads

to an increase in the intensity of the low and high temperature peaks. In addition, the high temperature peak shifts towards high temperatures while the low temperature peak shifts towards low temperatures. It is attributed to the change in crystallinity, Electrical treatment not only increases the number of charge traps, but also favours a greater depth of their occurrence, which in turn provides greater stability of the charges. Charges are injected into the composite during the polarization process from the inter-electrode spaces and from the electrodes [15]. As the polarisation voltage increases, the values of electret properties increase due to the increase in the number of injected carriers trapped inside the material. In addition, the mobility of macromolecules adsorbed on the filler is limited, which allows the charge to be more stable. At low field intensity applied to the sample, the charges coming out of the traps accumulate. It, in turn, creates a local internal field. When the field intensity $15 \cdot 10^6$ V/m is applied, a local field of maximum intensity is formed, which prevents the charges from leaving the traps. As a result, the intensity of the thermogram decreases. This agrees with the results of calculation of the accumulated volume charge depending on the applied voltage (Fig. 3).

Fig. 3 shows the dependence of the activation energy W of the release of charges from the traps, as well as the temperature of the maxima of the TSD peaks, as a function of the intensity of the electrical treatment. The activation energy represents the depth of the traps, i.e. the potential barrier that the charges have

to overcome when leaving the traps. As can be seen, the activation energy increases with increasing applied electric field, reaching a maximum value at 10^7 V/m and then decreasing at field intensity $1,5 \cdot 10^7$ V/m. Such a dependence of the activation energy is in agreement with the results of calculations of the dependence of the accumulated volume charge on the applied field. As can be seen from the same figure, the temperature of the thermogram maxima is synchronized with the course of the activation energy curves. In fact, according to [16],

the dependence between the activation energy and the temperature of the thermogram peak has the following form

$$E_t = 25kT_m \qquad (5)$$

That is, the change in activation energy is directly proportional to the peak temperature of the thermogram.
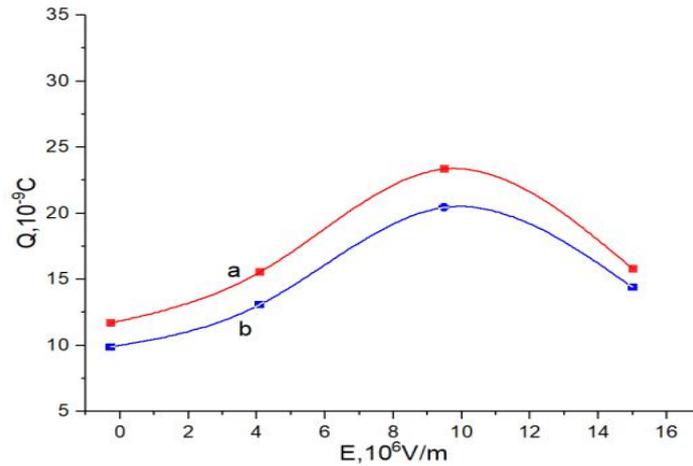

Fig. 2. Dependence of the magnitude of volume charges accumulated in the traps of the composite with the concentration of 3 vol.% ZrO_2 on the external electric field intensity: (a) charges accumulated by the traps corresponding to the high-temperature peak; (b) charges accumulated by the traps corresponding to the low-temperature peak. As can be seen from this figure, the magnitude of the accumulated charges increases with increasing field, reaching its maximum value at field intensity 10^7 V/m. Further increase of the external field strength leads to decrease of the accumulated charge.
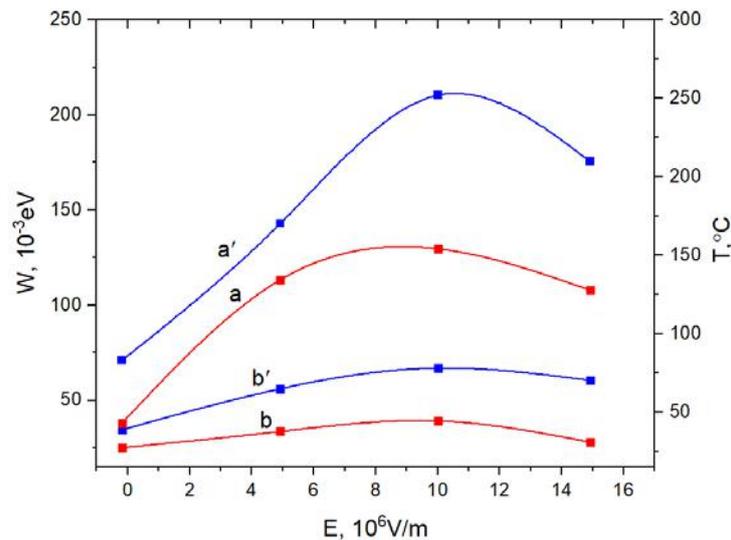

Fig. 3. Temperature of the maxima of the TSD peaks and activation energy W of charge release from traps as a function of the applied electric field intensity:

The magnitude of the charge is due to the amount of injected charge carriers trapped in deep bulk traps. The magnitude of the electret characteristics of polymers depends on the amount of injected charge carriers penetrating into the material during polarization fixed on energy traps of different nature.

The surface potential V as a function of time is well described by an exponential function of the form:

$$V_c = V_0 \exp(-t/\tau), \qquad (6)$$

where V_0 is initial value of the surface potential; τ is the relaxation time; t is time.

Relaxation time characterises the ability of an electret sample to retain charge over time. It depends on various factors. In particular, on the diffusion of charges inside the sample. In this case, the surface potential decreases.

Another reason for the decrease of the surface potential is the recombination of charges. In addition, the relaxation time is also influenced by the environment, temperature, and electron-ion processes. Calculations of the relaxation time according to the relation (6) are given in the form of points in Fig. 4.
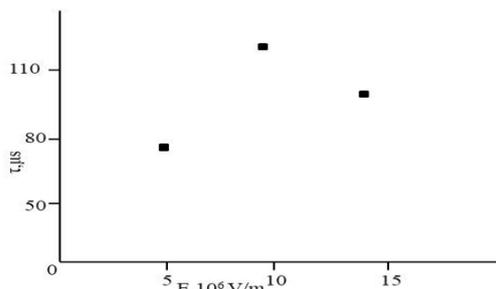

Fig.4. Relaxation time dependence on the intensity of the pre-applied field.

As can be seen, the maximum value of relaxation time is observed at the pre-exposure of an electric field with an intensity of 10^7 V/m. It is at this intensity of the field applied to the sample that greater electret durability of the nanocomposite sample is observed.

CONCLUSION

It is shown that increasing the applied electric field leads to an increase in the intensity of the termograms, reaching a maximum at 10^7 V/m and then decreasing at $1.5 \cdot 10^7$ V/m. The activation energy, the total accumulated charge and the relaxation time behave similarly. This is due to the increase in injected charges, but at higher field intensity of an internal field is formed which prevents this process.

In other words, the highest and most stable electret properties in the investigated nanocomposites are formed under the pre-exposure to an electric field with an intensity of 10^7 V/m

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