ELECTRET EFFECT IN BIODECOMPOSED POLYLACTIDE FILMS FILLED WITH NANOSCALE MAGNESIA

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In the paper, the results of studies in the charge relaxation mechanism in polylactide films with nanoscale hydrophilic filler (magnesia) have been obtained using thermally stimulated depolarization current (TSDC) and thermally stimulated surface-potential decay (TSSPD) methods. The loading of the hydrophilic filler (magnesia) was shown to result in the polymer conductance reduction, i. e., in the improvement of the electret properties of the composite. The optimal content of magnesia (4%) responsible for the highest electret state stability in polylactide films was determined. The values of the effective frequency factor and the activation energy of the deep traps for the injected charge being inherent to the polymer matrix were estimated by regularization technique. The obtained results demonstrate the capability of making active (long time retaining the organoleptic properties of the products) and biodegradable (solving the problem of recycling) packaging materials based on composite polylactide films with magnesia as a filler.

Key words: polylactide; hydrophilous filler; biodecomposed film; electret state; charge-dipole complex

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Introduction

Synthetic polymers have found wide application as a packaging material for food products. Recycling these polymer materials after use in packaging is a pressing problem since incineration leads to release of toxic gases and decomposition in soil can take over hundreds of years.

One way of solving this problem is using biodegradable polymers. To date, the most promising material for this purpose is polylactide (PLA), a polymer whose monomer (lactide $C_3H_4O_2$) is obtained from lactic acid. It has been established that if a stable electret state is formed in a polymer film, the packaging made of this material preserves the organoleptic properties of the products for a long time [1 – 3]. Such packaging is referred to as active [4, 5]. It is known that PLA's electret state is not sufficiently high in its initial form [6 – 8] but introducing various fillers, in particular, Aerosil SiO_2, into the polymer makes it possible to significantly improve the stability of the electret state in PLA-based films [9].

It should be noted that Aerosil is rather expensive to produce, which in turn raises the cost of products packed in PLA films with the Aerosil filler. For this reason, it is of interest to investigate the effect of other fillers on the stability of the electret state in PLA-based composite films. In this study, magnesium oxide was chosen as the filler. It is a hydrophilic filler like Aerosil but its production is cheaper [10].

Thus, the purpose of this study is to establish the nature of the electret state in composite PLA-based films with magnesium oxide as a filler (PLA + MgO system).

Experimental procedure

In this paper, we investigated PLA and PLA + MgO films, obtained by pressing in accordance with GOST 12019-66 at the Kazan National Research Technological University. The thickness of the films was 100–200 μm, the mass fraction of magnesium oxide varied and amounted to 0 %, 2 %, 4 %, and 8 %.

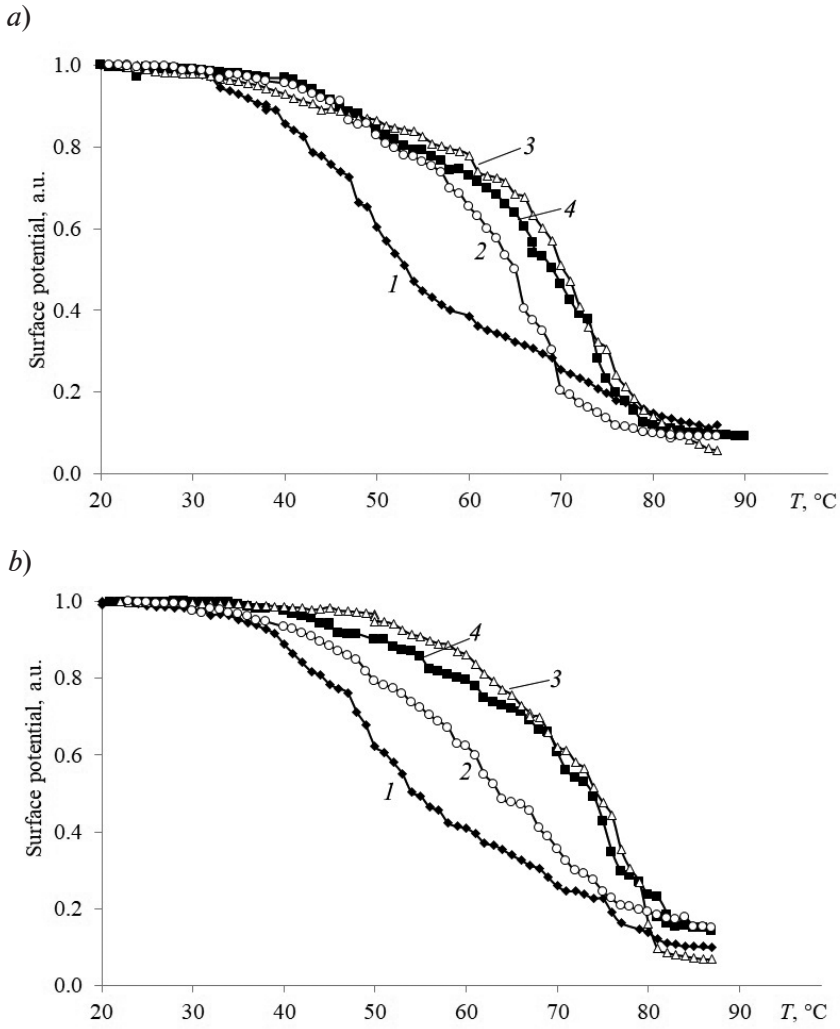

Fig. 1. TSSPD curves for films based on the initial PLA (*1*) and the PLA with filler (magnesium oxide) *(2 − 4)* for negatively (*a*) and positively (*b*) polarized corona electrode. The MgO concentrations, %: 2 (*2*), 4 (*3*), 8 (*4*)

The electret state in the films under investigation was achieved by exposing the film to a positive or negative corona discharge field for 5 min at room temperature. The stability and nature of the electret state were studied by methods of thermally stimulated depolarization currents (TSDC) and thermally stimulated surface potential decay (TSSPD).

The TSSPD method is based on recording the temperature dependence of the surface potential of samples under linear heating. The TSDC method is based on measuring the short-circuit current in samples under linear heating. (The electret state is formed in the samples in advance in both cases.)

Fig. 1 shows the TSSPD curves for PLA and (PLA + MgO)-based films with different filler contents, with the electret state induced by negative and positive corona charging.

It can be seen from the obtained curves that when the MgO filler is added, the stability of the electret state in composite PLA films increases and reaches its maximum at a mass fraction of MgO of 4% (curves *3* in Fig. 1). A further increase in filler concentration leads to a decrease in the stability of the electret state in composite PLA films with a hydrophilic nano-sized MgO filler (Fig. 2). The temperature stability of the electret state was estimated by processing the TSSPD curves

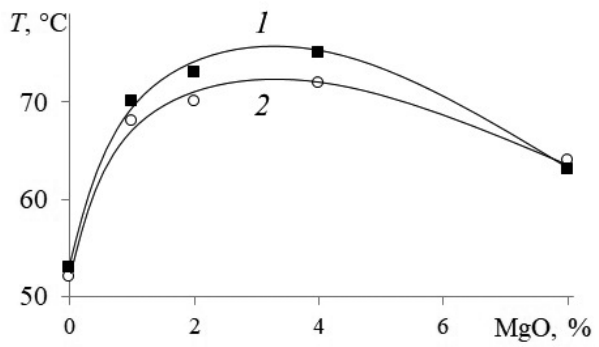

Fig. 2. Curves of temperature stability of the electret state (the temperature of the inflection point of the TSSPD curve) as a percentage of the MgO filler in composite PLA films; the curves were obtained with positive (*1*) and negative (*2*) corona discharges

(see Fig. 1): their temperature inflection points were determined.

For clarity, Fig. 3 shows a separate comparison of the TSSPD curves for composite PLA + 4 % MgO films with the electret state induced at different polarities of the corona electrodes.

It can be seen that the character of potential decay depends on the sign of the corona electrode polarity: a positively polarized electret state is more stable with positive polarity than with the negative one. This suggests that the decrease in the surface potential is governed by the release of the charge captured under electretization from near-surface traps. Evidently, the energy depth of the traps is greater for positive than for negative charge carriers.

The increase in the stability of the electret state with the filler added can be attributed to the presence of so-called charge–dipole centers in the polymer. The latter are formed as a result of the interaction of water molecules with polymer chains, which, on the one hand, have a dipole moment (i.e., they are capable of participating in dipole polarization), and, on the other hand, serve as traps for charge carriers (and thus determine the volume conductivity of the film) [11]. Since magnesium oxide is a hydrophilic filler, it can capture some of the water molecules, thus leading to a decrease in the concentration of charge-dipole centers in composite PLA films compared to the initial PLA (without filler), and, as a consequence, to a decrease in conductivity and a respective increase in the stability of the electret state.

The non-monotonic dependence of the temperature stability of the electret state of composite polylactide films on the percentage of the MgO nanoscale hydrophilic filler can be explained by the presence of two competing bulk conductivity mechanisms. On the one hand, as mentioned above, bulk conductivity decreases with increasing filler concentra-

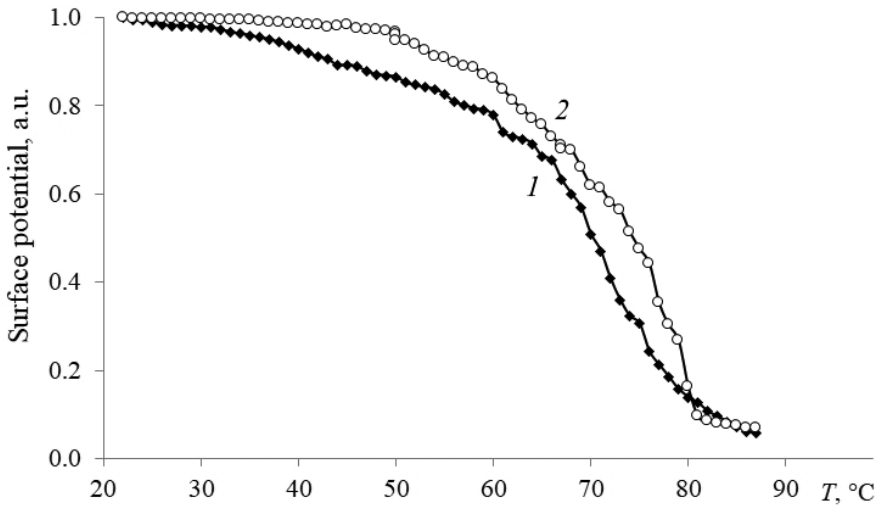

Fig. 3. TSSPD curves of composite PLA + 4 % MgO films obtained under negative (*1*) and positive (*2*) corona discharges

tion due to a decrease in the concentration of charge–dipole centers, which means that the stability of the electret state increases; on the other hand, bulk conductivity can increase due to increasing probability of conducting clusters forming over the filler particles, which, accordingly, should lead to a decrease in the stability of the electret state. Thus, there should be an optimal value of the MgO filler concentration in PLA-based films ensuring the greatest stability of the electret state in the films. In our case, the optimal concentration is 4 %.

Fig. 4 shows the TSDC curves of composite PLA + 4 % MgO films with the electret state induced by positive and negative corona discharges.

Two peaks are observed on the TSDC curves in composite PLA-based films. A low-temperature peak near 40 °C is associated with heterocharge relaxation (the orientation of charge-dipole centers in our model). The height of this peak, if compared with the data on the initial PLA films, is two orders of magnitude smaller [6]. This result agrees with the assumption that introducing a nanoscale hydrophilic MgO filler lowers the concentration of charge–dipole centers (the effect of MgO is similar to that of Aerosil SiO_2 described in the paper).

High-temperature peaks on the TSDC curves in composite PLA films correspond to homocharge relaxation. This suggests that these peaks are due to charge ejection from deep near-surface traps. The curves in Fig. 4 indicate that the depth (activation energy) of traps is less for negative charge carriers than for positive ones. This result is consistent with the TSSPD data. The calculated values of trap activation energy were $W = 0.84 \pm 0.03$ eV for positive charge carriers and $W = 0.76 \pm 0.03$ eV for negative ones (the frequency factor was equal to 10^{11} s^{-1} in both cases). Since the temperature position of the high-temperature peaks in composite PLA + 4 % MgO films coincides with the temperature position of similar peaks in the initial PLA films (see [6]), it can be concluded that the traps determining the potential stability of the electret state are inherent for the PLA polymer matrix.

The results obtained by TSDC in composite films based on PLA and MgO filler are similar to the TSDC dependences previously studied in composite PLA films filled with aerosil SiO_2 [6], the only difference being that the optimal (from the standpoint of the electret state stability) concentration was 2 % for the Aerosil filler, while for magnesium oxide this value is 4 %.

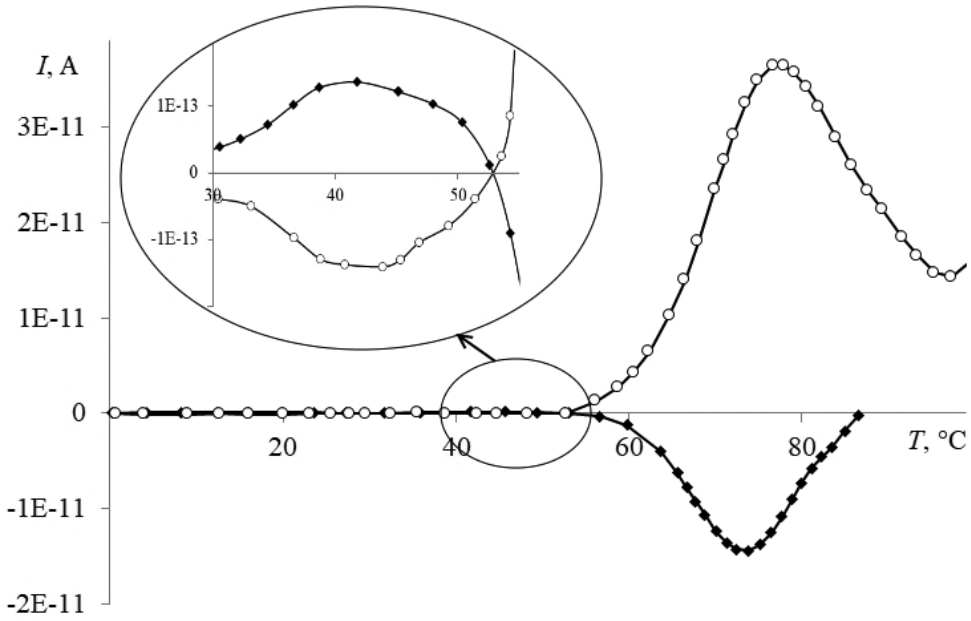

Fig. 4. TSDC curves in the corona electret system of a composite PLA + 4 % MgO film; the films were obtained under positive (*1*) and negative (*2*) corona discharges

Conclusion

A hydrophilic nanosized MgO filler can be proposed as a cheaper alternative to the Aerosil SiO_2 filler, improving the stability of the electret state in biodegradable PLA-based composite films used to create an active packaging material.

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