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Study of polylactic acid corona electrets

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Electret and surface properties of the PLA film treated in a negative or a positive corona discharge at two different temperatures were studied. Vibrating electrode method with compensation was used to measure the electret surface potential value. The changes in the surface free energy were investigated by means of contact angle measurements. The Bickerman's method was applied to determine the polar and dispersion components of the polymer surface free energy, FTIR-spectroscopy was used to analyze the polymer functional groups content. It was found that in all cases the corona treatment increases the polar component of surface free energy of polylactic acid. The effects of negative and positive corona polarities display some specific features which could be associated with different charged group introduced into the film during the corona treatment. The total final effect depends on the simultaneous action of the two competing factors – temperature and corona polarity. The most pronounced effect was observed for high temperature negative corona treatment.

Key words: electret, corona discharge, polylactic acid, surface free energy

INTRODUCTION

Electrets are dielectrics that possess excess or distributed charge and create constant electric field. They have found various applications in different industries. To manufacture electrets synthetic polymers are commonly used [1–3]. However, nowadays there is a demand in new advanced materials for their manufacturing since industrial polymers have long decomposition period resulted in increase of polymer wastes and environmental pollution [4, 5]. One of the solutions is application of biodegradable polymers e.g. polylactic acid (PLA) derived from renewable resources [6, 7].

One of the most popular techniques to produce electrets is polymer polarization in a corona discharge. Its advantages include high process rate and simple instrumentation. During unipolar corona discharge injection of charge carriers (electrons, ions) occurs into dielectric where these charge carriers are held by surface or volume traps.

Therefore, the objective of the paper was to produce film material based on PLA and study its electrets properties.

MATERIALS AND METHODS

The subject of research was L-polylactic acid (PLA) (Direct Corporation Lot # 902-57-1 with density 1.25 g/cm^3 and glass transition temperature 327 K (54°C)).

PLA films were solvent-casted using trichlormethane. The films thickness was about 5-10 μm measured by electronic micrometer Micromaster IP54, TESA SA, Switzerland.

The corona charging of the samples was carried out by the method of the negative and positive corona discharge shown in Figure 1. The distance between the grounded plate electrode and the grid was 10 mm, the distance from the grid to the corona electrode was 7 mm. The samples were divided in two groups.

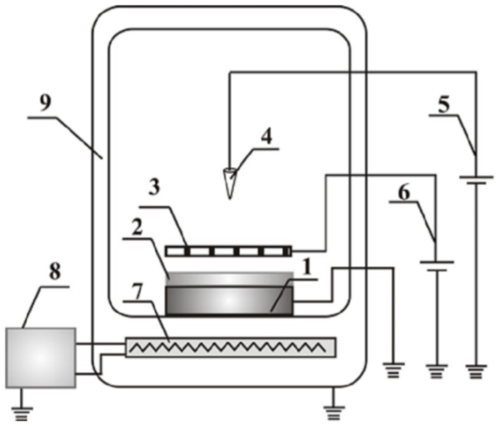

Fig. 1. Experimental set-up for corona treatment: 1 – grounded electrode; 2 – sample; 3 – grid; 4 – corona electrode (needle); 5 – corona electrode power supply; 6 – grid power supply; 7 – heating element; 8 – thermocontrol system; 9 – thermochamber

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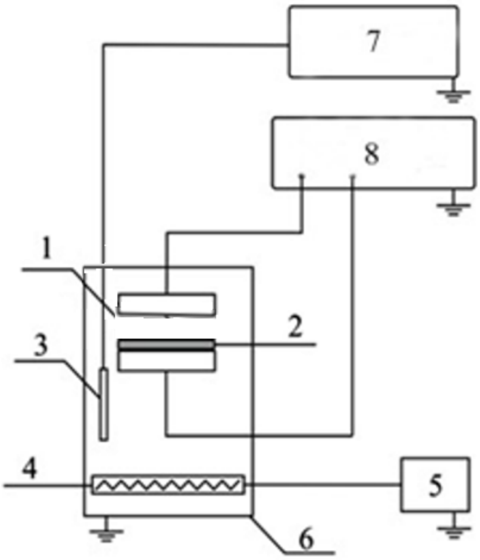

Fig. 2. Thermally stimulated surface potential relaxation measuring unit: 1 – upper vibrating electrode; 2 – sample; 3 – thermal couple; 4 – heating element; 5 – power suply with temperature control; 6 – thermochamber; 7 – digital multimeter; 8 – surface potential meter.

The samples of the first group were placed on the grounded plate electrode and were charged for 3 min at temperature 25ºC. Another group of samples was heated up to 90ºC, charged for 3 min at temperature 90ºC and then cooled to 25ºC in corona discharged for 30 minutes. Positive or negative 5 kV voltage was applied to the corona electrode. 1 kV voltage of the same polarity as that of the corona electrode was applied to the grid.

The surface potential values were measured using a vibrating electrode method with compensation. The estimated error was less than 5%. Thermally stimulated surface potential relaxation was measured by vibrating electrode method at constant heating rate of 1.65 degree/min. Figure 2 illustrates unit for measuring thermally stimulated surface potential relaxation.

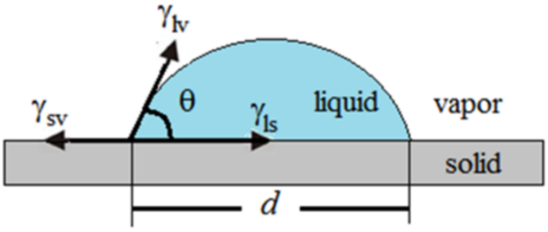

Fig. 3. Scheme of the surface energy: γ_{sv} at solid-vapor interface, γ_{ls} at liquid-solid interface, and γ_{lv} at liquid-vapor interface; θ is the contact angle; *d* is the drop diameter

Contact angle formation between a liquid drop and solid surface is presented in Fig. 3. The contact angle depends on the energies at the interfaces: solid-liquid (sl), solid-vapor (sv), and liquid-vapor (lv). The symbols γ with two indices describe the surface energy between the two phases in contact.

Following the theory of Owens and Wendt [8], and Kaelble and Uy [9], the surface free energy of a solid, γ_s, can be expressed as a sum of contributions from γ_s^d and “γ_s^p components. Both can be determined from the contact angle data of polar and non-polar liquids with known dispersion, γ_{lv}^d, and polar, γ_{lv}^p, parts of their interfacial energy:

$$\gamma_{lv}(1+\cos\theta) = 2\sqrt{\gamma_s^d\gamma_{lv}^d} + 2\sqrt{\gamma_s^p\gamma_{lv}^p} \qquad (1)$$

where $\gamma_{lv} = \gamma_{lv}^d + \gamma_{lv}^p$.

To measure the contact angle, θ, distilled water and diiodomethane drops with varying volume were inserted onto the solid PLA film surface, at room temperature, using a precise 10 μl micro syringe (Innovative Labor System GmbH, Germany) supplied with steel needle. The drop volume was from 2 μl to 6 μl. The drop diameters were measured with optical microscope (MBC-9, USSR) provided with a micrometer scale eyepiece (Fig. 4). For each drop volume, and each testing liquid, 5 measurements were performed at different places onto the sample surface. The same procedure was repeated with six different samples. The final value of the contact angle is the mean value of the six samples measurements. The estimated error was less than 5%.

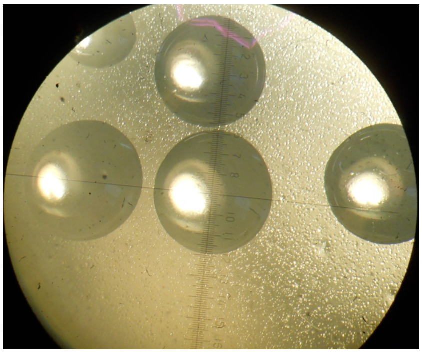

Fig. 4. Microscope drop image.

Bickerman's method [10, 11], in which the effect of gravity distortion is negligible and the drop may be considered as a segment of a sphere, was applied to derive the contact angle:

$$\frac{d^3}{V} = \frac{24\sin^3\theta}{\pi(2-3\cos\theta+\cos^3\theta)} \qquad (2)$$

where V is the drop volume, and d is the drop diameter.

RESULTS AND DISCUSSION

Charge behavior of PLA-based electrets produced at various polarization conditions is shown in Fig. 5.

Electrets properties depend on quantity of injected charges penetrating into the material during polarization in corona discharge and fixed to different energy traps. Initial sharp decay of the surface potential curve occurs due to escape of injected charge from small surface energy traps. Then charge stabilizes and surface potential changes slightly. Charge value in this case is determined by injected charge carriers captured by volume traps. Therefore, polylactic acid polar groups promote trapping of injected charge carriers by small surface energy traps resulting in rapid charge decay of corona electrets.

Differences in electret properties of negative- and positive-charged films are due to different nature of injected charge carriers that are formed during air ionization. According to [3], if positive corona occurs in air, the prevailing ions are of the type $(H_2O)_nH$ and n enhances with increasing relative humidity. In the case of low relative humidity values, the $(H_2O)_nNO^+$ and $(H_2O)_n(NO2)^+$ groups are dominant. If negative corona occurs in air, the most important ions are the CO_3^- ions, while at 50% relative humidity, 10% of all ions are of the type $(H_2O)_nCO_3^-$. In case of polar PLA films the most stable values of surface potential were observed for negatively charged electrets.

One can see (Fig. 5) that PLA electrets charged in negative corona discharge at 90°C performed the most stable surface potential values. At other polarization conditions, significant charge relaxation occurs in as little as 5 hours after polarization.

Higher surface potential values of the PLA corona electrets charged at 90°C compared to ones charged at room temperature were expected since initial heating is known [1,12] to enhance electrets stability. The reason for this is that charge carriers penetrate deeper into the bulk of a polymer due to greater chain mobility leading to increased electric conductivity.

More information on corona electret charge stability was obtained by the method of thermally stimulated surface potential relaxation. It includes measuring electrets surface potential during linear heating right after polarization. Figure 6 shows thermally stimulated surface potential relaxation curves for the samples positively and negatively charged at room temperature.

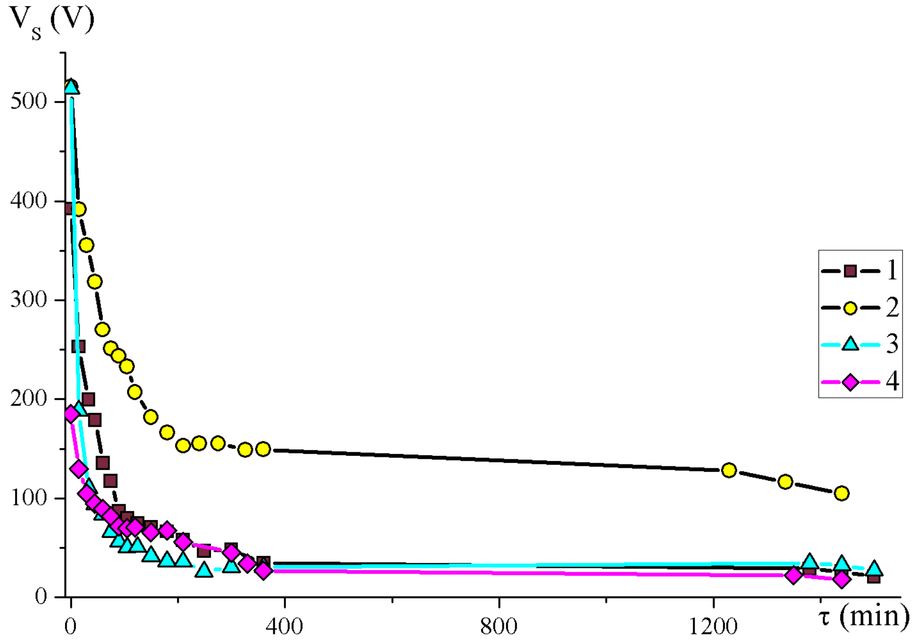

Fig. 5. Surface potential of PLA films vs. storage time: 1 – negatively charged at 25°C, 2 – negatively charged at 90°C, 3 – positively charged at 25°C, 4 – positively charged at 90°C.

Heating above 25°C was shown to cause sharp surface potential decay. Complete relaxation occurred at 50°C. Almost identical curves of surface charge decay in negative- and positive-charged PLA films indicate similar charge carrier trap nature. Complete charge relaxation temperature in PLA is close to its glass transition temperature (50–55°C). It means that dipoles in PLA macromolecules act as charge traps. Rise in temperature above this point enables polymer dipole group to move freely resulting in disappearance of dipole-group or dipole-segment polarization. It is reported in [13, 14] that electrets effect in corona electrets based on polar polymers is caused by both external (injected charge) and internal (dipole-group) polarizations. Therefore, above PLA glass transition temperature ordered dipole system breaks down and injected charge escapes i.e. electrets state relaxation occurs (Fig. 6). Thus, it is inefficient to produce electrets based on pure PLA. To enhance stability and values of electret performances different modifications may be used, e.g., fine filler addition [13, 15, 16].

Surface properties are ones of the most important application performances of any polymer film (including electret). Distilled water and diiodomethane contact angles on PLA films and calculated data on surface energy and its dispersion and polar components are given in Table 1.

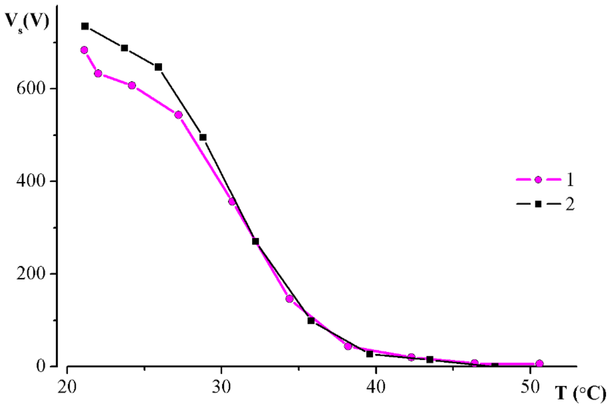

Fig. 6. Surface potential vs. Temperature for PLA electrets films negatively (1) and positively (2) charged when uniform heated at the rate of 1,65°?/min.

Polarization at room temperature increases polar and decreases dispersion component of the surface energy regardless of corona polarity (Fig. 3). It occurs due to formation of different oxygen containing groups on a polymer surface that contribute to surface energy polar component of the PLA films.

Temperature rise results in surface free energy increase of uncharged samples due to surface oxidation leading to increase in the amount of polar groups on the film surface. Meanwhile, surface free energy of electret samples reduces while the number of polar groups is grater compared to uncharged ones.

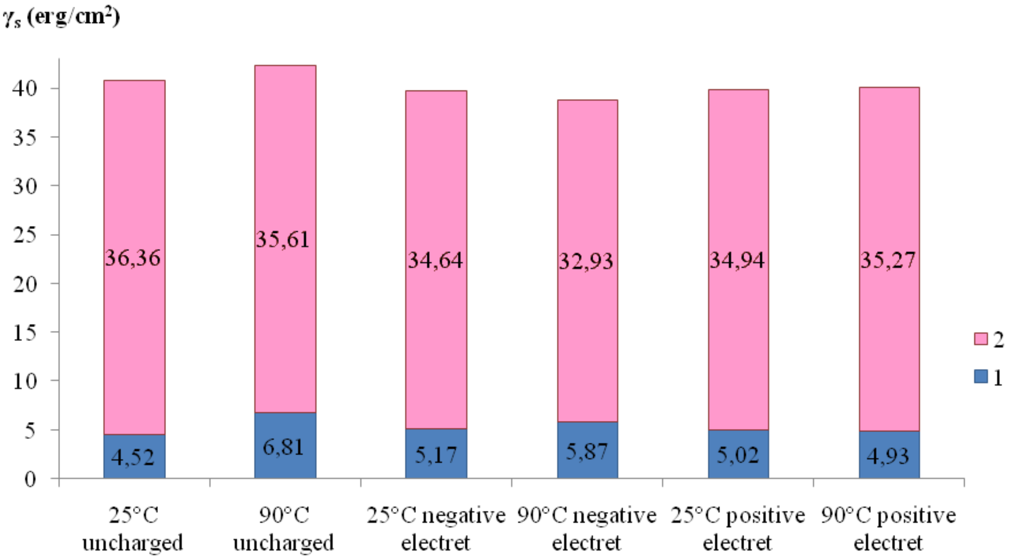

Fig. 7. Total surface energy of uncharged and electrets PLA films: 1 – polar component γ_s^p, erg/cm^2; 2 – dispersion component γ_s^d, erg/cm^2.

Table 1. PLA film surface properties

Film charge	T, °C	γ_s, erg/cm^2	γ_s^p, erg/cm^2	γ_s^d, erg/cm^2	Polarity	θ_{H_2O}	$\theta_{CH_2J_2}$
Uncharged	25	40.89	4.52	36.36	0.11	79,0° ± 0,6°	40,0° ± 0,6°
Uncharged	90	42.42	6.81	35.61	0.16	73,9° ± 0,3°	39,6° ± 1,3°
Negative	25	39.81	5.17	34.64	0.13	78,4° ± 0,6°	42,9° ± 0,8°
Negative	90	38.79	5.87	32.93	0.15	77,8° ± 1,0°	45,7° ± 0,6°
Positive	25	39.95	5.02	34.94	0.13	78,6° ± 0,7°	42,5° ± 0,4°
Positive	90	40.20	4.93	35.27	0.12	80,7° ± 0,7°	41,3° ± 1,3°

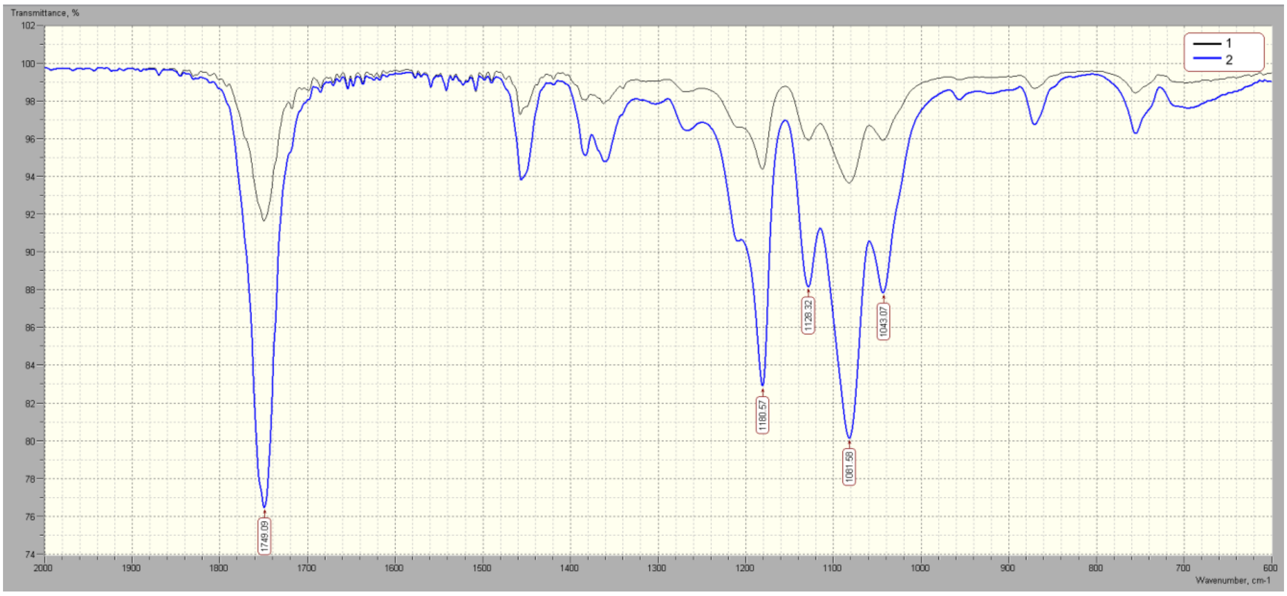

Fig. 8. Surface potential vs. Temperature for PLA electrets films negatively (1) and positively (2) charged when uniform heated at the rate of 1.65°C/min.

It is evidenced by transmittance peak intensity of the IR-spectra (Fig. 8) at 1749 cm $^{-1}$ corresponding to C=O stretch vibrations and at the range of 1200–1050 cm $^{-1}$ corresponding to C-C(O)-C stretching vibrations. It can be explained by the presence of the electrets surface charge that prevents drop spreading on the surface and thereby increasing contact angle.

CONCLUSIONS

Thus, optimal parameters to manufacture PLA electrets are negative corona discharge and initial heating at 90°C Injected charge carrier traps were shown to be dipole groups of PLA macromolecules oriented in corona discharge. When PLA electret sample is heated above glass transition temperature (about 50-55°C) complete charge relaxation occurs. Polarization at room temperature increases polar and decreases dispersion component of the surface free energy.

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ИЗСЛЕДВАНЕ НА КОРОНОЕЛЕКТРЕТИ ОТ ПОЛИМЛЕЧНА КИСЕЛИНА

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(Резюме)

Получаването на електрети на основата на полимлечна киселина привлича научния интерес, т.к. заменя синтетичните полимери, произведени от невъзобновяеми въглеводороди и оставя биоразграждащи се отпадъци без екологични вреди.

Изследвана е полимлечна киселина (ПМК) (Direct Corporation Lot #: 902-57-1). Филми с дебелина 10 µm са получени чрез изливане на 5% разтвор на ПМК в трихлорметан. Образците са зареждани в положителна и отрицателна корона с помощта на триелектродна система. Разстоянието между заземения електрод и решетката е 10 mm, а разстоянието между решетката и коронираща електрод е 7 mm. Част от образците се поставят на плоския заземен електрод и се зареждат 1 мин. Друга група образци се нагряват до 90°C, включва се полето на коронния разряд за 5 мин. и след това образците се охлаждат линейно в електричното поле за 30 мин. Положително или отрицателно напрежение 5 kV се подава на корониращия електрод. Напрежение 1 kV със същата полярност като на корониращия електрод се подава на решетката. Повърхностният потенциал на електретите се измерва по метода на вибриращия електрод с компенсация. Термично стимулираната релаксация на повърхностния потенциал се измерва по същия метод на вибриращия електрод при постоянна скорост на нагряване 1.65°/min.

Най-стабилен повърхностен потенциал е установен за филми от ПМК, отрицателно заредени при 90°C. При другите условия на зареждане е наблюдавана значителна релаксация на заряда за по-малко от 5 часа след поляризацията.

Електретните свойства на отрицателно и положително заредените филми се дължат на различния характер на инжектираните йони, които се образуват по време на коронния разряд. Съгласно [1], при положителна корона във въздух преобладаващите йони са от типа $(H_2O)_nH^+$ и n се увеличава с увеличаване на относителната влажност. При ниска относителната влажност групите $(H_2O)_nNO^+$ и $(H_2O)_n(NO_2)^+$ са доминиращи. При отрицателна корона във въздух най-важните йони са CO_3^-, а при 50% относителна влажност, 10% от всички йони са $(H_2O)_nCO_3^-$.

Повече информация за стабилността на електретния заряд е получена чрез метода на термично стимулираната релаксация на повърхностния потенциал. Установено беше, че нагряването над 25°C причинява рязко спадане на повърхностния потенциал, като пълна релаксация настъпва при 50°C. Наблюдаваните идентични експериментални криви за отрицателно и положително заредените филми от ПМК показват наличие на подобни носители на заряд, захванати в различни енергетични уловки. Температурата на пълна релаксация на заряда в ПМК е близка до температурата на встъкляване (50–55)°C. Това означава, че диполите в ПМК макромолекулите действат като захванати в уловки заряди.

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