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ELECTRET PROPERTIES OF NANOCOMPOSITES BASED ON POLYETHYLENE AND POLYLACTIDE

Abstract. *The electret state of nanocomposites based on two types of polyethylene (LDPE and UHMWPE) and polylactide has been investigated. It was found that an increase in the content of montmorillonite in polyethylene up to 3 vol. % leads to an increase in the absolute values of thermally stimulated currents. Laser treatment of the samples leads to a sharp increase (by 2-3 orders of magnitude) in the intensity of the TST peak, which corresponds to the melting point of polyethylene. The treatment of samples in a corona discharge leads to a significant increase in the effective surface charge density. It was found that the electret charge obtained during the processing of polylactide samples filled with nanodispersed hydroxyapatite in the field of a corona discharge, as well as those activated by laser radiation, has a small value and is weakly subject to change during processing.*
Keywords: *electret, nanocomposite, polyethylene, polylactide, montmorillonite, hydroxyapatite*

Introduction

An electret is a piece of dielectric with a quasi-permanent electric charge. The term "quasi-constant" means that the time constants characterizing the discharge of an electret significantly exceed the time intervals during which a given electret is studied [1].

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 [2-7]. All of these technical applications of electrets require materials with high magnitude and charge stability. 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 nanosized fillers on the stability and magnitude of the electret charge of polymers [8-14]. The presence of ultra- (nano-) dispersed fillers in the system leads to 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 (socialization of electrons, delocalization of electron density), thermodynamic (ability particles to be highly efficient traps for charge carriers) and other properties of fillers.

In a number of works, the electret properties of polymer nanocomposites based on polyethylene filled with carbon black (filler particle size 30–40 nm) were investigated [9, 15–18]. It is shown that the maximum effective surface charge density 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 [17, 18].

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 results 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 polymers polarization, including, first, surface and bulk modification of polymers, essentially at the level of chemical interactions, and second – the use of new methods of physical influence, such as, for example, laser radiation with different wavelengths.

The aim of this work is to study the electret state of nanocomposites based on polylactide and two types of polyethylene, subjected to polarization in a corona discharge and additional treatment with laser radiation. Corona electrets are among the objects most convenient from the point of view of studying polarization mechanisms in composite dielectrics. The scientific idea is to activate a polymer nanocomposite by laser radiation of a certain wavelength to create deeper (and higher concentration) energy traps, which make it possible to achieve higher values of the effective surface charge density and stability in time.

1. Materials and methods of research

To prepare the samples, we used powdered polyolefins – low dencity polyethylene (LDPE) and ultra-high-molecular-weight polyethylene (UHMWPE), which were mechanically mixed with finely dispersed (5-20 nm) montmorillonite (MMn) at a content of the latter from 0 to 5 wt %. Then, samples of films with a thickness of 150-200 μm were prepared by hot pressing.

As a matrix of composite materials, we also used PL18 polylactide (PLA), a biodegradable biocompatible thermoplastic polymer, raw materials for the production of which act such renewable resources as corn and sugarcane. The PLA filler was a finely dispersed (50-100 nm) hydroxyapatite (HA) mineral $Ca_{10}(PO_4)_6(OH)_2$ from the apatite group. Synthetic HA is used in medicine as a filler to replace parts of the lost bone, and as a coating for implants which promotes the growth of new bone. Investigated were four types of samples: PL18 with a content of HA 0; 0.5; 1; 1.5%. Samples in the form of films with a thickness of 50 μm were prepared using the solution technology at the Institute of Macromolecular Compounds of the Russian Academy of Sciences (St. Petersburg).

The samples were polarized in a corona discharge (positive and negative). The voltage across the needle electrode was 25 kV, while the field strength between the electrode and the sample was 10 kV/cm.

The samples were activated by laser radiation. A solid-state yttrium-aluminum garnet laser with a wavelength of 1064 nm and a maximum average power of 400 W was used for laser processing of the samples. The diameter of the laser beam at the exit from the resonator was 8 mm. A special holder was developed, installed on a movable laser rail for better fixation of samples and their quick change. Thus, laser radiation was performed by scanning the entire surface of the film under study in a pulsed mode.

The electret charge was measured by standard methods [19]. The effective surface charge density (ESCD) of the samples σ_{eff} was determined using a meter of electrostatic field parameters (ИПЭП-1, manufactured by MNIPI, Belarus, Minsk). The measurement was carried out with an electrode at a 2 cm distance from the sample under study. The measurement error (for each point from 5 to 8 samples) did not exceed 10%. Thermally stimulated depolarization was performed between two electrodes by heating the sample at a constant rate and measuring the thermally stimulated current (TSC). As a result, a TSC spectrum was obtained for each sample.

2. Results and discussion

The known data on the effect of the content of micro- and nanosized fillers on the magnitude and stability of the electret state of composites based on polylactide are contradictory [20, 21]. We also failed to establish the main laws governing the polarization of such materials. The most sensitive to polarization was the PL18 sample without a filler, which had the highest technological charge (the charge obtained during the production of films), and also a significant change in the charge was observed at various stages of the experiment (Fig. 1).

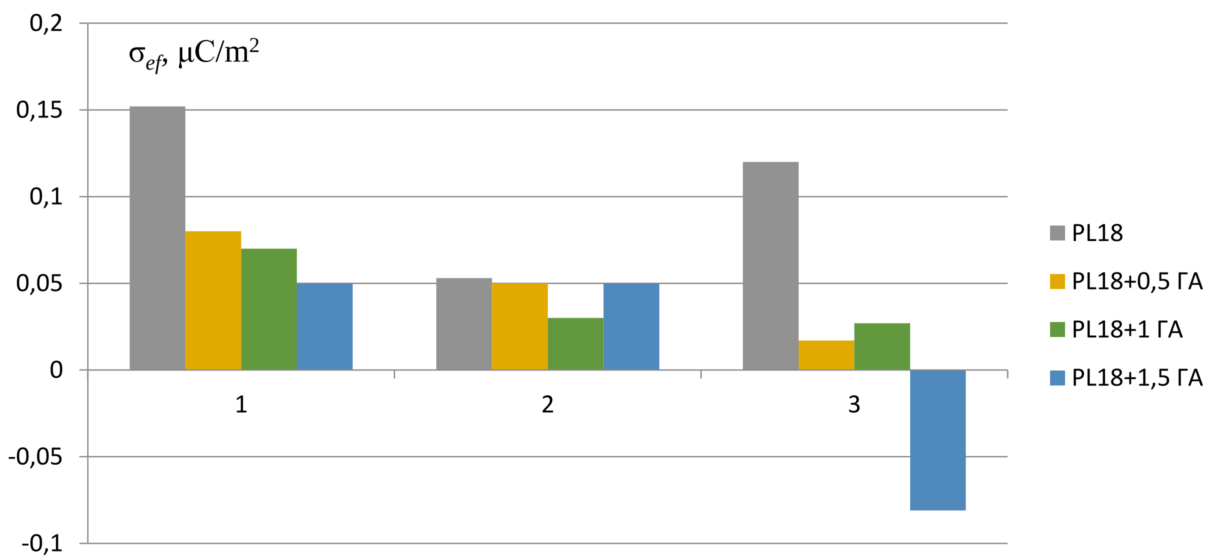


Fig. 1. **Effective surface charge density in films of various compositions. Column groups: 1 – initial value before film processing (technological charge), 2 – after activation by laser radiation, 3 – after sample processing in a corona discharge**

Estimating the value of the technological charge of electrets based on polylactide according to the experimental data, we can say that the electret charge obtained during the processing of samples in the field of a corona discharge, as well as those activated by laser radiation, has a small value and is weakly subjected to change during processing.

The situation is different with polyethylene-based nanocomposites. The experimental data on the value of the ESCD for various samples (LDPE and UHMWPE) are shown in Fig. 2. Based on the results obtained, the following conclusions can be drawn.

1) A small technological charge is formed on all samples (both UHMWPE and LDPE) after formation by hot pressing. It is somewhat higher in UHMWPE than in LDPE, and filling with montmorillonite only decreases its value, especially in UHMWPE. Perhaps this is due to the relaxation of the Maxwell-Wagner polarization at the filler/binder interface, which proceeds more intensively at an elevated temperature of sample formation.

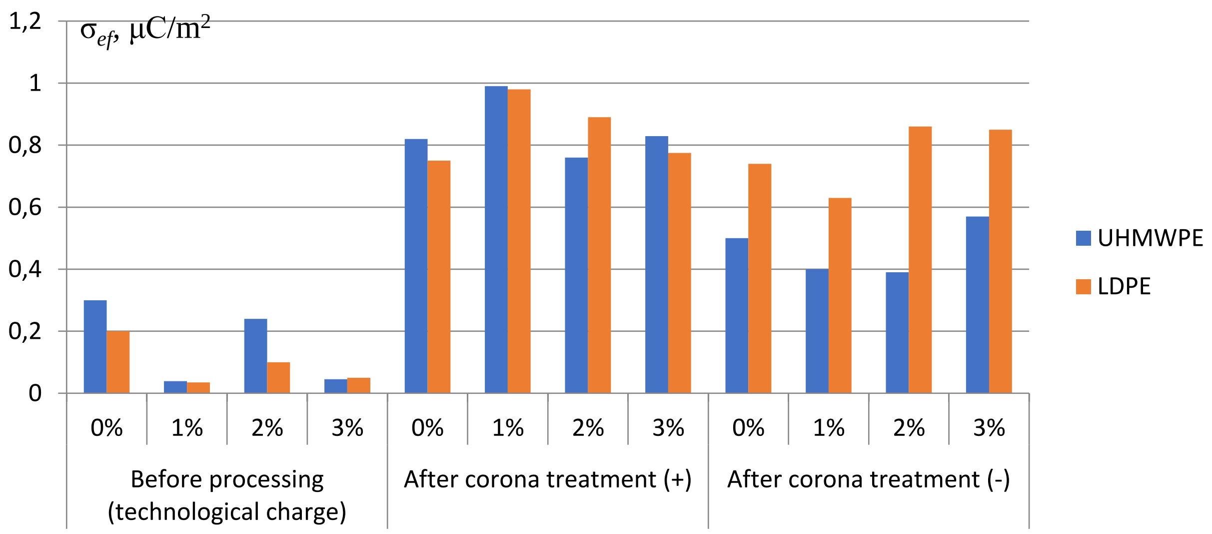


Fig. 2. **Values of ESCD in samples based on UHMWPE and LDPE with different MMn content before and after treatment in a corona discharge of positive (+) and negative (-) polarity**

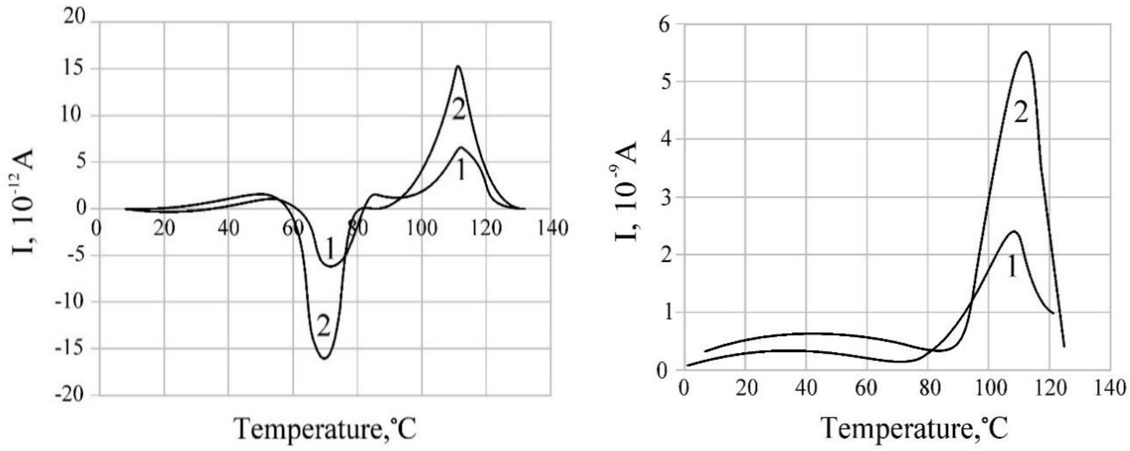
2) Treatment of samples in a corona discharge (both positive and negative polarity) leads to a significant increase in the effective surface charge density. The

UHMWPE and LDPE samples acquire approximately the same charge in the positive corona, and their modification with a filler slightly increases the charge. An insignificant increase in EITR at a filler content of 1 wt % is apparently due to the so-called "effect of low concentrations", when a significant improvement in the parameters of some physical-mechanical properties is observed in polymer nanocomposites at a low filler concentration [10]. The results obtained agree with the data of [9], which shows that the maximum effective surface charge density occurs at a filler content of about 4 vol. % (which corresponds to about 1% of the mass.).

3) Treatment in a corona discharge of negative polarity increases the EITR of UHMWPE samples much less than in a positive corona, and for LDPE the charge has approximately the same value. In general, taking into account the technological complexity of the manufacture of electret samples from UHMWPE in comparison with LDPE, as well as the higher indicators of the effective surface charge density of the LDPE samples, high pressure polyethylene should be preferred in the manufacture of electret films.

The generalized TSC spectra of LDPE samples after their formation by hot pressing are shown in Fig. 3, *a*. 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 content leads to an increase in the absolute values of the currents, which is most likely due to the Maxwell-Wagner polarization at the filler-matrix interface.

Laser treatment of the samples dramatically changes the picture of charge relaxation (Fig. 3, *b*). The intensity of the low-temperature peaks practically did not change on the TSC spectra of the samples after laser treatment, and the intensity of the peak corresponding to the melting temperature increased by 2–3 orders of magnitude (up to 10^{-9} A). Analyzing the TSC spectra of the samples, it can be assumed that laser radiation 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 polymer melting, when the crystalline phase is destroyed, all charges are released. In addition, an increase in the concentration of the filler in the sample positively affects the polarization.



a) *b)*

Fig. 3. **TSC spectra of LDPE films with different mass content of MMT before (*a*) and after (*b*) laser irradiation. MMt content: 2 wt. % (1) and 5 wt. % (2)**

Conclusion

The electret state of nanocomposites based on two types of polyethylene (LDPE and UHMWPE) and polylactide has been investigated. It was found that an increase in the montmorillonite content in polyethylene leads to an increase in the absolute values of thermally stimulated currents, which can be explained by the Maxwell-Wagner polarization at the filler-matrix interface. Laser treatment of the samples leads to a sharp increase (by 2-3 orders of magnitude) in the intensity of the TSC peak, which corresponds to the melting point of polyethylene. It can be assumed that laser radiation has a weak effect on the polarization in the amorphous regions and strongly affects the polarization of the crystalline phase. The treatment of samples in a corona discharge leads to a significant increase in the effective surface charge density. In the positive corona, the UHMWPE and LDPE samples acquire approximately the same charge, and their modification only slightly increases the amount of charge. It was found that the electret charge obtained during the processing of polylactide samples filled with nanodispersed hydroxyapatite in the field of a corona discharge, as well as those activated by laser radiation, has a small value and is weakly subject to change during processing.

Acknowledgment. The work was carried out with financial support from the Ministry of Education of the Belarus Republic (grant from the Ministry of Education, state registration no. 20210986).

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