Conference materials
UDC 620.22
DOI: https://doi.org/10.18721/JPM.163.234

Charge relaxation after exposure to barrier and corona discharge of polylactide films

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Abstract. In this work, it is shown that the effect of a corona discharge and a dielectric barrier discharge differs in depth of charge penetration and relaxation time. The relaxation time and the mechanism of charge relaxation in polylactide films were determined using thermally stimulated depolarization current (TSDC). Experimental data are analyzed based on modern ideas about the mechanism of charge relaxation. The activation energies are calculated based on a model that considers the intrinsic conductivity of the dielectric. By the method of computer modeling, the complex TSDC spectra are decomposed into separate elementary maxima, which are described by first-order kinetics, and the activation energies corresponding to them are determined.

Keywords: polylactide, relaxation, charge, plasma, film

Funding: Grant for young scientists the Ministry of Education and Science Russia MK-4346.2022.4.

Citation: Kamalov A.M., Borisova M.E., Charge relaxation after exposure to barrier and corona discharge of polylactide films, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 200–205. DOI: https://doi.org/10.18721/JPM.163.234

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Материалы конференции
УДК 620.22
DOI: https://doi.org/10.18721/JPM.163.234

Релаксация заряда после воздействия барьерного и коронного разрядов на полилактидные пленки

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Аннотация. В этой работе показано, что воздействие коронного разряда и разряда с диэлектрическим барьером различается по глубине проникновения заряда и времени релаксации. Экспериментальные данные проанализированы на основе современных представлений о механизме релаксации заряда.

Ключевые слова: полилактид, релаксация, заряд, плазма, пленка_

Финансирование: Работа выполнена в рамках гранта для молодых ученых при Министерстве науки и высшего образования РФ МК4346.2022.4-.

Ссылка при цитировании: Камалов А.М., Борисова М.Э. Релаксация заряда после воздействия барьерного и коронного разрядов на полилактидные пленки // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 200–205. DOI: https://doi.org/10.18721/JPM.163.234

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Introduction

Environmental, economic, and safety issues have initiated the work of scientists and manufacturers dealing with packaging problems to partially replace petrochemical-based polymers with biodegradable polymers.

It is known that under the influence of an electric field, the activity of microbial cells decreases, and consequently, metabolic processes slow down. In this regard several studies have been carried out, which confirmed that the polymer film, which has undergone preliminary electric charge, significantly increases the shelf life of various food products [1].

To modify polymer films, different forms of gas discharge are used: Townsend [2], barrier [3], sliding and corona. Corona discharge and barrier discharge at atmospheric pressure in the air are the most common methods of activation (charging) of dielectric materials [4].

Atmospheric pressure plasma can be created using an alternating electric field source from ultra-low to ultra-high frequencies. An increase in the frequency of discharge repetition leads to a more uniform modification of the polymer film surface.

The nature of the ions coming from the corona discharge at a constant electric field in the air to the surface of the dielectric is determined by the polarity of the corona electrode. The main ions to be considered in the reactive non-thermal plasma of dry air include cations $O_2^{+\cdot}$, $N_2^{+\cdot}$, O^+, N^+, NO^+ and anions $O^{-\cdot}$, $O_2^{-\cdot}$ $O_3^{-\cdot}$ [5]. The average kinetic energy of ions in the corona discharge coming to the surface of the film can reach values of 0.01–0.1eV [6]. When ions interact with the polymer surface, charging is carried out due to ion-electron emission (Auger neutralization).

Charges that are fixed in the near-surface region or in the volume of the dielectric are captured at energy levels (traps) located in the forbidden zone. In polymers, the existence of a set of many discrete capture levels with different 'depths' is assumed. Dielectric materials have either a purely amorphous or partially crystalline structure. The heterogeneity of the structure in these materials leads to an increase in many years.

The energy distribution of traps depends on the degree of ordering of the polymer structure, the lower the ordering, the more capture levels with high activation energy are formed.

The appearance of traps in the volume is due to the presence of defects and impurities in the polymer. Defects can be associated with the irregularity of the chain, the appearance of the boundaries of the amorphous and crystalline phase.

The accumulation of charge at the interface of phases with different values of conductivity and permittivity may be due to the Maxwell-Wagner-Sillars polarization. These boundaries can appear at the junction of the near-surface layer and the volume of the polymer, as well as between amorphous and crystalline phases.

The purpose of this work is to study the relaxation of the charge accumulated under the action of corona and barrier discharges in polylactide films. Determine the effective depth of the charge accumulated under the action of various discharges.

Materials and Methods

The objects of this study are samples of polylactide films, which thickness was 25±5 μm.

A dielectric barrier discharge (DBD) was created in an ionization cell, which consists of ceramic plates with electrodes divided by an air gap (1 mm thick). The method of DBD film surface treatment was shown in the previous work [7]. The PLA film was charged in DBD for 2 minutes at a voltage of 3 kV with a frequency of 25 kHz.

Corona discharge method allows to produce electrets with homocharge. The sample is placed on a ground electrode, the other electrode is a needle with a negative potential. A metal grid is placed between the needle and the sample. Biased by a negative potential supply, the grid limits the maximum voltage on the sample. The charging process ends with the potentials of the grid and the surface of the sample becoming equal [8]. The PLA film was charged in a corona discharge for 1 minute, there was a voltage of −6 kV on the corona electrode and −400V on the grid. The charging level is regulated by the grid potential.

To determine the electret potential difference, a compensation method with a vibrating electrode was used. The electret potential difference for the PLA film charged in DBD was −200V, and for the film charged in corona discharge −400V.

Charge relaxation processes were studied by the method of thermally stimulated depolarization current (TSDC) under heating of samples at a constant rate of 2 K/min. The TSDC was measured

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in an open circuit, as provided by an insulating layer of PTFE film 40 μm thick arranged between the charged film and the electrode.

Results and Discussion

When charging in a gas discharge, a homocharge will accumulate in the glassy state of the polylactide. The effect of the polylactide charging method on the relaxation of the homocharge has been studied by thermal activation spectroscopy. The spectra of TSDC are shown in Fig. 1.

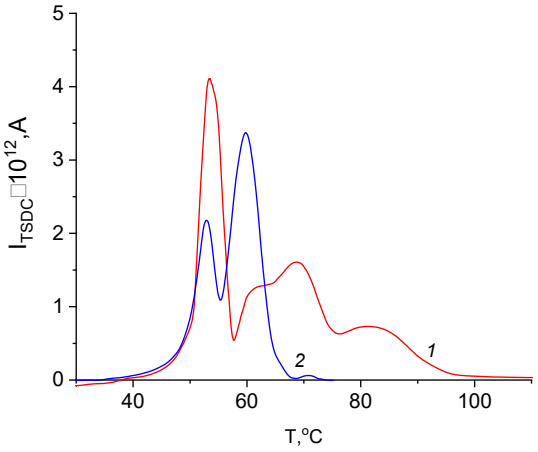

Fig. 1. TSD current for PLA film after: corona discharge (*1*), barrier discharge (*2*)

As can be seen from Fig. 1 (Curve *1*), three relaxation maxima are observed on the TSD spectrum for a PLA film pre-charged in a corona discharge. The position of the first (anomalous) sharp peak at 54 °C corresponds to the beginning of the transition process from a glassy state to a highly elastic one. The glass transition temperature T_g of polylactide is 50–60 °C [9], T_g determines the defrosting of the segmental mobility of the polymer. It can be assumed that the low-temperature peak is due to the relaxation of the homocharge in the region of the glass transition temperature. A similar result was obtained in the work [10].

The second (67 °C) and third (82 °C) peaks on the TSD spectrum can be associated with various relaxation processes. The main mechanisms of relaxation of the homocharge can be carried out either by releasing charge carriers from traps, or due to the intrinsic conductivity of the polymer.

The spectrum of the TSD current of a film charged in a barrier discharge is shown in Fig. 1 (Curve *2*). The spectrum has 2 distinct relaxation maxima in the region of 53 °C and 60 °C. Similarly, the low-temperature peak is caused by the relaxation of the homocharge in the region of the glass transition temperature of the PLA. To determine the mechanism of charge relaxation in polylactide films in high-temperature peaks, it is necessary to carry out a mathematical calculation of activation energies and relaxation times.

Mathematical analysis

The theoretical analysis of the TSDC spectra is based on the 'fitting method'. The calculated spectrum of TSDC is compared with the experimentally measured by varying three parameters, J_m, T_m, W. Complex curves of TSDC can be analyzed using the sum of discrete elementary Debye maxima $\Sigma n_{1,2,3} J_k$, described by first-order kinetics [11]. The current density of the TSDC J_{TSD} can be described by the expression

$$J_{TSD} = \frac{d\sigma_{ind}}{dt} = J_m \exp\left[\frac{W}{k}\left(\frac{1}{T_m} - \frac{1}{T}\right)\right] \exp\left\langle -\frac{W}{kT_m^2}\int_{T_m}^{T} \exp\left[\frac{W}{k}\left(\frac{1}{T_m} - \frac{1}{T'}\right)\right] dT' \right\rangle. \quad (1)$$

Current density value J_m by T_m:

$$J_m = \frac{\varepsilon\varepsilon_0\varepsilon_{lay}U_{e0}}{\left(\varepsilon h_{lay} + \varepsilon_{lay}h\right)}\exp\left\{-\frac{W}{kT_m^2}\int_{T_0}^{T_m}\exp\left[\frac{W}{k}\left(\frac{1}{T_m}-\frac{1}{T'}\right)\right]dT'\right\}, \quad (2)$$

where ε_{lay}, h_{lay} are the dielectric constant and thickness of gasket; k is the Boltzmann coefficient; T_0, T' are the initial and current temperature; T_m is the maximum current density temperature J_m; ε, h are the dielectric constant and thickness of experimental film; U_{e0} is the initial value of electret potential difference; τ_m is the relaxation time at maximum temperature, ε_0 is the permittivity.

The relaxation time is expressed as

$$\tau = \tau_m \exp\left(\frac{W}{kT} - \frac{W}{kT_m}\right). \quad (3)$$

Temperature dependence U_e expressed:

$$U_e(t) = U_e(0)\exp\left(-\int_0^{\infty}\frac{dt}{\tau_e}\right). \quad (4)$$

The theoretical calculation of the TSD current spectra was carried out based on the values of the current density J_m at the maximum and the temperature of the maximum T_m, determined from the experimental spectra of the TSD currents. In this case, the value of the activation energy W varies. Activation energies and relaxation times were calculated from ratio 4, which are presented in Table 1.

High values of activation energies may indicate the inapplicability of the Debye model in the field of defrosting of segmental mobility of polylactide. In the region of the glass transition temperature, there is a sharp increase in electrical conductivity, which causes an increase in the TSDC in this region.

The spectra of films pre-charged in corona discharge and DBD were measured by the method of TSDC in a closed circuit. The experimental data presented (Fig. 2) confirm the fact that the specific conductivity of the inner layers of the film is lower than the conductivity of the near-surface layers.

According to the TSD current curves (Fig. 2) measured at close contact, the effective depth δ of charge localization was calculated by the ratio based on the model of a three-layer electret [12]:

$$\delta = h\left[1 + \frac{\varepsilon\varepsilon_0 U_E S}{Qh}\right]^{-1},$$

where $h = h_1 + \delta$ is the film thickness, ε is the its dielectric constant, U_E is the initial value of the electret potential difference, Q is the charge calculated from the TSDC curve by integrating.

Table 1

Calculation parameters TSDC

Calculated maxima	$J_m \cdot 10^{-8}$, A/m^2	T_m, K	W, eV	τ_m,s
Corona charging				
J_{11}	3.3	327	9.5	30
$J_{12.}$	0.7	340	2.0	110
J_{13}	0.35	355	1.2	301
DBD charging				
J_{21}	0.9	326	7.0	346
J_{22}	1.8	333	4.0	97

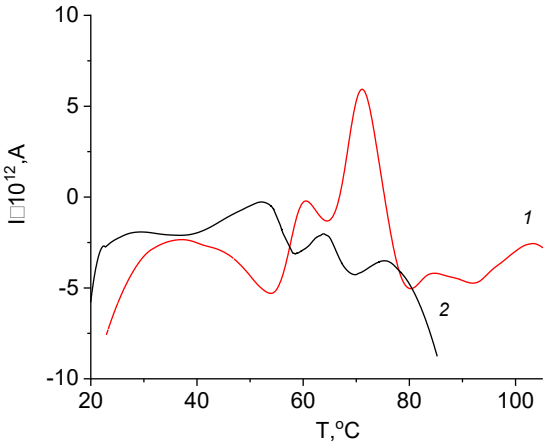

Fig. 2. TSDC at short circuit contact for PLA films charged in corona discharge (*1*) and DBD (*2*)

As a result of the calculations carried out, it was found that the value of δ depends on the method of charging polylactide films. The effective depth of the charge after treatment in the corona discharge is 1.5 ± 0.1 microns, and after charging in the dielectric barrier discharge 2.7 ± 0.2 microns.

Conclusion

It has been demonstrated that when polylactide films are charged at room conditions at atmospheric pressure, a homocharge accumulates in the corona and barrier discharge. Using the method of TSDC in the open circuit mode, it was found that the relaxation of the homocharge in the region of the glass transition temperature of the polylactide is due to the defrosting of segmental mobility (an increase in electrical conductivity). Likely the remaining peaks are associated with the release of the homo charge from the traps. When measuring the TSDC in an open and closed circuit, the currents have the opposite direction, therefore, the specific conductivity of the inner layers of the film is lower than the conductivity of the surface layers of the film. Using a three-layer dielectric model, the depth of the charge after exposure to corona and barrier discharge was calculated. The effective depth of the charge after treatment in the corona discharge is 1.5 ± 0.1 microns, and after charging in the dielectric barrier discharge 2.7 ± 0.2 microns.

However, it should be noted that under the action of a corona discharge in the presence of a grid, the polymer film is charged, while the action of the DBD in an alternating electric field leads to the processes of polymer destruction and its simultaneous charging, which is indirectly confirmed by the spectra of TSDC.

Acknowledgments

Grant for young scientists the Ministry of Education and Science Russia MK-4346.2022.4.

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Received 01.07.2023. Approved after reviewing 03.08.2023. Accepted 03.08.2023.

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