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Nature and mechanisms of relaxation processes in biocompatible polylactide films

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Abstract. The results of a TSRSP study of the electret properties of initial PLA films and PLA-based composite films with various hydrophilic nanoscale fillers are presented. It is shown that the introduction of a filler into the composite matrix changes the relaxation mechanism and leads to an improvement in the electret state stability in the PLA-based composite samples. The maximum possible value of the electret state stability in PLA-based composite film is provided by the proper electreting mode.

The nature and mechanism of relaxation, as well as the stability of the electret state, is obtained by the presence of charge-dipole centres in the polymer structure. The presence and distribution form of the charge-dipole centres in the polymer matrix of PLA composites was confirmed by FTIR-spectroscopy and the attenuated total reflectance (ATR) method.

Keywords**:** polylactide, polymer composite, charge-dipole centres, electret state stability, thermal activation spectroscopy, FTIR-spectroscopy, attenuated total reflectance (ATR).

Introduction

In the modern world, food preservation is impossible without the right packaging material. One way of advancing the field is the development of new polymeric materials with special properties. Such packages are called "active packaging materials". Active packaging materials refer to packaging systems used for food, pharmaceuticals and some other types of products (Galikhanov et al. 2005; 2014). They can contain various absorbents of moisture and odours, as well as antimicrobial enzymes and additives that have a targeted effect on products they contact (Fedotova et al. 2010).

The creation and comprehensive study of "active packaging materials" is of great interest; since the additive is not introduced into products, but into the structural matrix of a polymer film, it allows prolonging the products' shelf life in such a polymer shell, controlling freshness and increasing the safety and convenience (Fedotova et al. 2010).

Another equally interesting and important way of research and development is the creation of biodegradable materials. Earlier the efforts of scientists aimed at creating polymers resistant to various kinds of influences. Now the opposite trend is being formed. Biodegradable and biocompatible polymeric materials are increasingly being developed. However, such materials are inferior in their properties to traditional plastics, but the fact that they are biodegradable is their main advantage, since they are capable of decomposing into safe components via the action of biological environmental factors (Fomin, Guzeev 2001; Legonkova 2006). Interest in such technologies is growing due to the increase in human consumption of disposable products.

The most promising polymer is polylactide (PLA). PLA is a biodegradable, thermoplastic biopolymer, the monomer of which is lactic acid. It is mainly obtained for medical purposes, as well as for the manufacture of packaging materials and products with a short service life (Pihlajamaki et al. 2006). PLA is completely biodegradable in 45 days under industrial composting conditions (Ermolovich et al. 2005; Stein 1992).

Combining these two ways of investigations could lead to the creation of "active biodegradable packaging" based on PLA. Such packaging could allow prolonging shell life of food and maintaining its operational characteristics only during the period of consumption. Then they undergo physicochemical and biological transformations under the influence of the Earth's biosphere.

However, it is known that the shell life of food in PLA films is limited (Ignatyeva et al. 2015b). Possible ways to increase this time are the creation of polymer-based composites by introducing additional inclusions into the structure of the polymer matrix, as well as advance electreting of the polymer sample. Pre-electreting in the corona discharge field enhances the bactericidal properties of polymer films. The electret process has an inhibitory effect on microorganisms in food (Galikhanov et al. 2008). Thus, this makes it possible to use pre-electreted biodegradable polymer films as "active packaging materials".

Experimental procedure

In this paper, we have investigated the biodegradable initial PLA films and PLA-based composites with various hydrophilic nanoscale dispersed fillers (silicon dioxide, barium titanate, etc.). This research involved studying two types of PLA samples with different thickness: thin films (about 40 μm) and thick films (more than 180 μm).

In order to study the structure and basic electrophysical phenomena of PLA films (the processes of transfer, accumulation and relaxation of charge), as well as to refine the proposed model of the electret state stability and to estimate the parameters of relaxation processes, a combination of experimental methods was used. Combined application of FTIR-spectroscopy and thermoactivation spectroscopy methods (in particular, the method of thermally stimulated relaxation of the surface potential (TSRSP)) makes it possible to obtain detailed information on the nature and mechanisms of relaxation processes in PLA films.

In order to investigate the electret state stability by the TSRSP method, the PLA samples were preliminarily electreted for 10 minutes in a field of positive and negative corona discharges at room temperature and at a higher temperature (about 55–60 °C).

Results and discussion

Relaxation of the surface potential in the initial PLA films

Fig. 1 demonstrates the TSRSP curves of the initial PLA films (at the same heating rate) charged in the unipolar corona of positive and negative signs. The inflection point temperature on the TSRSP curve characterises the temperature stability of the electret state. In this study, this temperature is approximately 45–50 °C (Fig. 1), which indicates low electret stability. The sign of the surface charge for the PLA samples corresponded to the accumulation of homocharge.

Furthermore, it should be noted that the TSRSP curves obtained for different signs of the corona discharge are practically identical. This fact allows suggesting that the relaxation of the surface potential in the initial PLA films (without a filler) is preconditioned by the neutralisation of the homocharge. It is a characteristic feature of the charge relaxation process introduced with the corona effect due to the bulk conductivity of the initial PLA films (Ignatyeva et al. 2015a).

The TSRSP method made it possible to reveal that the initial PLA films (without fillers) have low electret properties. The electret state storage time of the initial PLA films was also estimated by direct measurements of the surface potential at room temperature (Fig. 2). Fig. 2 demonstrates that the electret state storage time of the initial PLA film is approximately 15 hours. This indicates the shell life of food products in electreted initial PLA packages is limited.

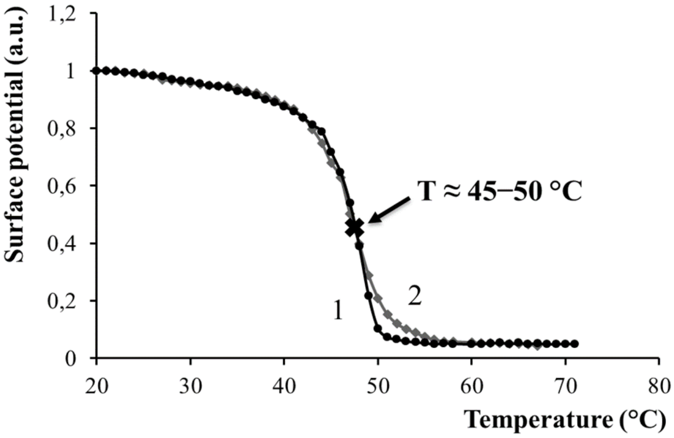

Fig. 1. TSRSP curves of initial PLA film (without fillers), electreted in the field of negative (curve 1) and positive (curve 2) corona discharge

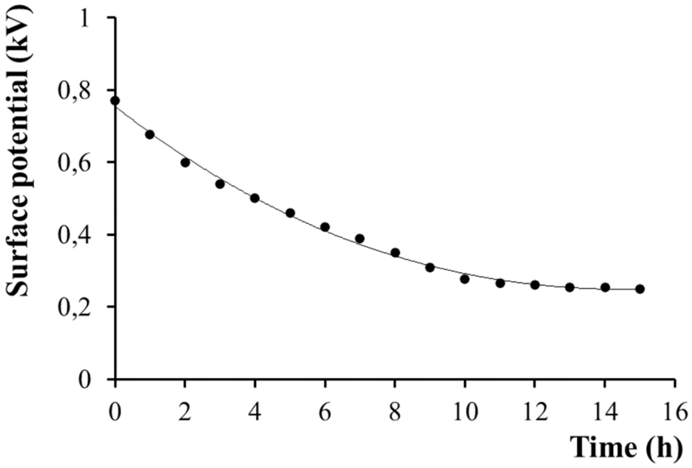

Fig. 2. Dependence of the surface potential on the electret state storage time of the initial PLA film

In studies (Gorokhovatskiy et al. 2017; Ignatyeva et al. 2015b), it was suggested that the structure of aliphatic polyesters may contain quasimolecular complexes, such as charge-dipole centres. Charge-dipole centres have a dual nature. On the one hand, due to the dipole structure, they can take part in polarisation. On the other hand, such centres are formed because of the interaction of charge carriers with H_2O, O_2, H_2 molecules dissolved in the polymer structure, as well as with structural defects, such as traps ("sticking centres") of charge carriers, thereby affecting the conductivity of polymeric materials.

Thus, it seems reasonable to suppose that the low electret state stability in the initial PLA films, which is preconditioned by increased bulk conductivity, is related to the presence of charge-dipole centres in the structure of the PLA sample (Gorokhovatskiy et al. 2017; Ignatyeva et al. 2015a; 2015b).

Relaxation of the surface potential in PLA-based composite films with hydrophilic nanoscale fillers

It was assumed that the introduction of a hydrophilic nanoscale filler (such as silicon dioxide, barium titanate, etc.) into the PLA polymer matrix would facilitate the capture of water by the filler particles. This process, in turn, should lead to a decrease in the concentration of charge-dipole centres. Thus, the conductivity of the polymer material should decrease and the electret properties of the composite should improve.

In (Ignatyeva et al. 2015a), it was shown that in PLA-based composite films with a hydrophilic nanoscale filler silicon dioxide (SiO_2) the decrease in the surface potential is determined by the release of the captured charge from near-surface traps. The energy depth of traps for charge carriers of opposite signs is different, since relaxation of the surface potential occurs at different temperatures. This is possible if the bulk conductivity in the PLA-based composite films is significantly lower than in the initial PLA films.

The relaxation of the surface potential has a two-stage form for PLA-based composite films (Ignatyeva et al. 2015a). The relaxation in low-temperature area (about 55 °C) occurs due to the reorientation of polar structures in the internal field of a side charge. In the high-temperature area, the relaxation of the surface potential for a PLA-based composite film, electreted in the positive corona discharge, occurs at T ≈ 80 °C, and in the negative corona discharge at T ≈ 70 °C. The asymmetry of the TSRSP curves is explained by the release of charges from the trapping centres, which are characterised by different parameters (activation energy and frequency factor) for positive and negative carriers.

Since the relaxation of the surface potential has a two-step form, preliminary electreting in the field of a corona discharge at a temperature of 55–60 °C, followed by cooling in a corona discharge to room temperature, was carried out. Subsequently, the surface potential of the sample was measured.

Fig. 3 shows the TSRSP curves of the initial PLA samples and PLA-based composite pre-electreted at a high temperature (55–60 °C) charged at the same heating rate in a positive corona discharge.

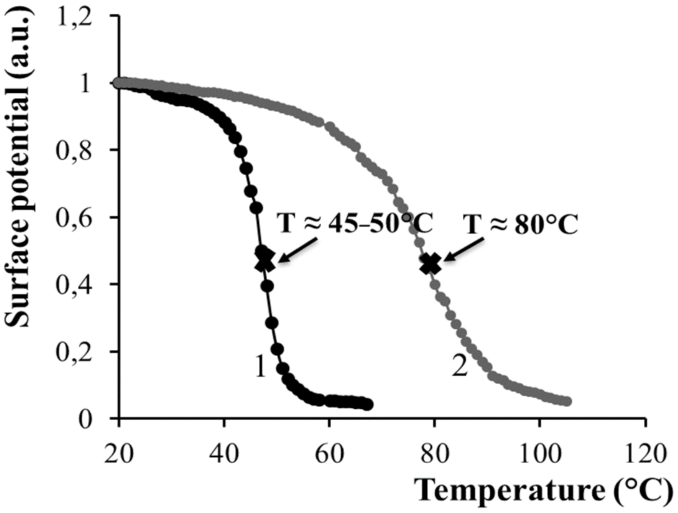

Fig. 3. TSRSP curves of samples charged in a positive corona discharge at the same heating rate: the initial PLA film (curve 1) and the PLA-based composite film (with 2% SiO_2) pre-electreted at a high temperature (55–60 °C, curve 2)

Thus, the introduction of a hydrophilic nanoscale filler reduced the concentration of charge-dipole centres, as well as preliminary preparation of the composite sample (advance electreting in a positive corona discharge at a high temperature) made it possible to increase the temperature electret stability from 50 °C to 80 °C (Fig. 3).

This procedure also allows increasing the temporal electret stability of the PLA-based composite (Fig. 4). It was experimentally revealed that the electret state storage time of the PLA-based composite sample at room temperature exceeds 4 months.

This result makes it possible to recommend PLA-based composite films with nanoscale filler SiO_2 (vol. 2%) pre-electreted at a high temperature (55–60 °C) for practical use as biodegradable active packaging.

The IR-transmittance spectra and the ATR spectra. Model of electret stability in initial PLA films and PLA-based composite films

The presence of charge-dipole centres in thin PLA films (about 40 μm) was established experimentally using the method of FTIR-spectroscopy (Ignatyeva et al, 2015b). Curve 1 (Figs. 5–6) corresponds to the IR-transmission spectrum of thin PLA film. The bands determined by the presence of charge-dipole

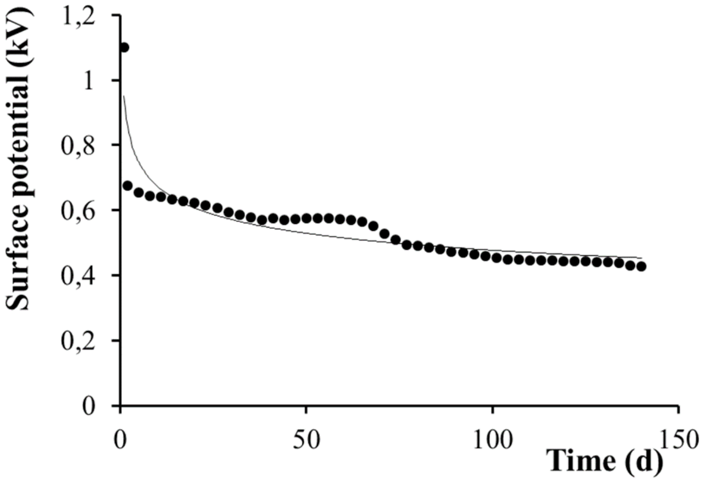

Fig. 4. Dependence of the surface potential on the electret state storage time of the PLA-based composite (with 2% SiO_2) pre-electreted at a high temperature (55–60 °C)

centres in the structure (1501 cm^{-1}, 1561 cm^{-1}, 1591 cm^{-1}, 3055 cm^{-1}) are presented in Figs. 5 and 6 (Ignatyeva et al. 2015b).

Lowering the bulk conductivity and, therefore, increasing the electret state stability is known to be achieved via the introduction of hydrophilic nanoscale fillers into the polymer matrix of the sample (Gorokhovatskiy et al. 2018).

This study presents the IR-transmission spectrum of the PLA-based composite with hydrophilic nanoscale barium titanate ($BaTiO_3$) (curve 2, Figs. 5–6). The intensity of the absorption bands corresponding to charge-dipole centres decreases due to the introduction of $BaTiO_3$ (Figs. 5–6). The particles of $BaTiO_3$ filler capture and bind water molecules in the near-surface regions of polymer matrix of PLA, which leads to the reduction of the concentration of charge-dipole centres in the PLA-based composite structure.

The fact of a decrease in the concentration of charge-dipole centres confirms the results obtained by the TSRSP method (relaxation mechanism and the model of the charge-dipole centres) and leads to an increase in the electret state stability.

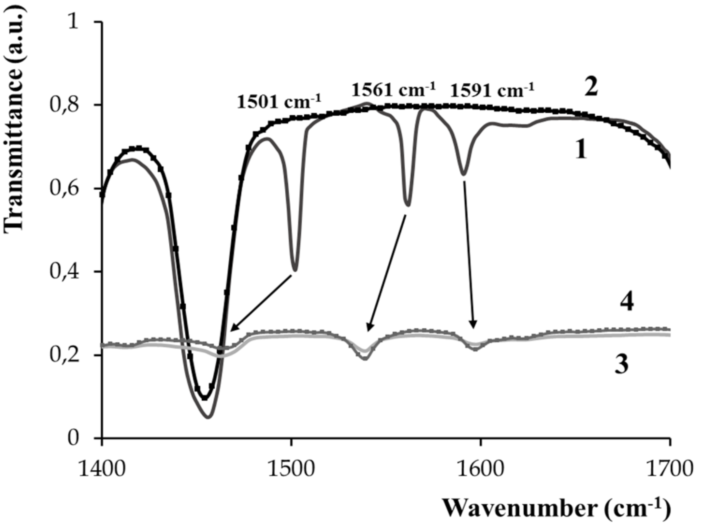

Fig. 5. The IR-transmittance spectra of the initial PLA (curve 1) and the PLA-based composite + $BaTiO_3$ (curve 2); the ATR spectra of the initial PLA (curve 3) and the PLA-based composite + $BaTiO_3$ (curve 4) in the range of wavenumbers 1400–1700 cm^{-1}

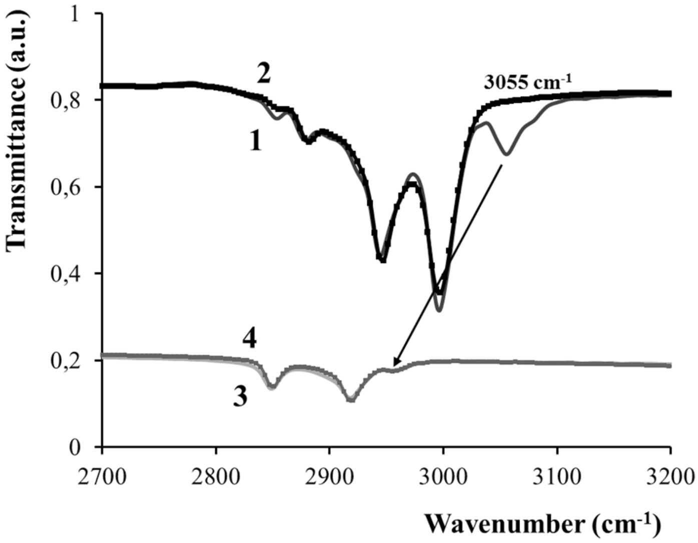

Fig. 6. The IR-transmittance spectra of the initial PLA (curve 1) and the PLA-based composite + $BaTiO_3$ (curve 2); the ATR spectra of the initial PLA (curve 3) and the PLA-based composite + $BaTiO_3$ (curve 4) in the range of wavenumbers 2700–3200 cm^{-1}

The experimental data of the TSRSP and FTIR-spectroscopy of thin PLA films (about 40 μm) are in good agreement with the proposed model of charge-dipole centres. However, during the study of thick PLA films (more than 180 μm) this model turned out to be not entirely correct.

Specifically, the absorption bands corresponding to charge-dipole centres are strongly weakened or not observed at all in the initial thick PLA films on the IR-transmission spectra (Gorokhovatskiy et al. 2019). It casts doubt on the fact of charge-dipole centres presence in these films and the proposed model. That is why the ATR method for the research composite PLA-based films with different thickness was used.

The presence of absorption bands corresponding to charge-dipole centres in the initial thick PLA films (curve 3, Figs. 5–6) was revealed by the ATR method. Previously, the presence of these bands in the IR-transmission spectra of a thick PLA films was not established, but these bands are presented in the ATR spectra. The ATR spectra of PLA-based composites with $BaTiO_3$ (curve 4, Figs. 5–6) also demonstrate bands associated with charge-dipole centres.

It is worth mentioning a shift of all absorption bands of ATR spectra to shorter region of wavenumbers (about 100 cm^{-1}).

Absorption bands associated with charge-dipole centres are present in all ATR spectra: both in the spectra of the initial PLA and in the spectra of PLA-based composites with different hydrophilic nanoscale dispersed fillers.

These experimental results obtained by the ATR method made it possible to trace the presence of charge-dipole centres in all samples of PLA and PLA-based composites (thin and thick films). This allows us to conclude that these centres are predominantly formed in the near-surface regions via constant contact with the molecules of atmosphere. It can also be assumed that the distribution of these centres has a saddle-like shape. A large concentration of these centres is observed in the near-surface zone, and decreases from the centre to the periphery.

Conclusion

All the presented results obtained by using a set of research methods allow us to draw the following conclusions.

The presence of charge-dipole centres in the initial thin PLA films and their disappearance in PLA-based composite films with a hydrophilic nanoscale filler is confirmed by the method of FTIR-spectroscopy. A decrease in the intensity of absorption bands corresponding to charge-dipole centres in the IR-transmission spectra is connected with capture of free molecules of water, oxygen, and hydrogen by the filler particles. Considering the limited possibility of registering the charge-dipole centres by FTIR-spectroscopy in thick PLA films, the ATR method was used, which also confirmed their presence in the structure of the initial thin and thick PLA films and PLA-based composites. The distribution of the charge-dipole centres in the polymer film has a saddle-like shape, and the maximum concentration is observed in the near-surface zone, decreasing from the centre to the periphery.

The model of the charge-dipole centres makes it possible to explain the nature and mechanisms of relaxation, as well as the stability of the electret state, in the initial PLA films and PLA-based composites, which were obtained by the TSRSP method.

The low stability of the electret state in the initial PLA films was established, The increased bulk conductivity in the initial PLA films is associated with the formation of charge-dipole centres in the polymer structure. The temperature of electret state stability in the initial PLA films is about 45–50 °C.

The TSRSP method allows establishing two areas of relaxation in PLA-based composite films:

- low-temperature area (T ≈ 55 °C), which is connected with the reorientation of polar structures in the homocharge field;
- high-temperature area (T ≈ 70–80 °C) (depending on the sign of the corona discharge), which is related to relaxation of the surface potential via ejection of the charge from deep near-surface traps.

Moreover, the proper electreting mode (allowing to increase the electret state stability) for PLA-based composite films was presented. The temperature stability of the electret state in pre-electreted at a high temperature (55–60 °C) PLA-based composite films in the field of a positive corona discharge is about 80 °C.

It was experimentally revealed that the electret state storage time of the PLA-based composite film at room temperature exceeds 4 months, which makes it possible to recommend it as an “active packaging material”.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

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