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THE EFFECT OF THE MONTMORILLONITE-BASED FILLER ON THE ELECTRET PROPERTIES OF POLYPROPYLENE

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Abstract. In the paper, the studies of electret properties of polypropylene with different percentages of montmorillonite have been carried out by methods of thermally stimulated potential relaxation and thermally stimulated currents. A significant effect of filler concentration on the electret state stability was revealed. The parameters of electrically active defects and the storage time of the electret state were determined. It was established that polypropylene with a 4% mass content of montmorillonite exhibited the best electret properties.

Keywords: electret, composite polymer film, electret state, polypropylene, montmorillonite

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ВЛИЯНИЕ НАПОЛНИТЕЛЯ НА ОСНОВЕ МОНТМОРИЛЛОНИТА НА ЭЛЕКТРЕТНЫЕ СВОЙСТВА ПОЛИПРОПИЛЕНА

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Аннотация. Проведены исследования электретных свойств полипропилена с различным процентным содержанием монтмориллонита методами термостимулированной релаксации потенциала и термостимулированных токов короткого замыкания. Выявлено заметное влияние концентрации наполнителя на стабильность электретного состояния. Определены параметры электрически активных дефектов и время хранения электретного состояния для разного содержания наполнителя в образцах. Установлено, что наилучшими электретными свойствами обладает полипропилен с 4 %-м массовым содержанием монтмориллонита.

Ключевые слова: электрет, полимерный композитный материал, электретное состояние, полипропилен, монтмориллонит

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Introduction

The field of application of polymer electrets is quite wide: electroacoustics, medicine, filtering devices, radioactive radiation sensors, etc. [1].

An important parameter for the practical use of a polymer as an electret material is the stability of the electret state formed in it [2]. The influence of the electret electric field on microorganisms and bacteria is described in Refs. [3, 4]. It has been found that the effect of the field on microorganisms leads to a slowdown in the processes of their vital activity and can significantly increase the shelf life of food products.

Currently, an effective and technologically advanced way to form a stable electret charge in polymer films is the method of charging films in a corona discharge.

Promising objects of research are polymer films based on polypropylene (PP). Low density, high mechanical strength and resistance to chemical influences, as well as low cost make polypropylene a popular and easily accessible material.

It is known that the addition of dispersed fillers to the polymer matrix has a positive effect on the stability of the electret state in the polymer under study. This leads to the creation of new materials with improved electret properties and opens up new possibilities for their application [5, 6].

The results of studies [7, 8] have shown that the introduction of fillers such as diatomite and aerosil into the polyethylene matrix significantly increases the stability of the electret state, while pure polypropylene does not exhibit its high stability. Another possible filler in the polypropylene matrix is montmorillonite (MM). Montmorillonite is a cheap material with sorption properties.

Previous studies [9 – 12] have shown that the introduction of montmorillonite has a significant effect on the complex properties of polymers. For example, when chrysotile or montmorillonite is added to the polymer matrix, it leads to a significant change in the electrophysical properties of the starting material. The hydrophilicity of the fillers used may be one of the reasons for this. In Ref. [13], it was shown that the addition of montmorillonite particles to chitosan increased the activation energy of the electrical conductivity of this material from 0.20 eV to 0.31 eV, and as a result, the specific electrical conductivity of this polymer decreased by reducing the concentration of free ions.

In this regard, the goal of this study was to introduce montmorillonite into polypropylene films and investigate the filler effect on the electret properties of the modified material.

Materials and methods

In this work, the initial polypropylene films of the PP4215M brand (EP1X35F) and composite films based on it have been studied.

Composites based on PP with 2 and 4 wt.% of montmorillonite were prepared in the melt at the laboratory station "Plastograph EC" of the company "Brabender" (Germany) with adjustable electric heating at a temperature of 190°C and rotor speeds of 50 – 150 rpm for 300 s. The samples were produced by pressing on a GotechGT-7014-H10C hydraulic press at 190 ± 5°C with a heating time of 5 min, a pressure exposure of 3 min, and subsequent cooling of 3 min. The sample thickness of the initial films and composites varied from 0.12 ± 0.05 to 0.14 ± 0.05 mm.

Montmorillonite (mark 15A) is a clay mineral belonging to a subclass of layered silicates. The three-layer structure of this mineral, consisting of two silicon-oxygen and one aluminum hydroxide layers, is provided due to sufficiently weak molecular bonds. As a result, water molecules can easily penetrate into the interlayer space, and the mineral itself has good sorption properties.

The electret properties of the samples were investigated by the following methods:

thermally stimulated relaxation of the surface potential (TSRSP),

thermally stimulated currents (TSC).

When studying the films by the TSRSP technique, the samples were pre-polarized in a corona discharge at a temperature of 80°C. Further, the temperature dependence of the surface potential in the linear heating mode was removed.

In the TSC procedure, polarization was carried out at room temperature also in a corona discharge. The result of the study was a graph of the depolarization current dependence on temperature. The maximal temperature positions of the thermally stimulated depolarization currents and the nature of the TSD curves made it possible to determine the activation energy and the effective frequency factor of electrically active defects, as well as to obtain information about the relaxation mechanisms of the objects under study.

Results and discussion

Fig. 1,*a* presents the dependences of the surface potential decay on temperature at a heating rate of 5°C/min for PP samples without filler charged in the field of positive and negative corona discharges.

From this graphs we notice that the decreasing curves of the surface potential at different polarities of the polarizing field turn out to be identical. This result indicates that the relaxation process of the charge state is associated either with the reorientation of the dipoles in the samples or with the neutralization of the trapped charge due to the intrinsic conductivity of the polymer [14].

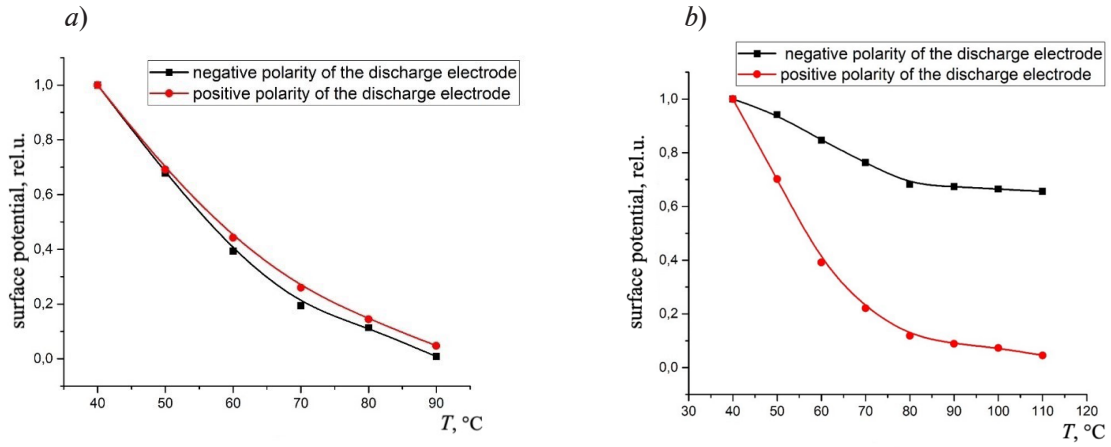

Fig. 1. Temperature dependences of the surface potential (relative units) for polypropylene (PP) charged samples without filler (*a*) and PP + 4 % montmorillonite (MM) charged composite films (*b*); they were treated in the field of positive and negative corona discharges in both cases (a heating rate was 5°C/min)

Fig. 1,*b* shows the similar dependences of the surface potential decay but for samples PP + 4 % MM charged in the same fields. In this case, the decline of the surface potential becomes strongly dependent on the polarity of the corona discharge. The process of surface potential decay for samples charged in the positive corona discharge field is more intense than that for samples charged in the negative one. It can be assumed that in this case, sufficiently deep electronegative traps are formed at the polymer–filler interface. A similar effect was observed in polyethylene films filled with talc [15], simultaneously with a decrease in the conductivity of the polymer due to the sorption properties of the filler [16].

An additional confirmation of the above-mentioned double effect of the hydrophilic filler on the charge relaxation in the polypropylene is the temperature dependences of the current for PP films with different percentages of MM, pre-polarized in the negative corona discharge field at room temperature (Fig. 2).

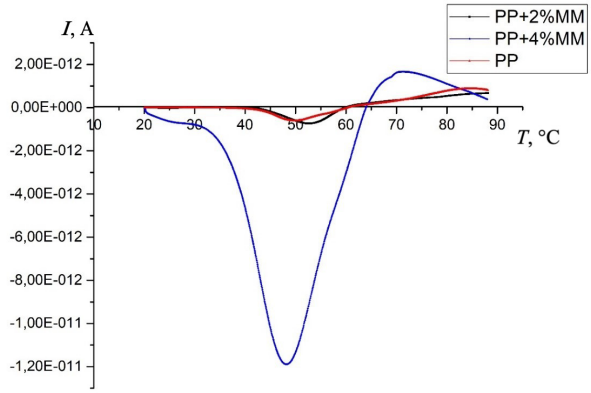

Fig. 2. Thermostimulated currents for the initial films, composite films PP + *n* MM (*n* = 2 and 4 % by weight), polarized in the field of the negative corona discharge field (a heating rate was 9°C/min)

Here the intensity of the TST peaks grows significantly with an increase in the percentage of filler from 2 to 4 % (not proportional to the percentage), which can be explained not only by an increase in the quantity of traps at the polymer – montmorillonite boundary, but also by a decrease in the conductivity of the polymer.

The activation energy and frequency factor of the electrically active defects responsible for relaxation processes in both the initial and filled polymer samples were calculated using the method of varying the heating rate. As an example, Fig. 3,*a*,*b* shows the TSC curves for two heating rates for the initial PP films and PP ones with 4% of the filler mass.

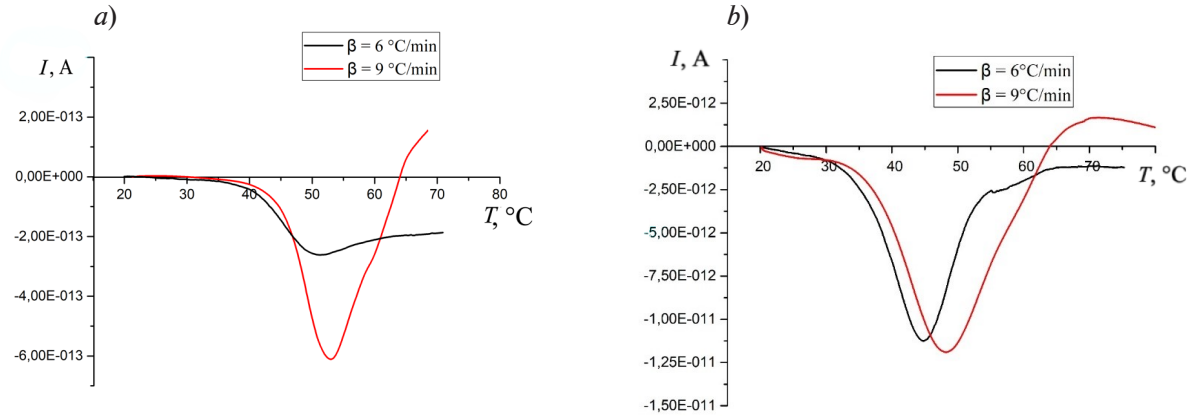

Fig. 3. Thermostimulated currents for PP + 4 % MM composite films (4 % by weight) (*a*) and the initial polypropylene films (*b*) polarized in the negative corona discharge field at different linear heating rates (6 and 9°C /min)

The formula for finding the activation energy W of relaxers by the temperature positions of the peaks at two heating rates has the form:

$$W = \frac{kT_{m_1}T_{m_2}}{T_{m_1} - T_{m_2}} \ln \frac{\beta_1 T_{m_2}^{\ 2}}{\beta_2 T_{m_1}^{\ 2}}, \quad (1)$$

where T_{m1}, T_{m2} are the temperature values of the maximal currents; β_1, β_2 are the heating rates; k is the Boltzmann constant.

The value of the frequency factor ω was determined by the following formula:

$$\omega = \frac{W\beta}{kT_m^{\ 2}} \exp\left(\frac{W}{kT_m}\right), \quad (2)$$

where T_m is the temperature of the maximal current at the heating rate β.

The calculation results show an increase in the activation energy W for the composite polymer compared to the initial one from 0.75 ± 0.05 to 1.01 ± 0.05 eV at a frequency factor ω of the order of 10^{11} s^{-1}. Obviously, such results should increase the relaxation time τ_p of the electret state in the MM-filled polymer compared to the initial one.

Indeed, calculated the relaxation time of the electret state by the formula

$$\tau_p = \frac{1}{\omega} \exp\left(\frac{W}{kT_k}\right) \quad (3)$$

at room temperature, increases from 4 min (for PP without filler) to 256 hrs (for PP + 4% MM).

The temporary stability rise of the electret state when filling polypropylene with montmorillonite is accompanied by an increase in temperature stability. The temperature dependences of the surface potential in relative units for samples with different percentages of montmorillonite charged in the negative corona discharge field are shown in Fig. 4.

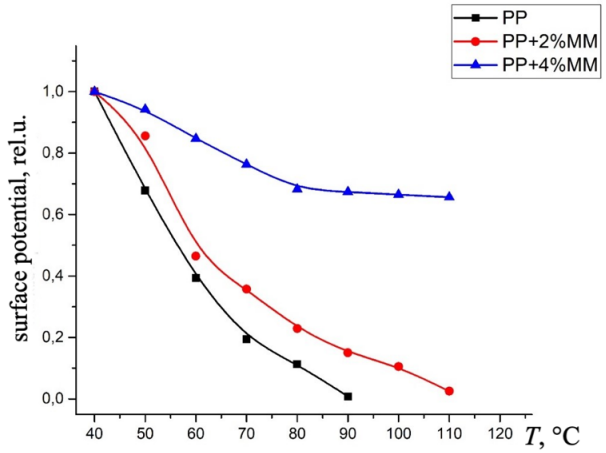

Fig. 4. Temperature dependences of the surface potential for PP films and PP + n MM (n = 2 and 4 % by weight) composite films charged in the negative corona discharge field

Similarly, according to the current spectroscopy data presented in Fig. 2, a significant change in the decline of the surface potential with an increase in temperature occurs when 4 wt. % MM is added., as well as the curve at 2 wt.% of the thermally stimulated relaxation of the potential almost coincides with a similar dependence for the initial polypropylene.

Conclusion

The electret properties of the initial polypropylene films and composite polypropylene ones with montmorillonite filler were studied by the TSRP and TSC methods.

It was revealed that the stability of the electret state increases compared to the initial PP with an increase in the percentage of montmorillonite to 4 wt.% in polypropylene films. This results from two reasons: the formation of sufficiently deep charge traps at the polymer–filler interface and a decrease in the conductivity of the polymer due to the sorption properties of the MMT filler.

The relaxation time of the electret state in the PP films with 4 wt.% of montmorillonite is about 256 hrs at room temperature; this result makes it possible to use these composite polymer films as an active packaging material for food products.

Further studies of the electret properties of polypropylene with a high percentage of montmorillonite will allow us to determine the optimal percentage of the filler.

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