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ELECTRET CHARGE IN NANOCOMPOSITES BASED ON POLYETHYLENE

Abstract: The electret state of nanocomposites based on low density polyethylene has been investigated. It was found that the increase of montmorillonite content in the samples leads to an increase in the absolute values of thermally stimulated currents. The treatment of samples in a corona discharge leads to an increase in the effective surface charge density. In the positive and negative corona discharges, the LDPE samples acquire approximately the same charge, and their modification with montmorillonite slightly increases the amount of charge. A relationship has been established between the initial value and the relaxation rate of the technological charge of the electret. The higher the technological charge, the faster its decline occurred.

Key words: polyethylene, nanocomposite, electret, technological charge, charge relaxation.

Language: English

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Introduction

An electret is a piece of dielectric with a quasi-permanent electric charge. The term "quasi-permanent" means that the time constants characterizing the discharge of the electret significantly exceed the time intervals during which the given electret is studied [1, p. 11]. The study of the electret effect began at the beginning of the last century after the discovery of electrets in 1919 by the Japanese physicist Eguchi [2], although theoretically the existence of electrets was predicted by the English physicist Heaviside back in 1892 [3].

Electrets have been studied most intensively since the 1960s, due to the wide possibilities of their practical application in electronics, electrical engineering, biology, medicine, and many other fields of science and technology [4-11]. For example, in mobile communication systems, electro-acoustic converters on electrets have almost completely replaced converters of other types due to the high economic efficiency of their production, as well as because of the advantages in their consumer properties (miniature size, low power consumption) [12].

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It should be noted that for all of these technical applications of electrets, materials with high density and charge stability are required. Therefore, the problem of stabilizing the electret charge and increasing its density is relevant for physics and materials science, both from a scientific point of view and in terms of wider use of electrets.

In recent years, a line of research has been intensively developing related to the study of the effect of ultra- and nanodispersed fillers on the stability and magnitude of the electret charge of polymers [13-18]. The presence of such fillers in the system determines the manifestation of so-called size effects due to the anomalous structural characteristics of nanosized particles (distortion of the crystal lattice due to changes in interatomic distances and bond angles), special physical (collectivization of electrons, delocalization of electron density), thermodynamic (the ability of particles to be highly efficient traps for charges carriers) and other properties of fillers.

It is obvious that the creation of stable electret materials based on polymers should be based on the principles of complex modification of these polymers, including various types of effects on them. It is preferable that these effects contribute to the formation of electrically active centers in polymers, which could disturb the local electrical equilibrium, create a nonzero electrical moment and cause forced polarization in microvolumes of the polymer matrix, including with the participation of injected (introduced from the outside) carriers of electric charge [13, 15, 16, 18-20].

In a number of works, the electret properties of polymer nanocomposites based on polyethylene filled with carbon black (filler particle size 30–40 nm) have been investigated [14, 21, 23]. It is shown that the maximum effective surface charge density σ_{ef} occurs at a filler content of about 4 vol. %. It is characteristic that the stability of the electret state also significantly increases in LDPE filled with carbon black (4 vol.%), in comparison with unmodified LDPE [22, 23].

An interesting fact is that the content of the filler is 4 vol. % is optimal in terms of the magnitude and stability of the electret charge both for nanodispersed carbon black and for larger filler particles (talc, titanium dioxide, silicon dioxide). Moreover, the nature of the filler particles (conducting or dielectric) also does not play a significant role in this case. This can only be explained by the fact that the main role in creating a stable electret state of polymer composites is played by the transition layer at the polymer-filler interface, which is the concentration of energy traps of various depths for injected charge carriers.

Analysis of the literature data indicates that the introduction of nanosized additives into polymers by the methods of volumetric and surface modification can significantly increase the charge, time-, and thermal stability of polymer electrets. However, the experimental material accumulated to date does not

allow making any generalizing conclusions about the mechanisms for increasing the magnitude and stability of the electret charge in polymer nanocomposites, especially since in some cases such an increase is not observed. Nevertheless, the prospects for improving the electret properties of polymer nanocomposites look promising, and they consist, first of all, in an integrated approach to the process of polarization of polymers, including, first, surface and bulk modification of polymers, including at the level of chemical interactions, and -second, the use of new methods of physical influence, such as, for example, laser irradiation with different wavelengths. It is known, for example, that laser treatment of fillers for polymer composites increases the indices of physical, mechanical and tribotechnical properties [24].

The aim of this work is to study the charge state of polyethylene-based nanocomposites polarized in a corona discharge. Corona electrets (obtained as a result of processing the samples under study in a corona discharge) are among the objects most convenient from the point of view of studying polarization mechanisms, especially in composite dielectrics.

Materials and research methods

For the preparation of samples, powdered low density polyethylene (LDPE) was used, which was mechanically mixed with a filler at a content of the latter from 0 to 3 mas %. Highly dispersed montmorillonite (MMn) with an average particle diameter of 20 nm was used as a filler. Samples of films with a thickness of 150-200 μm were prepared by hot pressing.

The samples were polarized in a corona discharge (positive and negative) in several stages: 1) heating the furnace together with the sample to a temperature of 80 °C and fixing it; 2) switching on the corona discharge and holding the sample in it for 15 minutes; 3) natural cooling of the furnace to 25 °C, while the corona discharge was not turned off. The voltage across the needle electrode was 25 kV, while the field strength between the electrode and the sample was 10 kV/cm.

The electret charge was measured by standard methods [25]. The effective surface charge density (ESCD) of the samples σ_{eff} was determined using an IPEP-1 meter of electrostatic field parameters (manufactured by OAO MNIPI, Belarus, Minsk). The measurement was carried out with an electrode at 2 cm from the test sample. The measurement error (for each point from 5 to 8 samples) varied for each of the groups of samples and will be discussed below. Thermally stimulated depolarization of the samples (electret-thermal analysis) was carried out between two electrodes by heating the sample to 120 °C at a constant rate and measuring the thermally stimulated current (TSC). As a result, a TSC spectrum was obtained for each sample.

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Results and discussion

In Fig. 1 one can see that immediately after the formation by hot pressing, a sufficiently large charge appears on all samples (group I), which decreases over time and stabilizes after about 200 minutes (group II). We called this steady-state electret charge as a

technological. It is somewhat higher in samples containing MMn, which is possibly due to the Maxwell-Wagner polarization at the filler-binder interface, which proceeds more intensively at an elevated temperature of sample formation.

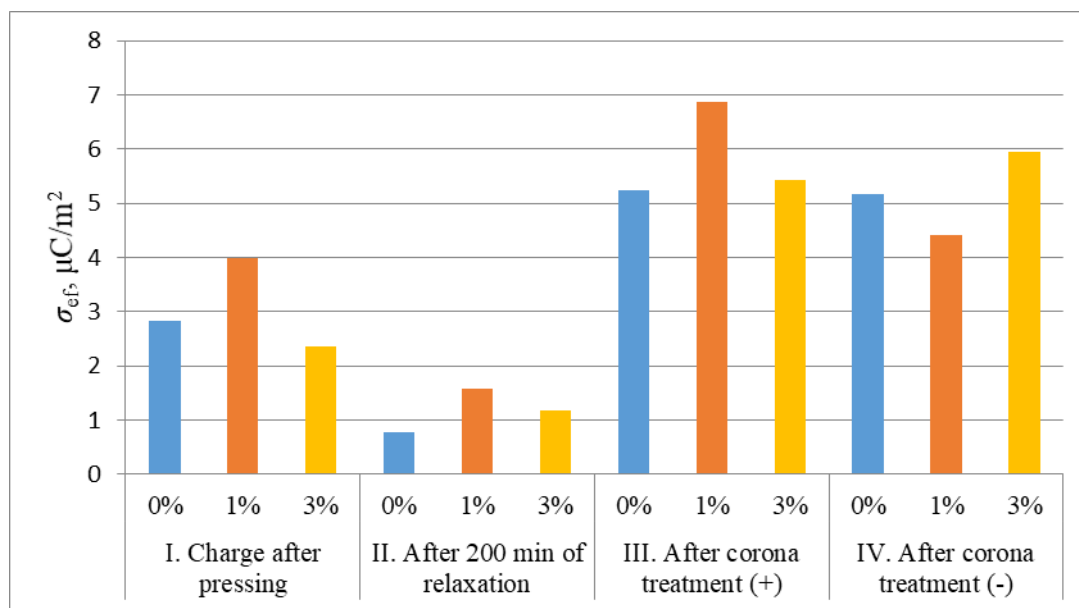


Fig. 1 – ESCD values in LDPE-based samples with different MMn concentration, before and after corona treatment with positive (+) and negative (-) polarity

The treatment of samples of group II in a corona discharge of positive polarity (group III) leads to a rather significant increase in ESCD, and the modification with a filler slightly increases the charge. An insignificant increase in ESCD at a filler content of 1 mas % is apparently due to the so-called “effect of low concentrations”, when an increase in the parameters of some physical-mechanical properties is observed in polymer nanocomposites at a low filler concentration [26]. The results obtained agree with the data of [14], which shows that the maximum effective surface charge density occurs at a filler content of 4 vol. % (which corresponds to about 1% of the mass.).

The processing of samples in a negative corona (group IV) also leads to an increase in ESCD, and the maximum charge is formed in composites with a filler concentration of 3%. This is confirmed by the results of electret thermal analysis.

The Fig. 2 shows the generalized TSC spectra of LDPE samples after their formation by hot pressing and charge stabilization. The first peak of TSC in the temperature range of about 70 °C corresponds to the relaxation of the technological charge concentrated

mainly in the amorphous part of the polymer. The second peak at a temperature of about 110 °C corresponds to the melting point of the crystalline phase of polyethylene and is caused by charge carriers of the opposite sign. An increase in the MMn concentration leads to an increase in the absolute values of the currents, which is due to the Maxwell-Wagner polarization at the filler-matrix interface.

The treatment of samples in a corona discharge changes the picture of charge relaxation and leads to a sharp increase in TSC (Fig. 2, b), and the intensity of the peak corresponding to the melting temperature increases by 2-3 orders of magnitude (up to 10⁻⁹ A). Analyzing the TSC spectra of the samples, it can be assumed that treatment in a corona discharge has a weak effect on the polarization in the amorphous regions and a strong effect on the polarization of the crystalline phase: in the region of the polymer melting temperature, all charges are released upon destruction of the crystalline phase. In addition, an increase in the concentration of the filler in the sample positively affects the polarization.

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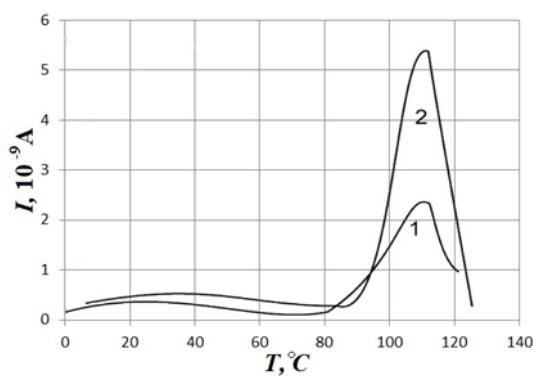
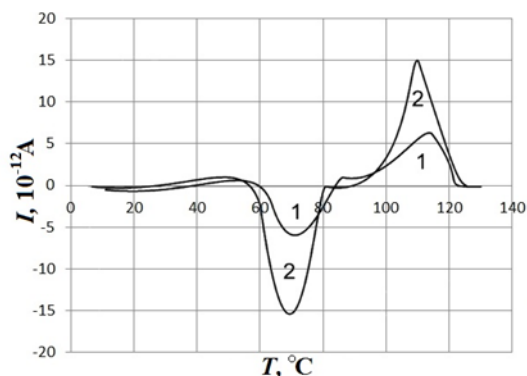


Fig. 2 – TSC spectra of LDPE films with different MMn concentration before (a) and after (b) treatment in a corona discharge of negative polarity. MMn concentration: 1 mass. % (1), and 3 mass % (2)

When making electrets, it is important to obtain samples that retain their properties for a long time. Consequently, not only the value of the charge is important, but also its relaxation in time, reproducibility in experiments, etc. Therefore, several additional parameters were used in the work, namely:

- the spread of ESCD values during manufacture (in %) within a certain group of samples; the higher this parameter, the stronger the samples in the group differ from each other, respectively, the lower the predictability of the result when they are polarized;
- change in the charge of the electret over time – an absolute value showing the difference between the charge of the electret immediately after manufacture and after some time, in a steady state;
- rate of charge change, $\mu C/(m^2 \cdot min)$, it shows the rate at which the electret charge changes over a certain period of time;

– the value of the charge changes in relation to the initial one, in percentage terms, it shows what fraction of the charge from the initial one the electret lost after a certain period of time; the higher this parameter, the more the electret is “discharged”.

Comparing the obtained values of ESCD within the groups, we determined the scatter of σ_{eff} values in relation to the mean (Fig. 3). It can be seen that, with an increase in the filler concentration in the sample, the spread of the ESCD values decreases. The highest scatter (54%) is for pure films, and for samples with a filler concentration of 3%, ESCDs differ from the average value by only 10%. Consequently, a more accurate (predictable) result of polarization can be obtained in the manufacture of filled films.

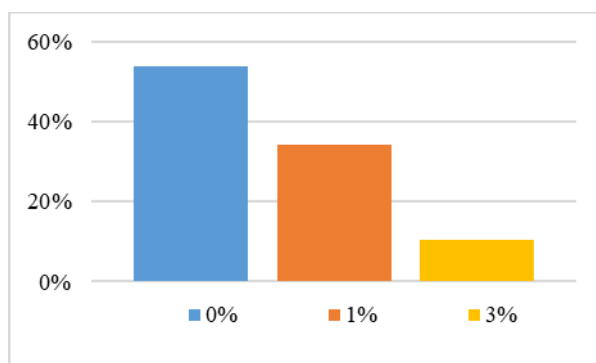


Fig. 3 – The spread of the charge values after the preparation of samples with different filler concentration

The charge relaxation process occurs most intensively during the first 200 minutes after sample preparation. During this time interval, the highest rate of charge decrease was recorded for samples with a filler concentration of 1% (Fig. 4). It is noteworthy that the technological charge of these samples was the highest after manufacture (see Fig. 1). In other groups

of samples, the change in charge occurred at approximately the same rate, more than half that of samples with a filler concentration of 1 mas %. Here one can observe the following tendency: the greater the initial value of the sample charge, the higher the charge relaxation rate.

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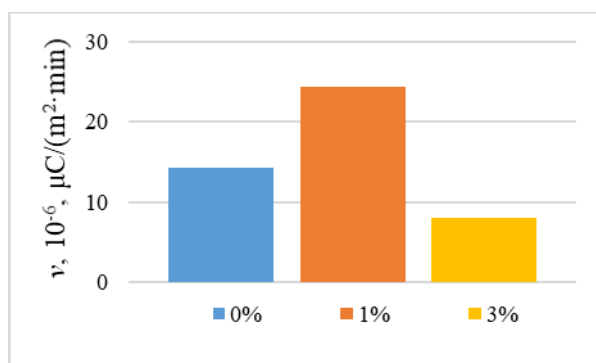


Fig. 4 – Average decay rates of ESCD for samples with different filler concentration

As a result of the relaxation of the charge after 100 days, the pure polyethylene had less than 30% of the ESCD of the initial values (Fig. 5). A significant decrease in σ_{ef} is also observed for samples with a filler concentration of 1%, while these samples, as already noted, differed from other groups of samples

by the highest initial technological charge. In the group of samples with a filler concentration of 3%, the charge loss was 50% of the initial value – the smallest value in the group.

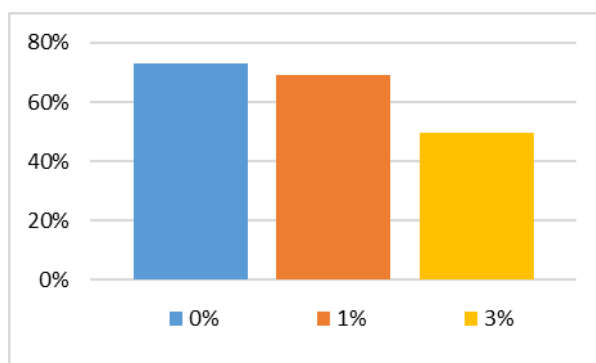


Fig. 5 – The relative decrease in the charge of the samples in relation to the initial value after 100 days

The results obtained indicate that polyethylene films acquire a high electrostatic charge during the manufacturing process, therefore, immediately after manufacturing, it is difficult to estimate the purely electret charge, since the surface density of the technological charge in this case will depend not only on the magnitude of homo- and hetero-charges, but and from electrostatic charge.

The cycle of "discharge" of the electret can be realized according to the following mechanism. In the first hours of the electret's life, the surface electrostatic charge, easily interacting with the environment, quickly relaxes. Then, for a longer time, relaxation of more equilibrium electret charges occurs. At the same time, it was found that filled films have a lower ability to accumulate an electrostatic charge.

Conclusion

The electret state of nanocomposites based on high-pressure (low density) polyethylene has been investigated. It was found that an increase in the montmorillonite concentration in the samples leads to an increase in the absolute values of thermally stimulated currents, which can be explained by the

Maxwell-Wagner polarization at the filler-binder interface. The treatment of samples in a corona discharge leads to an increase (by 2-3 orders of magnitude) in the intensity of the TSC peak, which corresponds to the melting point of polyethylene. In addition, the treatment of samples in a corona discharge leads to an increase in the effective surface charge density. In the positive and negative corona discharges, the LDPE samples acquire approximately the same charge, and their modification with montmorillonite slightly increases the amount of charge. A relationship has been established between the initial value and the relaxation rate of the technological charge of the electret. The higher the technological charge, the faster its decline occurred.

Based on the data presented, it can be argued that nanodispersed montmorillonite can be used as a filler to increase the stability and value of the electret charge in polyethylene. At low filler concentration, an increase in the ESCD is observed, the charge decay and the spread of the ESCD values of the samples decrease.

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