EFFECT OF HEAT TREATMENT ON POLYPROPYLENE AND METAL OXIDE (PP+ZrO_2) NANOCOMPOSITES

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The presented research work specifies the charge state before and after heat treatment of nanocomposites composed of isotactic polypropylene and metal oxide nanoadditive ZrO_2. It has been established that PP+3% ZrO_2 nanocomposites have the ability to retain a greater charge. The parameters of the electret state of a nanocomposite of a given composition at different temperature values have been obtained by the TSD method. It is concluded that the maxima in the region of low and high temperatures are due to charges accumulated in crystalline and amorphous phases and boundaries of polymer nanocomposites. The results of the conducted studies correlate with the results of the SEM.

Keywords: : nanocomposites, polypropylene, electrothermal polarization, thermally stimulated depolarization curren.
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INTRODUCTION

Polymers are widely used in modern science and technology as electret materials. Examples include radiation transducers, electroacoustic devices, small electret microphones, etc. Polymer electrets are commonly used in mechanical, electrical, acoustic transducers, storage devices, electric motors, generators as elements, friction zones, filters and membranes, anti-corrosion structures and medicine [1, 2]. The main advantage of these devices is the high internal resistance and the lack of an additional power supply. This feature ensures that the size and weight of the device will be small. For further development of such a promising field, it is necessary to obtain new electret materials with a high charge density and the ability to store this charge. For this reason, one of the main goals of modern condensed matter physics is to obtain polymers capable of holding more electret charges. It has been established that when polymers are modified with various substances, including metal oxides, high-density and stably charge-retaining electrets are obtained [3,4]. Modifications can cause a change in the supramolecular structure, provided that the chemical composition is maintained. Thus, in the case of these modifications, oxides of elements are formed in the polymer in the form of nanogroups, and the electret state increases significantly. In the presented research work, the electret state and its parameters obtained after heat treatment using isotactic polypropylene and the metal oxide nanoadditive ZrO_2 as a matrix have been determined.

EXPERIMENTAL METHODOLOGY

When obtaining the nanocomposites under study, first the required amount of isotactic polypropylene (Dema Import and Export Co. Ltd., China) in the form of granules 5 mm in size is weighed with an accuracy of 10^{-4} and dissolved in toluene up to the melting temperature of the polymer (≈175°C). Then, to ensure uniform distribution of the nanoadditive inside the matrix, after its melting, ZrO_2 metal oxide nanoparticles (Sigma-Aldrich, USA) 20-25 nm in size with a monoclinic structure in an amount of 1-15%, stabilized by YtO_3, are added to a completely transparent liquid. After cooling, nanocomposites are obtained by hot pressing under a pressure of 15 MPa for 3 minutes. In the fast cooling mode at a rate of 20-35 ° C/sec, the nanocomposites with the foil are placed in an ice-water mixture. The thickness of the samples is 50-70 μm. The change in charge state after heat treatment at various temperatures was determined by the method of thermally stimulated depolarization (TSD). TSD currents were determined at a rate of 4 ° C/min in the temperature range of 50-230°C. The activation energy of the particles was calculated by the Garlick-Gibson method using formula $\frac{d\ln I(T)}{d(1/kT)} \approx -W$ (1) based on the slope of the tangents drawn to the TSD currents.

RESULTS AND DISCUSSION

Figure 1 shows TSD curves for PP and PP+ZrO_2 nanocomposite depending on the percentage of nanoadditive. Analysis of the curves shows that they consist of two regions of maximum – low-temperature (20-40°C) and high-temperature (120-150°C). That is, on these curves, along with the peaks corresponding to the PP, other peaks are also observed. According to the results of comparative analysis of TSD spectra, it was found that depolarization maxima appearing in the spectra arise both in the polymer itself and in the layers of PP+%ZrO_2 nanocomposite as a result of relaxation of charges stabilized at the interfacial boundary at characteristic temperatures. The peaks formed in the low temperature region can be attributed to the currents generated by charges released due to heating from defects in the nanocomposite during fabrication. They can be formed as a result of the movement of linked molecular chains in the amorphous phase and free rotation between the lamellae. The maxima in the high temperature region are due to currents created by charges accumulated in

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the phase between the polymer and the nanoadditive. The increase in the electret properties of polymers with the addition of ZrO_2 can be explained by the formation of new structural elements that can act as new traps. Moreover, when nanoparticles are added to a polymer, they can serve as crystal nucleation agents or cause crystal defects. As it is seen from the figure, the TSD currents increase up to 3% of the amount of nanoadditive, but at subsequent percentage amounts a decrease in these currents is observed. This is due to the aggregation of the nanoadditive in a given percentage amount.

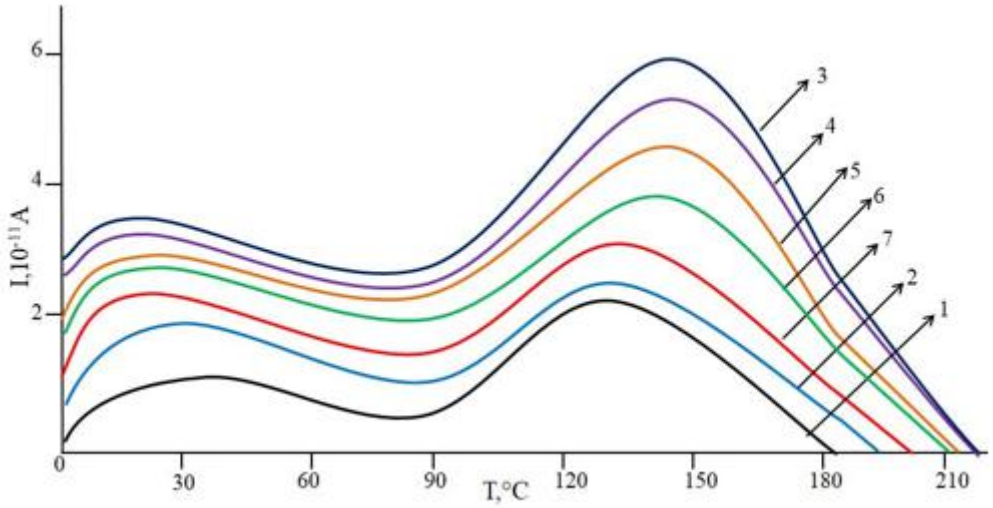


Fig. 1. TSD spectra before heat treatment depending on the percentage of PP and nanoadditive 1 - PP, 2 - PP+10%ZrO_2, 3 - PP+15%ZrO_2, 4 - PP+5%ZrO_2, 5 -PP+1%ZrO_2, 6 - PP+3%ZrO_2, 7 - PP+15%ZrO_2

Let's note that we used formula (2) to calculate the maximum charge

$$Q = \frac{1}{\beta}\int_{T_1}^{T_2} I(T)dT \qquad (2)$$

Here β is the linear heating rate of nanocomposites, T_1 and T_2 are the lower and upper temperature limits of the presence of charges, respectively.

Considering the above, it can be determined that the electret state can be changed by adding a certain percentage of nanoadditive to the PP, and also the parameters characterizing this state can be clarified. However, from the studies carried out it is clear that the relaxation of electret charges weakens when up to 3-10% of a nanoadditive is added to the matrix. When adding 15% nanoadditive, the electret state and the parameters characterizing this state decrease. This is explained by the fact that with a small amount of nanoadditive it acts as a nucleus inside the matrix, and with an increase in the percentage, it acts as a filler [5]. If we examine the table, we can see that the charges accumulated in the surface traps increase up to 3% of the nanoadditive. If we observe the TSD spectra, we will notice that the maxima are obtained between 30-60 °C and 120-150 °C. If we compare the spectral regions of 30-60°C, we will observe that the maxima shift towards lower temperatures and the intensity of the current generated by the TSD tends to decrease. This change can be explained by an increase in the degree of crystallinity depending on the percentage of nanoadditive. The maxima formed in high-temperature regions may be due to space charges generated in the polymer and thermal activation of charge carriers located at the boundary of the polymer nanocomposite.

Figure 2 represents the TSD curves obtained by heating the PP+3%ZrO_2 nanocomposite. To obtain an electret, these samples must be heated to different temperatures and for this reason, the nanocomposite is heated to 60, 100 and 140°C for 2 hours. From the nature of the above curves, it is evident that the heat treatment temperature affects the thermal stability of the nanocomposites. It is clear from the experiments that the electret parameters of thermoelectrets obtained only by heating are less stable. The generated TSD current is due to the self-charges of the polymer and matrix leaving their places under the influence of heat. When the samples are heated, the amount of charge released from the traps begins to change. As the temperature rises, charges begin to release even deep traps, and relax, accelerating in their fields. The frequency of charges released from traps is determined by Boltzmann's law:

$$\omega_t = \omega_0 \exp(-E_k / kT_m) \qquad (3)$$

$$W \approx 25kT_m \qquad (4)$$

where ω_0 is the frequency factor, E_k is the kinetic energy of charges released from traps, k is the Bolsmann constant, and T_m is the maximum temperature in the TSD curves (3). As it can be seen from the formula with increasing temperature, the release frequency from the traps increases exponentially, and the capture time decreases accordingly. On the other hand, according to formula

(4), an increase in temperature leads to an increase in the kinetic energy of charges releasing the traps. The effect of temperature is associated with an increase in the intensity of thermal movement of groups, segments and other kinetic units, which are the main factors influencing the electret state. The presence of maxima in the high temperature region can be explained by an increase in the specific conductivity of the nanocomposite.

Table 1.

Electret parameters of PP and PP+%ZrO_2 nanocomposites depending on the amount of nanoadditive

Nanoadditive %	q, (10^{-6} C/m^2)		Q(nC)		E(eV)		Temperature (°C)	
	I max	II max	I max	II max	I max	II max	I max	II max
0	1,18	1,87	9,42	13,68	0,024	0,068	43	130
1	1,26	18,5	9,68	14,45	0,026	0,075	32	135
3	2,07	2,97	9,89	15,78	0,029	0,083	29	138
5	2,00	2,43	8,45	14,95	0,023	0,079	27	141
10	1,08	2,95	7,45	13,45	0,089	0,061	20	143
15	1,16	2,02	8,39	13,76	0,099	0,084	17	147

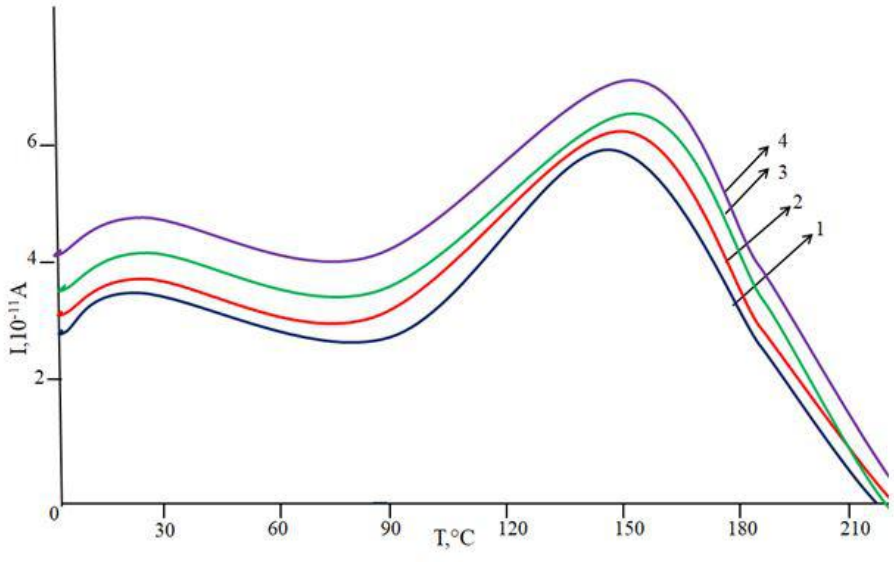


Fig. 2. TSD curves of PP+3%ZrO_2 nanocomposites subjected to heat treatment at different temperatures.

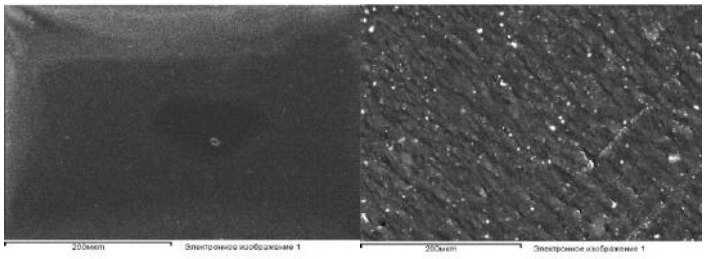
Table 2.

Parameters calculated from the TSD curves of PP+3%ZrO_2 nanocomposites after heating at different temperatures

Heat treatment	q, (10^{-6} C/m^2)		Q(nC)		E(eV)		Temperature (°C)	
	I max	II max	I max	II max	I max	II max	I max	II max
T=293K	2,07	2,97	9,89	15,78	0,029	0,063	25	135
T=333K	1,84	4,07	9,98	15,96	0,034	0,088	23	153
T=373K	1,98	4,2	10,5	16,3	0,039	0,9	20	155
T=413K	2,04	4,8	14,4	18,1	0,045	0,16	18	160

Table 2 summarizes the parameters calculated from the TSD curves of PP+3%ZrO_2 nanocomposites after heating at various temperatures. In the region of relatively low temperatures (30-60°C), a slight increase in the depolarization current intensity is observed. Relaxation of the accumulated charge occurs preferentially in those temperature regions where relaxation transitions are formed. This shows that the electrical and molecular relaxations in polymers are coupled. The presented table shows that these parameters have a smaller value only in the case of polymer and at low temperature. However, an increase in temperature is accompanied by an increase in the activation energies of charges released from traps. But it was determined that if the electret lifetime is 35 minutes at a temperature of 100 °C, then this time is reduced to 16 minutes at a temperature of 140 °C [6]. When heating without applying an external field, we slow down the polarization process so that the charges displaced relative to each other relax in the internal field of the electret. Thus, the studies carried out show that very small area electret states are observed in the nanocomposite due to the effect of temperature [7]. Indeed, the temperature we applied can only induce oscillations of the CH chains of the polymer and the nanocomposite.

If we examine the SEM images of the investigated nanocomposites, we can see agglomerations formed on the surface after two-hour heat treatment, which is a manifestation of defect formation in the nanocomposite. In general, if crystallite melting and structure rearrangement occur during the first hours of heat treatment, then the accumulation of particles of a certain structure is noticed during the subsequent intensification of the heat treatment effect. Figure 3 shows the SEM images before and after heat treatment.



a) b)

Fig. 3. SEM images of PP+3%ZrO_2 nanocomposite before (a) and after 2-hour heat treatment (b).

Thus, the conducted studies allow us to conclude that by introducing nanometaloxides into polymers it is possible to regulate the stability of the electret states of these substances, and also that the maxima on the TSD curves after temperature treatment are achieved due to the charges possessed by the polymer and nanocomposite, which are accelerated and leave the material as a result of thermal effects.

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