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Improvement of polylactic acid electret properties by addition of fine barium titanate

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ABSTRACT

The effect of $BaTiO_3$ on properties of polylactic acid composites was studied. Measurements of surface potential, electric field strength, effective surface charge density, and isothermal and thermally-stimulated potential relaxation showed that corona-charged films of the PLA – $BaTiO_3$ composites had more stable electret properties compared to PLA films. Addition of $BaTiO_3$ particles resulted in higher thermal stability of the charge, but it did not affect transition temperatures in the polymer according to differential scanning calorimetry data. IR-spectra revealed that filler addition accounted for disappearance of the charge–dipole complex bands. Homo- and heterocharge depth in the material was studied as well.

1. Introduction

Packaging has become essential part of any product. It is hard to imagine a good without package, especially food one. However, generally the final stage of food package usage is its disposal [1].

Majority of packaging wastes (over 40%) are polymer materials [2] which separation from municipal solid wastes followed by washing, sorting and recycling presents a challenge due to hard-to-remove impurities. Typically, packaging wastes are landfilled [3] expecting them to degrade in a short term, that, in fact, does not occur.

In this regard advanced packaging material that are easily assimilated and quickly-degraded without damaging the environment are constantly developed. There are two ways to accelerate degradation of polymer packaging materials. The first one involves degrading commercial packaging materials – polyethylene, polypropylene – e.g. by addition of fine fillers such as starch that lead to faster polymer chain breaking [4–6]. The second way is to use biodegradable polymers derived from renewable sources (corn, potato, sugarcane) as packaging materials. The key requirement to these polymers is physical, mechanical and barrier properties competitive with traditional industrial polymers [7–11]. One of these materials is polylactic acid (PLA) that is derived from corn starch and used as packaging material for food (tea bags, trays, containers, bags, tableware) [9–11].

Another trend in packaging industry is developing packages with additional functions, including smart and active ones that can elongate shelf-life of a product owing to direct impact of the package on the product [12–16]. We suppose polymer electrets to be promising material for manufacturing food package [17–19] that elongate food shelf-life by means of negative effect of electric field it creates on pathogenic microorganism vital activity. There are data on studying electret biodegradable materials based on synthetic polymers and fillers providing polymers with capability to be assimilated by soil microorganisms [20–22].

Electret properties of PLA corona electrets were studied in [23], where their low stability and values were shown. PLA thermoelectrets investigated in Ref. [24] had dominantly heterocharge and performed the applicable electret properties after 4 months being polarized at $E_p > 16.7$ MV/m. However, thermoelectret manufacturing method described in the paper is cost-

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intensive and energy-consuming as it required gold or aluminum deposition on the electrodes and polarization for a long period of time at high electric field intensity and heating. Corona discharge treatment, on the other hand, is a very inexpensive and fast process that requires simple equipment [25]. Studies [26–30] showed that one of the methods to improve electret state stability is addition of fine filler.

The objective of the paper was to improve electret state stability of the PLA film by adding fine filler.

2. Materials and methods

2.1. Materials and sample preparation

L-polylactic acid (produced by Direct Corporation, Lot #: 902-57-1) was the subject of research. Barium titanate (density 6.08 g/cm^3, Curie point 120 °C) was chosen to be a ferroelectric filler because it was shown [29,30] to improve electret properties of a material significantly.

PLA films were solvent-casted. Chemically pure chloroform was used as a solvent. After polymer grains dissolving at constant stirring the solution was casted in glass molds and dried for 48 h. Thickness of the samples was between 30 μm and 100 μm measured by "Mitutoyo" dynamic micrometer with uncertainty of ±1 μm.

Compositions of the PLA and 2%, 4% and 6% $BaTiO_3$ were produced by mixing the filler with 5% polymer solution in chloroform.

2.2. Scanning electron microscopy

Filler particle size and distribution were monitored with scanning electron microscope Zeiss EVO *40* to an accuracy of 0.1%.

2.3. Corona charging

Charging of the films was performed by the method of corona discharge using a point-to-plane three-electrode corona discharge system (Fig. 1). Metal grid inserted between point corona electrode and a sample allowed charging film uniformly. The final sample voltage is less or equal to the grid voltage [25]. Distance between the grounded electrode and the grid was 10 mm; the distance from the grid to the corona electrode was 7 mm. Samples were charged for 1 min. Positive or negative 5 kV voltages were applied to the corona electrode. Grid voltage of the same polarity as that of the corona electrode was 1 kV. Samples were stored in paper boxes at room temperature.

2.4. Electret properties

Electret surface potential of the charged samples was measured by the vibrating electrode method with compensation by which the estimated error was better than 5%.

Electric field strength and effective surface charge density were measured by electrostatic fieldmeter IPEP-1. Its working principle is based on periodic shielding of the receiving electrode located at a certain distance from the electret surface. Measurement error did not exceed 3%

Isothermal and thermally-stimulated potential relaxation methods were applied to investigate time and thermal stability of the electret state. During thermal stability test polarization of the samples was carried out at room temperature followed by heating at constant rate (5.4 °C/min) with simultaneous temperature and surface potential recording. During time stability study surface potential measuring was performed at 60 °C.

2.5. Charge depth

Charge penetration depth in PLA was measured according to the procedure as follows. Double-layered films with a varied thickness of the top layer were produced and charged in the negative corona discharge. After electret properties being measured, the top layer was removed with the solvent, samples were dried and electret properties of the second layer (the support) were measured. If the removed top layer thickness is greater than injected charge carrier depth the substrate will have no charge.

There are certain requirements to the support material. It should be resistant to the solvent and chemically similar to the polymer studied. PET film was chosen as the support. PLA solution was casted on the support varying the thickness from 10 μm to 30 μm.

To charge samples another corona discharge system was used that allowed charging bigger area. It consisted of 196 needles uniformly distributed at 5 mm distance at square area of 49 cm^2. Sample charged area was 7 × 7 cm as well. The distance between the sample and corona electrodes was 2 cm. Polarization time was 30 s, polarization voltage 30 kV. Before samples were charged in negative corona discharge, they were heated at 90 °C for 10 min.

2.6. FTIR-spectroscopy

Structure of the charged and uncharged films was studied using Fourier spectrometer FSM-1202 within the wavenumber range of 400–5000 cm^{-1} to an accuracy of 0.1%.

2.7. Differential scanning calorimetry

Phase transitions in the polymer were studied using differential scanning calorimeter Q-200TA. Heating rate was 10 °C/min.

3. Results and discussion

To analyze the relaxation process corona electrets were obtained in the negative and positive corona discharge. Studies performed showed pure PLA to have weak and unstable electret properties (Fig. 2, Table 1).

Weak and unstable electret properties of polylactic acid arise from chemical composition and structure of the polymer. Polylactic acid being a polar polymer is not charged well in the corona discharge because of the polar groups that promote capturing injected charge carriers by shallow energy traps resulting in fast charge relaxation. To check this assumption charge penetration depth in PLA was studied.

Fig. 3 illustrates the effective surface charge density behavior of the PLA-PET double-layered films with PLA layer thickness ranging

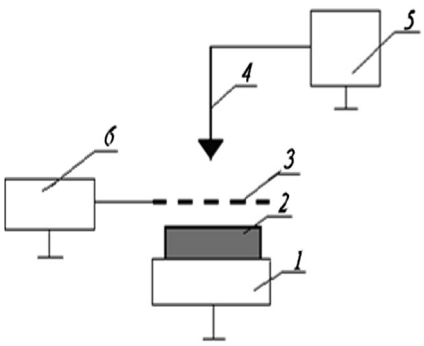

Fig. 1. Experimental corona discharge system: 1 – Grounded electrode, 2 – Sample, 3 – Grid, 4 – corona electrode (needle), 5 – Power supply to the corona electrode, 6 – Power supply to the grid.