Investigation of the electret properties of PDLA/PEC porous composite films

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In the present paper the influence of both time and low pressure on the surface potential decay of porous composite films of poly(D-lactic acid) and poly(ε-caprolactone) was investigated. The samples were charged in a corona discharge by means of a corona triode system under room conditions. Positive or negative voltage was applied to the corona electrode and voltage of the same polarity as that of the corona electrode was applied to the grid. After charging, the initial surface potential was measured using the method of the vibrating electrode with compensation. Two groups of tests were performed. In the first group, after charging, the electrets were placed into a vacuum chamber where the pressure was reduced step by step in the range from 1000 mbar to 0.1 mbar. At each step the samples were stored for 1 minute. After that the electrets were removed from the vacuum chamber, their surface potential was measured again and the normalized surface potential was calculated. The influence of low pressure was analyzed by the equation that describes processes of desorption from the electret's surface. In the second group, after charging, the electret surface potential was measured by the time of storage. The possible surface potential decay mechanisms responsible for the electret's behavior were discussed. It was established that the surface potential decay depends on both corona polarity and type of films. It was shown that the samples charged in a positive corona are more stable than those charged in a negative corona.

Keywords: corona discharge, porous composite films

INTRODUCTION

Over the last two decades, biodegradable polymers, such as poly(lactic acid) PLA, poly(glycolic acid) PGA and poly(ε-caprolactone) PEC, belonging to the family of poly(a-hydroxyesters), have emerged as a class of biomaterials of growing interest for application in surgery, drug delivery, tissue engineering, food industry, etc. [1, 2]. Polymer blending of two different kinds of biopolymers in different ratios has been demonstrated to improve the film properties, when compared to pure films [3, 4]. Different modification methods such as corona discharge treatment and lyophilizing [5-7] can further improve biocompatibility and assist in the creation of stable porous structures. In order to obtain stable electrets for different applications the influence of different factors as time of storage, temperature, humidity, low pressure, etc., on the charge decay has been studied [8]. In this paper the influence of time of storage and low pressure on the surface potential decay of porous composite films PDLA/PEC was investigated.

MATERIALS AND METHODS

Sample preparation

In the present paper two biodegradable polymers were used. Poly(D-lactic acid) (PDLA) was purchased from Sigma-Aldrich and poly(ε-caprolactone) (PEC) from Lactel Absorbable Polymers (USA). Both polymers were dissolved in 1,4 dioxane at 10 % w/v and the resulting solutions were used for the creation of a mixture at the desired mass ratio of 50/50. Additionally, two further films of pure PDLA and PEC with the same polymer concentrations were also created. All solutions were placed in Petri dishes in a freezer at -16 °C until completely frozen. After that the frozen solution was placed in a lyophilizer for 3 days and dried until the solvent evaporates. The obtained films were kept for 24 hours in a desiccator at room temperature and relative humidity.

Corona charging and surface potential measurement

Samples with 30 mm diameter were cut from the composite films. The charging of the samples in a corona discharge was carried out by means of a conventional corona triode system consisting of a corona electrode (needle), a grounded plate electrode and a grid placed between them. The samples were charged under room conditions for 1 minute. Positive or negative 5 kV voltage was applied to the corona electrode. Voltages of 1 kV of the same polarity as that of the corona electrode were applied to the grid. The electrets surface potential of the charged samples was measured by the vibrating electrode method with compensation and the estimated error was less than 5%. The

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normalized surface potentials V/V_0 were calculated, as the value V_0 is the initial surface potential measured about 1 minute just after charging the electrets.

Low-pressure measurement

After charging to the initial surface potential V_0, the samples were placed into a vacuum chamber, consisting of isolated bases and a jar bell, at low pressure. The pressures created in the vacuum chamber were 0.1 mbar, 1 mbar, 5 mbar, 10 mbar, 20 mbar, 40 mbar, 66 mbar, 120 mbar, 250 mbar, 500 mbar, 750 mbar and 1000 mbar. The pressure in the vacuum chamber was reduced step by step in the range from 1000 mbar to 0.1 mbar. At each step the samples were kept at the respective constant pressure for 1 minute. After that the electrets were removed from the vacuum chamber, the surface potential V was measured again and the normalized surface potential V/V_0 was calculated.

Differential scanning calorimetry (DSC)

A method of differential scanning calorimetry was applied for determining the phase state of the samples. The measurements were carried out with DSC 204F1 Phoenix (Netzsch Gerätebau GmbH, Germany) which was calibrated with an indium standard (T_m=156.6 ºC, ΔH_m=28.5 J/g). About 5 mg of the films were placed and sealed in an aluminium pan. An identical empty pan was used as a reference. The measurements were performed in argon atmosphere in the temperature range from 20 °C to 250 °C at a heating rate of 10 °C/min. The DSC thermograms were analysed by Netzsch Proteus – Thermal Analysis software.

The degrees of crystallinity for PEC (χ_{PEC}) and PDLA (χ_{PDLA}) compounds in the films were calculated based on the equation:

$$\chi_{PEC/PDLA} = \frac{\Delta H_m(PEC/PDLA)}{\Delta H_m^0(PEC/PDLA) \cdot \omega_{PEC/PDLA}} \cdot 100 \quad (1)$$

where $\Delta H_m(PEC/PDLA)$ is the specific melting enthalpy [J.g^{-1}] of the PEC or PDLA; ΔH_m^0 is the melting enthalpy of 100 % crystalline polymer ($\Delta H_m^0 = 139.3$ J.g^{-1} for PEC [9]) and $\Delta H_m^0 = 106.0$ J.g^{-1} for PDLA [10], and $\omega_{PEC/PDLA}$ is the mass fraction of PEC/PDLA, respectively.

The total crystallinity was calculated according to equation (2):

$$\chi = \omega_{PEC}\chi_{PEC} + \omega_{PDLA}\chi_{PDLA} \quad (2)$$

RESULTS AND DISCUSSION

According to the experimentally obtained thermograms, the melting transitions of the two components in the mixed films take place at temperatures of 67 °C and 155 °C, which are the melting temperatures of the pure substances. This observation indicated that PEC and PDLA were not miscible at molecular level. Similar results were reported by other authors [11].

The degrees of crystallinity of PEC and PDLA, and the total degree of crystallinity of the composite films are presented in Figure 1.

Based on the findings presented in Figure 1, it is evident that introducing PDLA into PEC leads to an augmentation in crystallinity. Likewise, the incorporation of PEC into PDLA has a similar, albeit more pronounced, impact on elevating crystallinity. Consequently, one could speculate that the introduction of inhomogeneities and the existence of two phases within the mixtures result in a nucleation effect and contribute to the heightened degree of crystallinity. The total crystallinity of the films decreases when the content of PDLA increases.
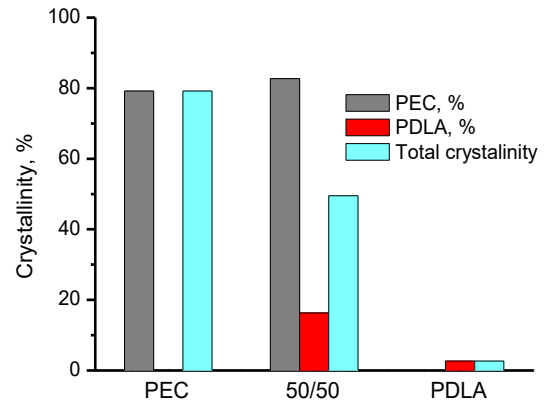

Figure 1. Degrees of crystallinity of PDLA/PEC films.

Time storage influence on the electrets surface potential decay

The normalized surface potential (dependence) on the storage time for positively and negatively charged PDLA, 50/50 and PEC electrets was studied for 6 hours. The surface potential was measured once every 5 minutes for the first 30 minutes, during which the charge was rapidly decaying. After this period, the surface potential was measured more rarely, with the steady-state values of the normalized surface potential (6 hours) stabilizing for all investigated electrets. The steady-state values of the surface potential for PDLA, 50/50 and PEC electrets are presented in Figure 2.
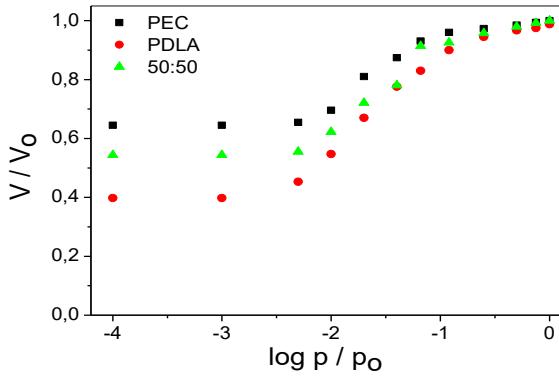
Figure 2. The steady-state values of the normalized surface potential at a time of 6 hours for all investigated electrets.

The obtained experimental results demonstrate the following features:

✓ The steady state values of the normalized surface potential for the samples charged in a positive corona are higher than those for the samples charged in a negative corona for all investigated samples. This was observed earlier in [12].

✓ The steady state values of the normalized surface potential are highest for the PEC electrets irrespective of the corona polarity.

This is probably due to the different degrees of crystallinity, determined by DSC method (see Figure 1).

Low-pressure influence on the electrets surface potential decay

The dependences of the normalized surface potential V/V_0 on the low pressure for positively and negatively charged PDLA, 50/50 and PEC films were investigated. The dependences are presented in Figures 3 and 4.
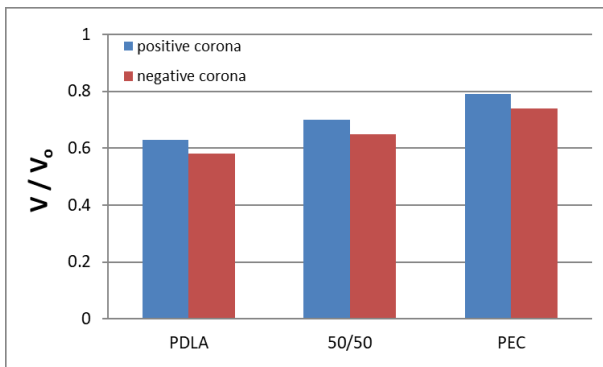

Figure 3. The normalized surface potential dependences on the normalized pressure for positively charged porous composite electrets.

In Figures 3 and 4 the symbol p_0 marks the atmospheric pressure and p is the pressure created in the vacuum chamber. Each point in the figures is a mean value of 5 samples. The calculated standard deviation was 5 % better than the mean value with confidence level 95 %.
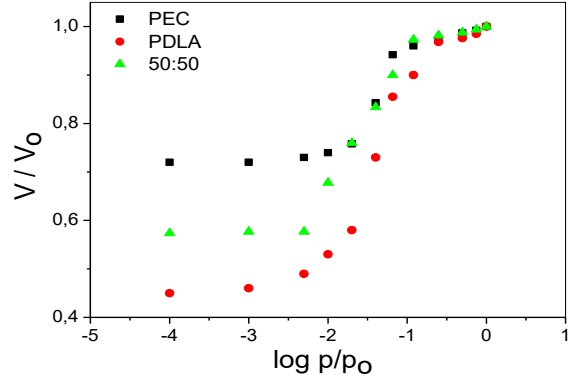

Figure 4. The normalized surface potential dependences on the normalized pressure for negatively charged porous composite electrets.

Table 1. The steady-state values of the normalized surface potential at a pressure of 0.1 mbar for all investigated electrets.

Samples	V/V_0	
	Positive corona	Negative corona
PDLA	0.45	0.4
50/50	0.57	0.54
PEC	0.72	0.65

The results presented in Figures 3 and 4 and Table 1 show that:

✓ Each curve consists of three parts. Similar behavior has also been observed in [13].

✓ The steady-state values of the normalized surface potential at a pressure of 0.1 mbar for the samples charged in a positive corona are higher than those for the samples charged in a negative corona independently of the sample type.

✓ The steady-state values of the normalized surface potential at a pressure of 0.1 mbar are highest for PEC samples independently of the corona polarity. We assume that this is due to the different structures of the polymers, which leads to the formation of different localized surface states that capture charges.

Table 2. Values of the parameters *a*, *b*, *c* and *d* obtained by fitting data to the equation 3.

Samples	Positive corona				Negative corona			
	a	*b*	*c*	*d*	*a*	*b*	*c*	*d*
PDLA	0.46± 0.02	0.53± 0.02	-1.42± 0.02	0.45± 0.02	0.39± 0.01	0.59± 0.01	-1.62± 0.01	0.61± 0.01
50/50	0.57± 0.02	0.43± 0.02	-1.60± 0.02	0.51± 0.02	0.54± 0.02	0.45± 0.02	-1.53± 0.02	0.51± 0.02
PEC	0.73± 0.01	0.26± 0.01	-1.38± 0.01	0.27± 0.01	0.64± 0.01	0.35± 0.01	-1.62± 0.01	0.45± 0.01

The results presented in Figures 3 and 4 were analyzed by the equation that describes the processes of desorption from the electrets surface accompanied with surface diffusion. This equation was earlier described in [14].

$$\theta = a + \frac{1}{2}b\left(1 + erf\left(\frac{x-c}{\sqrt{2}d}\right)\right) \qquad (3)$$

where $\theta = V/V_0$ is the normalized surface potential, $x = \log(p/p_0)$ and *a*, *b*, *c* and *d* are parameters. The parameter values for all investigated samples were obtained by fitting and they are presented in Table 2.

If one knows the initial surface potential value of different porous composite electrets, the data obtained for the parameters could be used to determine the pressure range in which the potential sharp decay is occurring. This has a practical benefit because of the fact that these composite films can be used under conditions of reduced pressures.

CONCLUSION

In this study the influence of different factors on the surface potential decay of porous composite films PDLA/PEC was investigated. It was established that the steady-state values of the normalized surface potential for PEC electrets are the highest compared to other investigated samples. This may be due to the highest value of the degree of crystallinity determined by the DSC method. It was also established that the low-pressure curves consist of three parts and these curves were analyzed by the equation that describes the processes of desorption from the electrets surface accompanied with surface diffusion. The results show that the obtained porous composite films PDLA/PEC possess excellent electret properties.

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