EFFECT OF ELECTROTHERMOPOLARIZATION ON RELAXATION TIMES OF NANOCOMPOSITES BASED ON PP AND PE

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The effect of electrothermopolarization on the surface density of electret charges and the relaxation time of the charge from the reciprocal temperature for a number of nanocomposites based on PP and PE are studied. It is shown that the addition of a nanofiller (1% MnO_2, 0.5% MnO_2, 7% ZrO_2, 2% TiO_2, 1% $PbCrO_4$) leads to an increase in the values of the electret potential difference of nanocomposites, and then decreases. This character of the dependence is explained by a change in the physical structure of the boundary layer of the polymer matrix and a change in the interphase interaction on the strength of the polarization field. The dependence of the charge relaxation time on the reciprocal temperature for all samples has approximately the same slope.

Keywords: nanocomposite, polyethylene, polypropylene, relaxation, electrothermopolarization.
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INTRODUCTION

The study of nanocomposite materials consisting of polymer matrix and nanoscale filler is currently a rapidly developing scientific area of the physics of macromolecular compounds. The use of nanocomposites instead of pure polymers is becoming especially important due to the fact that nanosized filler gives the material properties that are unattainable by "conventional" polymer composite materials. One of the most common large-scale polymers is polyethylene and polypropylene; this fact made them very promising materials for obtaining electrets and became decisive in the choice of research objects. It is no coincidence that a large number of works on the study of the electret effect in nanocomposites are devoted to these polymers [1-5].

The introduction of nanofillers has a significant effect on the physicochemical characteristics of polymeric materials [6-7,9]. This is largely due to the appearance of interfacial layers of the polymer matrix near the filler surface. The study of their properties is necessary to improve the physical, mechanical and operational properties and to improve their processing technology. Changes in the electret potential difference, effective surface charge density and its sign (homo- or hetero-charge) depending on the parameters of electrothermopolarization were determined [6-11]. It is shown that small amounts of nanofillers introduced into the polymer play the role of artificial nuclei of crystallization, which leads to an improvement in the properties of the nanocomposites. With the introduction of a significant amount of fillers, the properties of the nanocomposite material are determined both by structural changes in the polymer matrix and changes in the near-surface layer of the nanofiller. Nanofillers affect the rate of crystallization or hardening, the temperature of relaxation transitions, electrical, mechanical, thermophysical and other properties. In this regard, the study of relaxation and charge formation processes in electret nanocomposite materials is important.

OBJECTS AND METHODS OF EXPERIMENT

It is known that for the practical application of nanocomposite materials, an important parameter that characterizes the properties of materials is the electret difference in surface potentials and the lifetimes of electret charges, determined by various methods, of which the induction method is the most widespread one. The surface charge density is calculated by the formula:

$$\sigma = \frac{\varepsilon\varepsilon_0 U}{\delta}$$

where ε - is the dielectric constant of the composition, ε_0 - is the electrical constant equal to $8{,}85\cdot10^{-12}$Kl/(Nm^2), U - is the electret potential difference equal to the compensating voltage; δ - sample thickness.

Obtaining a sample of the nanocomposite is carried out by hot pressing at a polymer melting temperature and a pressure of 15 MPa for 10 minutes, followed by cooling to room temperature under pressure. The hot pressing process is characterized by three main technological parameters - pressure, temperature and holding time in the molten state. The nanocomposites were preliminarily subjected to electrothermopolarization at a temperature of T_p = 373K for an hour. To obtain the samples under study, the composite is first heated to the polarization temperature T_p, then a constant electric polarization field E_p is applied and kept for the time t_p in the field, after which, without removing the field, it is cooled to room temperature. This method of polarization makes it possible to vary the energy value and the concentration of injected charges in the nanocomposites in a wide range. The film was cooled to room temperature under the action of an electric field of strength $E_p=7\cdot10^6$V/m.

In this work, we investigated nanocomposites of polyethylene (PE) containing 1% volume content of $PbCrO_4$ nanofiller and polypropylene (PP) containing

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0.5% and 1% volume content of MnO_2 nanofiller and 7% of ZrO_2, 2% TiO_2.

The dependences of the relaxation time on the reciprocal temperature for nanocomposites are also investigated.

RESULTS AND THEIR DISCUSSION

By changing the isothermal modes of pressing the crystallization conditions, it is possible to vary the supramolecular structure of polymers in polymers and composite systems, which is very important when creating highly efficient composite materials for various converters. Also, the introduction of nanofillers can create in the polymer new artificial nuclei of crystallization and new trap centers for the electric charge, which can contribute to an increase in the surface density of electret charge and the lifetime [7, 8, 10].

Developed electret polymer nanocomposites based on PP, PE and nanoparticles 1% MnO_2 (PP/1% MnO_2), 0.5%MnO_2(PP/0.5%MnO_2), 7%ZrO_2 (PP/7%ZrO_2), 2%TiO_2 (PP/2%TiO_2), 1%$PbCrO_4$ (PE/1%$PbCrO_4$) showed an electret effect, which is noticeably superior in its characteristics to the known traditional analogs, which makes it possible to use these nanocomposites to obtain highly efficient electret microphones, electroacoustic devices, etc. Figure1 shows that the presence of nanoparticles significantly affects the manifestation of the electret effect in polypropylene and polyethylene.

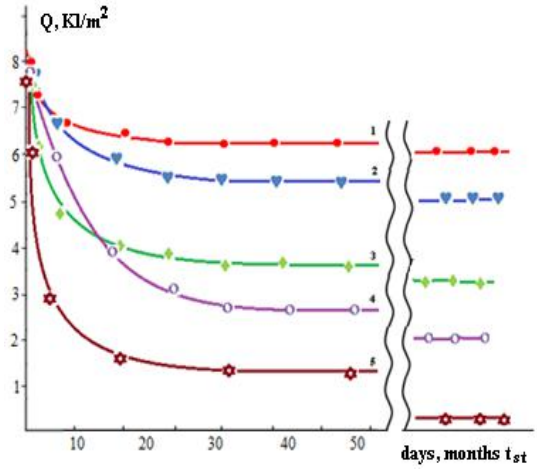

Fig.1. Dependence of the surface density of electret charges (Q) on the storage time t_{st} of nanocomposites: 1.PP/1%MnO_2; 2.PP/0.5%MnO_2; 3.PP/3%TiO_2; 4.PP/5%ZrO_2; 5.PE/1%$PbCrO_4$.

The data obtained indicate that the addition of nanofillers (1%MnO_2, 0.5% MnO_2, 7%ZrO_2, 2%TiO_2, 1%$PbCrO_4$) leads to an increase in the values of the electret characteristics of the nanocomposite, but only to a certain extent (Fig.1), after which some decrease is observed. Because the introduction of the nanofillers into the polymer matrix leads to changes in their supramolecular structure, they have a significant effect on the mobility of various kinetic units of macromolecules and on the spectrum of their relaxation times. In this case, the general course of the dependence of the electret potential difference of electrets on the nanofiller content first slightly increases and then decreases. This character of the dependence is also explained by a change in the physical structure of the polymer matrix of the interphase layer and a change in the interphase interaction on the strength of the polarization field.

It is known that the relaxation of the electret state is accompanied by a decrease in the magnitude of the excess charge accumulated in the electret, the surface potential, the flow of current in the bulk of the sample, and other phenomena. It can occur both at a constant temperature and when it rises over time according to a certain law.

Polarization and homocharge change exponentially with time. If we measure σ_{ef} (t) at different temperatures, then by plotting the dependence of logσ on 1/T, we can find the relaxation time of the charge τ. The relaxation time at the operating or storage temperature (~ 20 ° C) is obtained by extrapolating the dependence $\lg\tau = f(1/T)$.

The stability of the electret charges of nanocomposites in this work was investigated at relatively high temperatures. This was due to the fact that it took a lot of time to determine the lifetime of electret charges at room temperature [11]. Deep traps at room temperature can store charges at this level for several months or even years. As the temperature rises, the probability of carrier escape from the trap increases sharply. Therefore, in order to establish the real lifetime of electrets by extrapolation, the lifetime at room temperature was determined using the following relationship:

$$\tau = \tau_0 \cdot \exp\left(-\frac{E}{kT}\right)$$

where τ- is the lifetime at a given temperature; τ_0 - lifetime at room temperature; E - activation energy of electret charges; k - Boltzmann's constant.

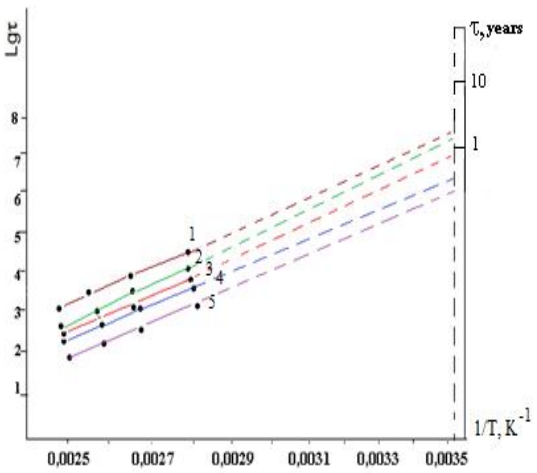

Fig. 2. Dependence of the charge relaxation time on the reciprocal temperature and the lifetimes of nanocomposites: 1.PP/1%MnO_2; 2.PP/0.5%MnO_2; 3.PP/3%TiO_2 ; 4.PP/5%ZrO_2; 5.PE/1%$PbCrO_4$.

In Figure 2. the dependences of the relaxation times of the charge on the reciprocal temperature and the lifetimes for a number of nanocomposites are presented. At the intersection of the extrapolated straight lines with the dashed vertical, corresponding to the storage temperature of the electret (room temperature), we obtained the expected lifetimes of the electret charge when stored under these conditions.

It was found that the lifetime of polymer nanocomposites based on PP/1%MnO_2 is 575 days, for nanocomposites based on PP/0.5%MnO_2 - 487 days, for PP/ZrO_2 - 225 days, for PP/TiO_2 - 321 days, and for nanocomposites based on PE/$PbCrO_4$ - 134 days. The dependences of E and τ_0 on time are highlighted taking into account their independence from each other.

In reality, they are connected in a complex way due to the presence of the process of displacement of charge carriers and polarization in the internal field of the electret. With such estimates of the lifetime, the lifetime of the hetero - and homocharge, as well as the individual components of these charges, should be separated.

It can be seen that the dependence on the reciprocal temperature for all samples has approximately the same slope, but the relaxation times are different. Because with an increase in the temperature of electrothermopolarization of the compositions of electrets, the size of the "cells" in the polymer network decreases, which leads to a decrease in the values of the dielectric relaxation time.

Thus, it follows from the above experimental results that nanofillers (1%MnO_2, 0.5% MnO_2, 7% ZrO_2, 2%TiO_2, 1%$PbCrO_4$) can create new traps for electric charge in the polymer (PP and PE), which can contribute to an increase in the surface density of electret charges and the lifetime. The experimental results show that the stabilization of charges in composites is determined by the supramolecular structure of the polymer matrix, which is controlled by changing the crystallization conditions, as well as by the formation of a high surface density of electret charges, characterized by the value of Q. Also, the dependence of the charge relaxation time on the reciprocal temperature for all samples has approximately the same slope, but relaxation times are different.

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