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Gas discharge activation of new poly(lactic acid) packaging composite films

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Abstract. This work focuses on new poly(lactic acid) electroactive packaging composite films with different mass percentages of a filler. Hydroxyapatite (HA), Poviargolum (PA) and vapor-grown carbon fibers (VGCF) were used as fillers. The films were produced by extrusion. Mechanical, electric and electretic properties were studied. Time dependences of the electretic potential differences were identified. The properties of the samples were compared and the most suitable films (0.5% HA, 5% PA, 0.5% VGCF) were chosen.

Keywords: polylactide, electret, composite material, hydroxyapatite, Poviargolum, vapor-grown carbon nanofibers

Introduction

In recent years, polymers have become an essential part of our life. Their outstanding mechanical and electrical properties make them irreplaceable in many industries. Mass production of petroleum-based polymers leads to a problem with their disposal, e. g., polyethylene breakdown in the natural environment can take several hundreds of years. A possible solution to this issue is biodegradable materials.

Made from lactic acid, polylactide (PLA) is one of the most popular biodegradable polymers (Fig. 1). It can quickly break down in a special compost, leaving only carbon dioxide, water and other harmless substances (Valdes et al. 2014; Yu et al. 2006). PLA is widely used as a material for 3D printing, surgical threads (due to its high biocompatibility) and food packaging (Cabedo et al. 2006; Garlotta 2001).

Another growing trend is the usage of active packaging. Electroactive polymer materials have bactericidal qualities, which positively affect the shelf life of a product. Dielectrics that provide such qualities due to a static electric field are called electrets (Borisova, Kojkov 1979). Polylactide has poor electretic properties (Guzhova 2016; Urbaniak-Domagala 2013). Thus, the goal of this work was to develop new PLA-based composite material and identify the optimal mass percentage of each filler with the best electretic properties.

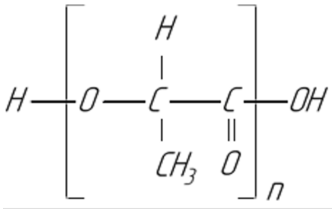

Fig. 1. The structural formula of PLA

Materials and methods

To improve the electretic properties of PLA, hydroxyapatite (HA), Poviargolum (PA) and vapor-grown carbon fibers (VGCF) were added as fillers. Two types of PLA matrix were used: PURAC PL18 (100% L-lactide) and Nature Works PLA 2003D (96% L-lactide, 4% D-lactide). The latter was used in composites with the addition of PA. The film samples were produced in the Institute of Macromolecular Compounds RAS. PLA and fillers were mixed in a double-screw microextruder DSM Xplore.

Hydroxyapatite is a mineral form of calcium apatite. Being a major component of human bones and dental enamel, it is frequently used in dentistry and fracture treatments. The mass percentage of hydroxyapatite in the composites varied from 0% to 3% (0%, 0.5%, 1%, 1.5%, 3%).

Poviargolum is a highly dispersed silver stabilized with polyvinylpyrrolidone (PVP). The silver to PVP ratio is approximately 8/92. Due to its antiseptic properties, it is often used in clinical practice. The mass percentage of Poviargolum varied from 1% to 5% (1 and 5%).

Vapor-grown carbon fibers (VGCF) have great mechanical properties. They are frequently used in composite materials to improve their electrical and thermal conductivity. The mass percentage of VGCF varied from 0.5% to 5% (0.5%, 1%, 3%, 5%).

A corona discharge was used to create an electret state in the samples (Borisova, Kamalov 2016). This is a widely spread method of electret production, which does not require any special equipment or environmental conditions. The compensation method with a vibrating electrode was used to measure the surface potential of an electret, as in our previous work (Pavlov et al. 2020). The goal was to conduct a one-week test to determine the most suitable samples. This period was chosen deliberately: most foods do not last longer than a week.

There are two mechanisms of charge relaxation in polymer dielectrics. It can occur due to the charge carriers moving through the sample (the intrinsic conductivity theory), or due to the charge carriers being released from the traps (the dispersion transport theory). Using the acquired time dependences of the electretic potential differences, the prevailing mechanism in each sample can be determined.

According to the intrinsic conductivity theory, the conductivity of the sample (γ) can be achieved using (1) (Borisova et al. 2004):

$$\gamma = -\varepsilon\varepsilon_0 \frac{dU}{dt} \tag{1}$$

The dispersion transport theory suggests that a dielectric material is ideal ($\gamma = 0$). The charge carrier mobility can be determined using the following formulas (Borisova 2014), where h is the thickness of the sample and μ is the charge carrier mobility (m^2/(V*s)).

$$\mu(t) = -2\frac{\mathrm{h}^2}{U^2(t)} \times \frac{dU(t)}{dt}, t \le t_\lambda \tag{2}$$

$$\mu(t) = -\frac{\mathrm{h}^2}{2U^2(t)} \times \frac{dU(t)}{dt}, t \ge t_\lambda \tag{3}$$

$$U(t_\lambda) = \frac{U(0)}{2} \tag{4}$$

The prevailing relaxation mechanism can be assumed by comparing the achieved $\mu(t)$ and $\gamma(t)$ curves and using (5), where n is the quantity of electrons and e is the elementary charge.

$$\gamma = ne\mu \tag{5}$$

If the curves have similar shapes, then we can suggest that the dispersion transport mechanism is prevailing in the sample.

The developed materials should be at least as durable as the original PLA matrix in order to be suitable for use in packaging. The mechanical properties of the film samples were investigated when they were stretched on an Instron 5943 tensile testing machine. The basic length of the test samples was 30 mm, width 4 mm, thickness about 20 µm. The stretching speed was 5 mm/min.

Results and discussion

The first test was 1 hour long. It helped to determine the most stable samples. The charging time for each sample was 60 seconds (at room temperature); the surface potential reached 500 V.

Fig. 2 shows the time dependences of the electretic potential differences of the samples with different mass value of HA (0%, 0.5%, 1%, 1.5%, 3%).

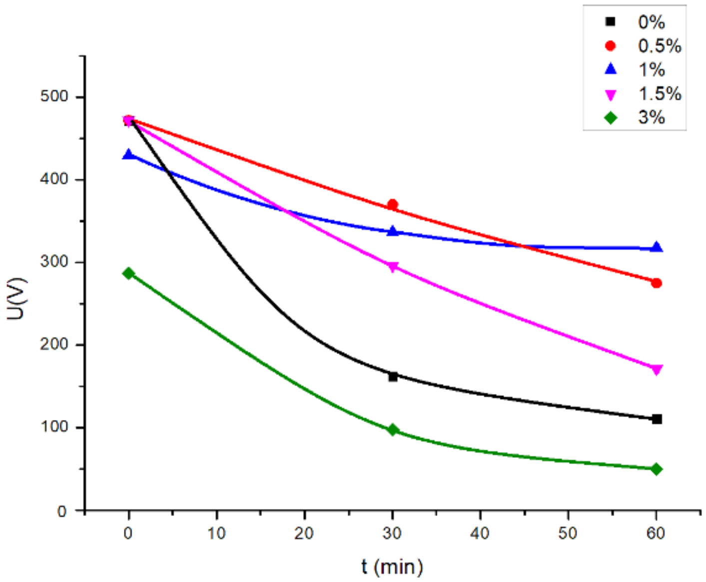

Fig. 2. Time dependences of the electretic potential differences of the samples with HA (0%, 0.5%, 1%, 1.5%, 3%)

The plot suggests that samples with 0.5% and 1% HA preserve the charge better compared to the other samples. The samples with 0%, 1.5% and 3% HA fully discharged the next day.

The charged samples with PA and VGCF were put to the same test (Fig. 3).

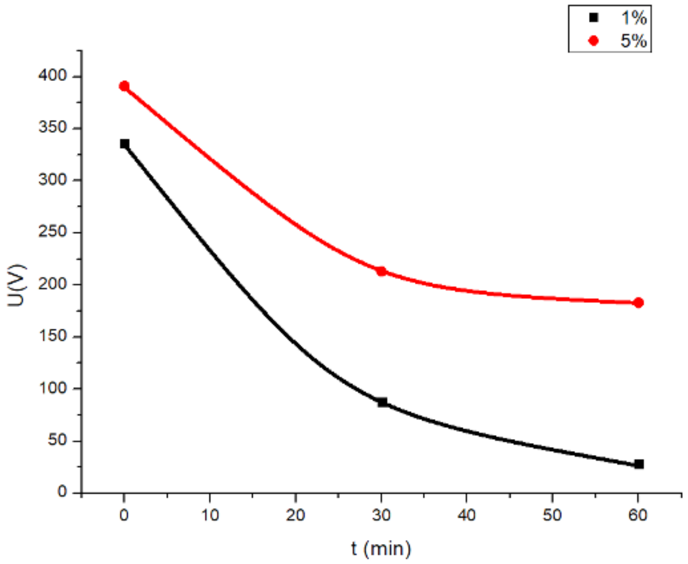

Fig. 3. Time dependences of the electretic potential differences of the samples with PA (1%, 5%)

The sample with 1% PA fully discharged the next day (Fig 4).

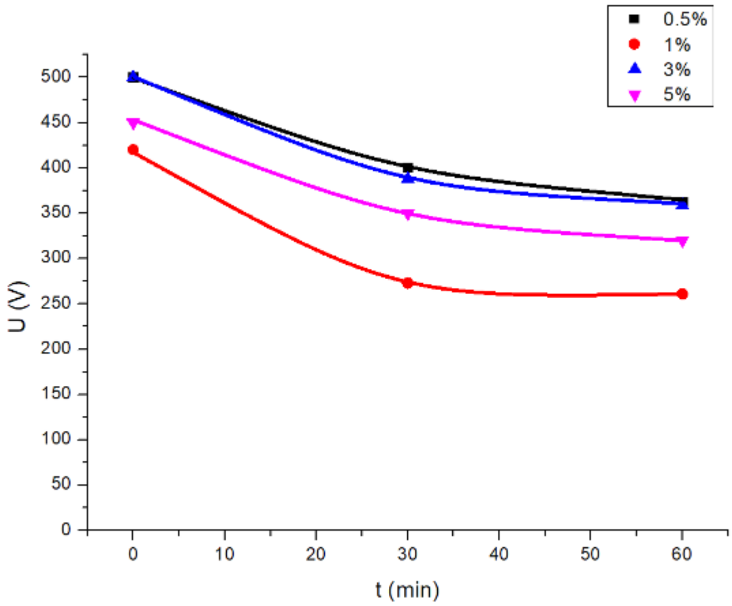

Fig. 4. Time dependences of the electretic potential differences of the samples with VGCF (0.5%, 1%, 3%, 5%)

The plot suggests that all samples with VGCF have good charge preservation capability.

The second test was one week long and was conducted upon the chosen samples from the former test.

Fig. 5 shows the time dependences of the electretic potential differences of the samples with HA (0.5%, 1%) and PA (5%).

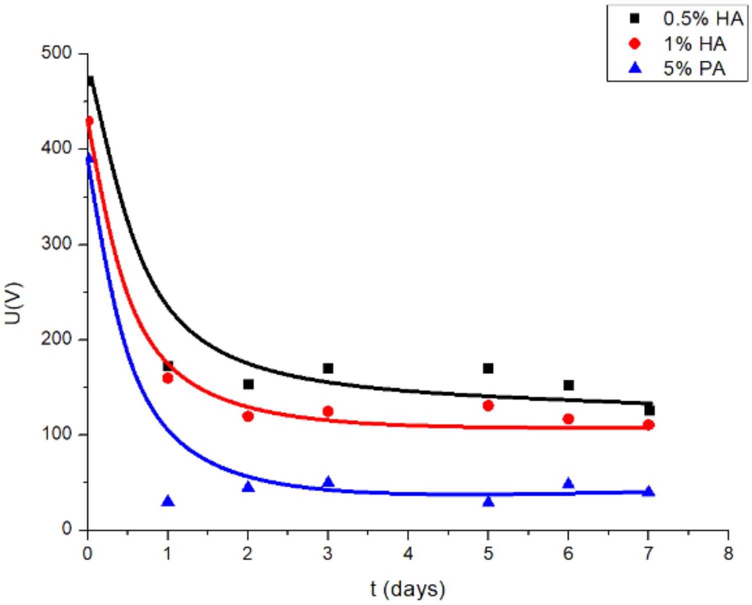

Fig. 5. Time dependences of the electretic potential differences of the samples with HA (0.5%, 1%) and PA (5%)

Using the plot, we can assume that the optimal mass value of HA is 0.5%.
The sample with 0.5% VGCF seems to have the longest charge relaxation time (Fig. 6).

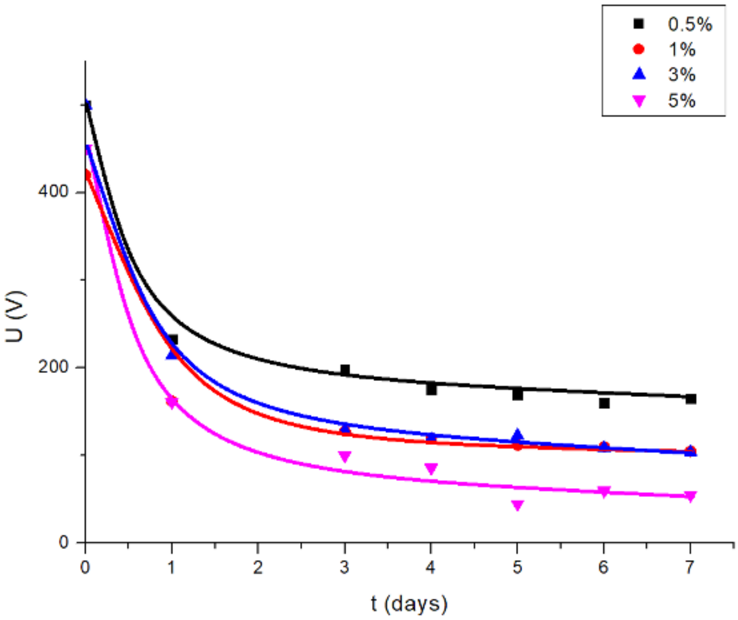

Fig. 6. Time dependences of the electretic potential differences of the samples with VGCF (0.5%, 1%, 3%, 5%)

The speed of discharge can be compared using the time period when the electretic potential difference is one half of the initial (Pavlov et al. 2021): 24 h for the samples with 0.5% HA and 5% PA, 30 h for the 0.5% VGCF sample, 45 min for the original PLA sample.

The intrinsic conductivity (Fig. 7) and the charge carrier mobility (Fig. 8) were calculated for the remaining samples (0.5% HA, 5% PA, 0.5% VGCF).

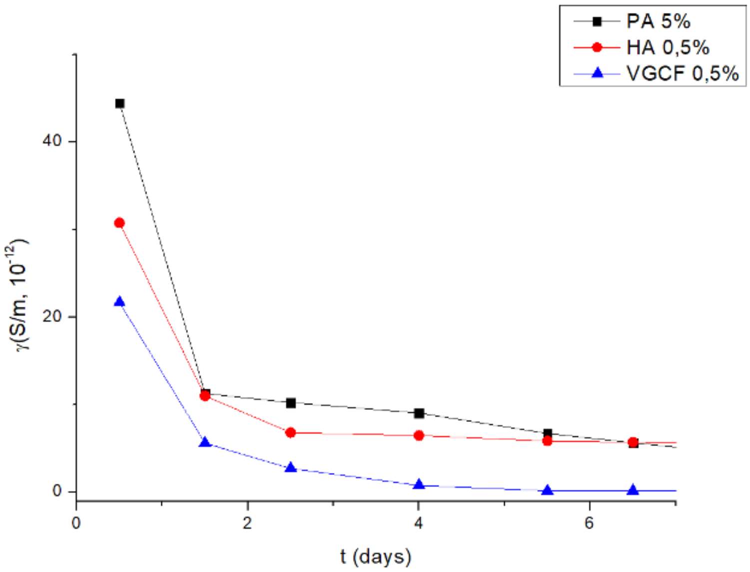

Fig. 7. Time dependences of the intrinsic conductivity of the samples with 0.5% HA, 5% PA and 0.5% VGCF

These exponential curves are characteristic for polymer dielectrics.

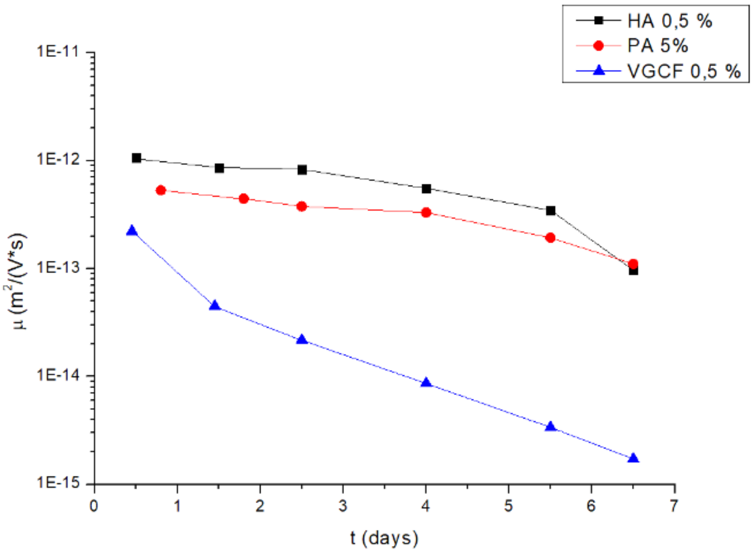

Fig. 8. Time dependences of the charge carrier mobility of the samples with 0.5% HA, 5% PA and 0.5% VGCF

Comparing the curves in Fig. 7 and Fig. 8 and using (5), we assume that charge relaxation in the sample with 0.5% VGCF mostly occurs according to the dispersion transport theory. In the samples with HA and PA the charge carrier mobility does not change much, so it might be suggested that the intrinsic conductivity of these samples is the main reason for charge relaxation.

The mechanical properties of the film samples are shown in Table 1, Table 2, and Table 3.

Table 1. Mechanical properties of HA samples

Properties	**Samples**				
	PL18	**0.5%**	**1%**	**1.5%**	**3%**
Strength, MPa	41 ± 3	40 ± 3	25 ± 3	30 ± 4	19 ± 3
Elastic modulus, GPa	1.8 ± 0.2	1.9 ± 0.2	1.5 ± 0.1	1.6 ± 0.2	1.4 ± 0.2
Deformation before rupture, %	6 ± 1	6 ± 1	8 ± 1	7 ± 1	6 ± 3

Table 2. Mechanical properties of PA samples

Properties	**Samples**		
	PLA	**1%**	**5%**
Strength, MPa	26 ± 3	25 ± 2	24 ± 2
Elastic modulus, GPa	1.6 ± 0.4	1.6 ± 0.2	1.7 ± 0.2
Deformation before rupture, %	6 ± 1	10 ± 7	12 ± 7

Table 3. Mechanical properties of VGCF samples

Properties	**Samples**				
	PL18	**0.5%**	**1%**	**3%**	**5%**
Strength, MPa	41 ± 3	41 ± 4	44 ± 1	38 ± 5	25 ± 3
Elastic modulus, GPa	1.8 ± 0.2	1.6 ± 0.3	1.6 ± 0.3	1.5 ± 0.2	1.3 ± 0.1
Deformation before rupture, %	6 ± 1	33 ± 6	26 ± 6	20 ± 3	16 ± 3

Table 1 shows that with an increase in the concentration of HA, the strength gradually decreases. With the addition of 1% HA the strength drops to 25 MPa. It should also be noted that the addition of HA does not affect the values of the modulus of elasticity and the deformation before rupture.

The films with the addition of Poviragolum were made from packaging PLA, so the strength values differ. Table 2 shows that Poviargolum does not affect the strength and the elastic modulus of the films. They remain at 25 MPa and 1.4 GPa respectively. The changes in the deformation before rupture of the films are at the same level.

The addition of VGCF significantly increases the deformation before rupture of the films. The strength and the elastic modulus of the samples gradually decrease with the further addition of the filler.

The addition of 0.5% HA and 5% PA has almost no effect on the mechanical properties of a composite, which makes them suitable for use in food packaging. The addition of 0.5% VGCF makes the value of the deformation before rupture 5 times greater; this may be explained by the high dispersive ability of fibers. This sample is the optimal choice due to its superior electretic and mechanical properties.

Conclusion

The optimal mass percentage of each filler to produce the best electretic properties was found (0.5% HA, 5% PA, 0.5% VGCF). The addition of each filler creates new charge traps in the PLA matrix, which increase charge relaxation time. The stability of the electret state in the developed composite materials showed a ten times increase.

The mechanisms of charge relaxation in the samples were determined (intrinsic conductivity for the samples with HA and PA, dispersion transport for the PLA + VGCF samples); the mechanical properties of the film samples were investigated. Based on the obtained results, the chosen samples are seen to have suitable properties for their use in active packaging and can be recommended for practical testing.

Conflict of Interest

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

Author Contributions

Andrey A. Pavlov, Almaz M. Kamalov and Margarita E. Borisova developed the concept, conducted the study, wrote the original draft and managed the project.

Konstantin V. Malafeev and Vladimir V. Yudin conducted the study, reviewed and edited the article.

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