

## Charge depth in polylactic acid electret filled with fine filler

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Charge depth of corona electrets based on polylactic acid was studied. Model of homo- and heterocharge distribution in the polymer was offered according to the observed electret behavior. Three different levels are specified in bulk of the polymer. At the first level dipole polarization that occurs due to surface oxidation dominates. At the second level injected charge carriers prevail. At the third level there is no injected charge carriers. For polylactic acid film first level thickness is up to 10  $\mu\text{m}$ , for the second one it is up to 20  $\mu\text{m}$

**Key words:** corona electrets, polylactic acid, charge depth

### INTRODUCTION

Modern technology has created the plastic age. Most of package is made from plastics. However, wide spread of polymers resulted in significant increase of plastic wastes and environmental pollution since plastic decay time is more than a hundred years. Biodegradable plastics are advanced materials that allow to meet this challenge and reduce decay period many times. Thus, they help to deal with the problem of waste disposal [1].

Another advanced materials used in packaging industry are polymer electrets – dielectric materials that have a quasi-permanent electric charge or dipole polarization and generate internal and external electric fields [2].

Polylactic acid (PLA) – a plastic substitute made from fermented plant starch (usually corn) - is quickly becoming a popular alternative to traditional petroleum-based plastics that are the basic material for electret production [1]. Application of PLA for manufacturing electrets offers opportunity for different industries including packaging [3, 4].

However, PLA being polar polymer may not perform characteristics required for industrial use of electret materials [5, 6]. In order to improve electret properties of PLA it is necessary to understand mechanisms of charging and charge relaxation. Fine filler particles are known to increase electret properties of polymers [7–12].

Hence, the objective of the paper is to study charge carrier (homo- and heterocharge) depth in corona electrets based on polylactic acid and estimate fine filler effect on it.

Nowadays there are a few techniques to determine charge distribution in the bulk of a polymer such as sectioning and chipping method, thermal impulse method, method of charge neutralization by light and etc. [13–16]. Nevertheless, these techniques are either indirect or involve mechanical treatment of the samples requiring certain assumptions that affect significantly the results of experiments. Following technique [17] may be considered to be the most reasonable for measuring charge depth: double-layered films are manufactured from different polymers with varied top layer thickness. Then samples are polarized in the field of negative corona discharge. After measuring electret characteristic of the samples top layer is removed by the solvent, under layer (substrate) is dried and electret properties are measured again. There is no charge on a substrate if the removed top layer thickness exceeds injected charge carrier depth.

This technique requires selection of compatible polymer pairs. Basic requirements to substrate are resistance to applied solvent (or minimum swell value) and chemical nature similar to polymer studied.

### MATERIALS AND METHODS

L-polylactic acid (PLA) was studied. Polyethylene Terephthalate (PET) was used as substrate; trichloromethane (chloroform) was used as a solvent. To begin, 5% solution of PLA or PLA+4%BaTiO<sub>3</sub> in trichloromethane was made. Then, top layer of the polymer studied of various thickness was solvent-casted to the PET under layer followed by solvent removal. Top layer thickness was measured by micrometer MK.

Samples were charged in the field of negative corona discharge after being heated at 90°C for

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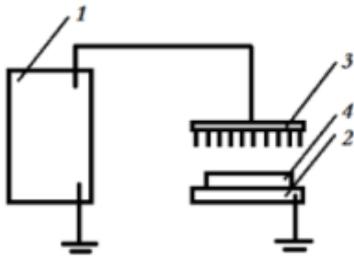


Fig. 1. Experimental set-up for corona treatment: 1 – corona electrode power supply; 2 – grounded electrode; 3 – corona electrode; 4 – sample.

10 min. Corona treatment unit is shown in Fig. 1. Corona electrode consists of 196 needles equally spaced on 49 cm<sup>2</sup> area. The gap between corona electrode and the sample was 20 mm, polarization time was 30 s, polarization voltage – 30 kV.

Samples were stored under room conditions in paper envelopes.

Surface potential  $V_s$ , electric field strength  $E$  and efficient surface charge density  $\sigma_{ef}$  were measured by IPEP-1 unit. Its working principle is based on periodic shielding of receiving electrode located at a certain distance from the electrets surface. Measurement error did not exceed 3%.

Top layer was removed from the samples with solvent (trichloromethane) under extract ventilation.

Thermal stability of electret state was investigated by thermally stimulated potential relaxation (TSPR) technique [18] that involves measuring surface poten-

tial of the samples being heated at the constant rate of 0,08 K/s right after polarization. Surface potential curves were normalized and given at relative unit  $V_s/V_{s0}$ , where  $V_{s0}$  is initial value of the sample surface potential.

## RESULTS AND DISCUSSION

It was shown earlier in [5, 6] that polylactic acid performs poor electrets properties. Surface potential of PLA electrets decays in two-three days. Heating above 50°C results in complete electret charge relaxation. Studying thermal stability of PLA electret state showed that surface potential decay curve falls into three regions: region of the surface potential relative stability, region of sharp drop and complete surface potential relaxation region. (Fig. 2, curve 1).

One can see that at 307 K (34°C) PLA surface potential sharp drop region begins, while at 317 K (44°C) complete charge relaxation occurs (Fig. 2, curve 1). The fact that this temperature is close to PLA glass transition temperature allows to suggest that during polarization in corona discharge charge carriers entering the polymer polarize nearby dipoles and their orientation occurs in injected charge field [19]. At that, most of charge carriers are located at surface traps. Relaxation time of this dipole polarization is short, while temperature increase results in relatively free rotation of PLA macromolecule units. When PLA glass transition temperature is reached ordered dipole system breaks with the release of injected charge i.e. electret state relaxation occurs.

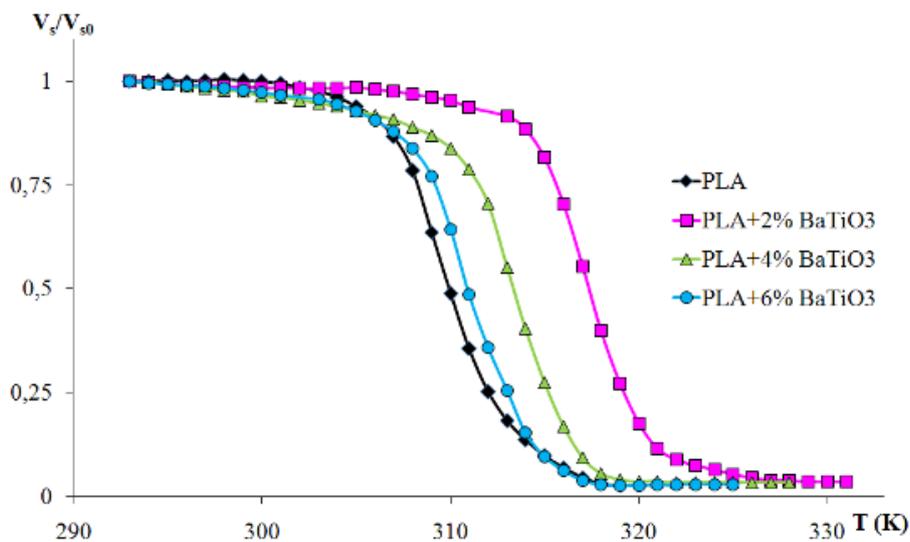


Fig. 2. Thermally stimulated potential relaxation curves of PLA compositions with barium titanate.

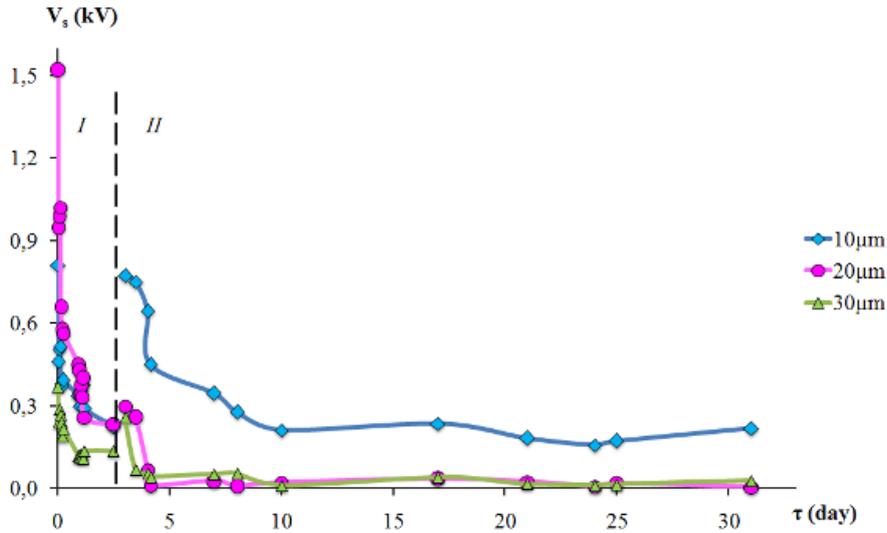


Fig. 3. Surface potential vs. storage time before (I) and after(II) PLA layer removal.

Figure 3 shows the results of charge depth study in the polymer. It is obvious that PLA layer removal affects significantly electrets properties of the samples. In one case substrate efficient surface charge density is higher (Fig. 3, curve 1), while in other cases it is lower (Fig. 3, curves 2 and 3) than for double-layered corona electrets.

The same behavior showed surface potential and electric field strength of the samples. Their values are given in Table 1.

Observed behavior can be explained by model of homo- and heterocharge distribution in polymer corona electrets described in [17] allowing for polylactic acid to be polar polymer. According to the model given in Fig. 4 three different levels are specified in bulk of the polymer. At the first level (Fig. 4,

lvl.1) dipole polarization of polar groups dominates that occurs due to surface oxidation during corona treatment. At the second level injected charge carriers prevail (Fig. 4, lvl. 2). There are dipoles in the bulk of PLA as well. They can be oriented during corona discharge treatment, but this polarization is limited by hindered mobility of the polymer macromolecules at the given conditions. At the third level there are no injected charge carriers. (Fig. 4, lvl. 3).

At the second level injected charge carriers prevail. For polylactic acid film first level thickness is up to 10  $\mu\text{m}$ , for the second one it is up to 20  $\mu\text{m}$ . When PLA is filled with BaTiO<sub>3</sub> fine particles heterocharge influence increases resulting in less injected charge penetration depth.

Table 1. Electret properties of double-layered PLA-PET films vs. storage time.

Electret Properties	PLA layer thickness, ( $\mu\text{m}$ )	before PLA layer removal			after PLA layer removal	
		0 day	1st day	3rd day	4th day	31st day
$V_s$ , kV	10	0.81	0.3	0.24	0.67	0.2
	20	1.52	0.34	0.20	0.67	0.01
	30	0.37	0.15	0.14	0.06	0.03
$E$ , kV/m	10	48.4	21.9	14.3	40.2	13.1
	20	86.9	27.0	14.6	0.4	0.4
	30	21.9	7.3	8.5	3.5	1.4
$\sigma_{ef}$ , $\mu\text{C}/\text{m}^2$	10	0.43	0.19	0.13	0.36	0.12
	20	0.58	0.24	0.13	0.00	0.00
	30	0.2	0.00	0.08	0.03	0.01

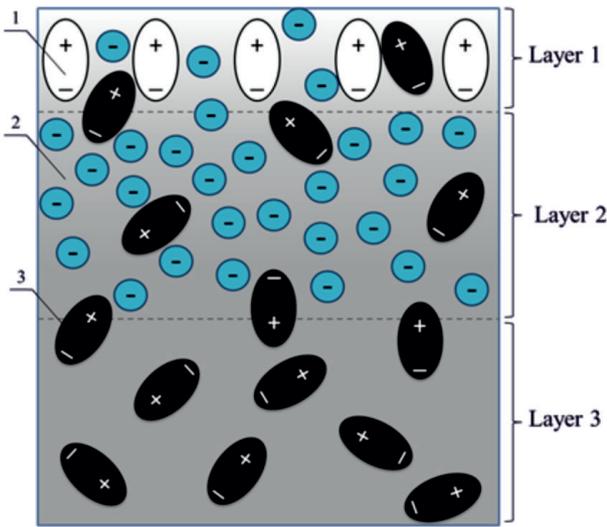


Fig. 4. Model of homo- and heterocharge distribution in PLA: 1 – dipoles formed due to surface oxidation; 2 – injected charge carriers; 3 – dipoles in the bulk of a polymer.

Electret performances of the samples increase after removal of the PLA layer where dipole polarization due to oxidation prevails since it contributes negatively to the electret total electric field value. In the case of PLA this layer thickness is about  $10\ \mu\text{m}$  (Fig. 3, curve 1).

When removed layer thickness is greater, injected charge carriers composing homocharge are removed as well resulting in almost complete charge decay shown in Fig. 3 (curves 2 and 3).

Therefore, it may be concluded that heterocharge depth in PLA that appears due to surface oxidation is  $10\ \mu\text{m}$ , while homocharge depth is up to  $20\ \mu\text{m}$ .

It was mentioned above that fine filler is often used to enhance electret properties of the polymers [7–10]. Research conducted showed that filling PLA

with barium titanate affect significantly stability and values of electret properties. It is seen (Fig. 2, curve 2) that 2%  $\text{BaTiO}_3$  added to the polymer shifted the beginning of surface potential sharp decay region at 313K ( $39^\circ\text{C}$ ), while complete charge relaxation occurs at 326K ( $53^\circ\text{C}$ ).

PLA electret properties enhance when filled with barium titanate can be explained by formation of new structural elements that can act as charge carrier traps (phase boundary, polymer loosened adsorption layer near filler surface). Increased number of injected charge traps contributes to the ability of dielectric to be polarized in corona discharge and enhances stability of the surface potential. Fillers affect mobility of different polymer kinetic units and relaxation time range. It occurs due to macromolecule adsorption on the solid surface to form adhesion polymer-filler bond resulting in macromolecule fixation and motion restriction at the surface adjacent segments. In other words, in filled PLA there is macromolecular layer with limited mobility near barium titanate surface. It hinders dipole polarization relaxation in PLA compositions and increases thermal stability of their electret properties (Fig. 2).

However, when barium titanate content in PLA is more than 2 wt.% gradual decrease of the surface potential stability is observed (Fig. 2, curves 3-4), although composition surface potential is more stable compared to pure polymer. It is worth mentioning that the trends of electret performance dependence on filler content (with maximum at 2-4% dispersion component load) are common for polymer-filler systems [7–9, 20]. Reducing surface potential stability at greater filler content can be explained by two factors. Firstly, it is ferroelectric domain orientation that forms heterocharge. Secondly, it is content reduc-

Table 2. Electret properties of double-layered PLA+4% $\text{BaTiO}_3$ -PET films vs. storage time.

Electret Properties	PLA layer thickness, ( $\mu\text{m}$ )	before PLA layer removal			after PLA layer removal	
		0 day	1st day	3rd day	4th day	31st day
$V_s$ , kV	10	1.25	0.29	0.08	0.23	0.06
	20	1.70	0.56	0.17	0.34	-0.20
	30	1.14	0.52	0.11	0.66	0.14
$E$ , kV/m	10	78.1	18.3	4.5	14.7	3.7
	20	101.8	35.1	10.8	21.3	-12.2
	30	71.2	33.7	6.7	41.5	9.1
$\sigma_{ef}$ , $\mu\text{C}/\text{m}^2$	10	0.69	0.16	0.04	0.13	0.03
	20	0.67	0.31	0.10	0.25	-0.10
	30	0.63	0.29	0.06	0.37	0.08

tion of the component polarizable in corona discharge (polymer).

It should come as no surprise that structural modification affects charge depth in polylactic acid composite. At 4% BaTiO<sub>3</sub> content heterocharge contribution increases due to filler domain structure with high polarizability. It reduces charge penetration depth (Table 2).

Reduced homocharge penetration depth should result in decrease of polymer electret characteristics. However, injected charge carrier capture energy of composite structural elements is higher compared to pure polymer that was shown earlier in [20].

### CONCLUSIONS

Therefore, polylactic acid performs insufficient electret characteristics. Heterocharge depth in PLA that appears due to surface oxidation is up to 10 μm, while homocharge (injected charge) penetration depth is up to 20 μm. Fine filler addition enhances surface potential stability of PLA composites. The most stable values of the surface potential were observed for PLA compositions with 2 wt.% BaTiO<sub>3</sub>. Charge penetration depth in PLA composite is less owing to barium titanate domain structure with high polarizability.

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