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Electret and Dielectric Properties of Lyophilized Polymer Films

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Abstract. Polymer electrets are one of the most important types of electrets, which are widely used both in academic research and industrial applications. The effect of trapped charges on dielectric properties of the polymer electrets is crucial for more intelligent utilization of these materials. The aim of the present paper is to investigate the lyophilization effect on electret and dielectric properties of polymer films. The properties of one synthetic polymer (polystyrene – PS) and two biopolymers (polyactic acid – PDLA and poly-ε-caprolactone – PεC) were investigated and compared. The samples were analyzed by means of dielectric relaxation spectroscopy in the range of 20 Hz – 1 MHz using QuadTech 1910 Inductance Analyzer. The frequency dependences of the impedance magnitude and the phase angle were measured.

Regarding the electret properties, the samples were charged in a conventional three-electrode corona system. Positive and negative 5 kV voltage was applied to the corona electrode and 600 V voltage with the same polarity was applied to the grid as to the corona electrode. The results showed that the lyophilization increases time relaxation of the trapped charges. It was established that the samples charged in a positive corona are more stable than those charged in a negative corona.

1. Introduction
The increased industrial interest on the dielectric and electret properties of polymers reflects the increasing use of these materials in electronic devices, optoelectronic switches, printed circuit boards, microwave radar systems, batteries, fuel cells and many others. Polymer electrets are one of the most important types of dielectrics, which are widely used in scientific research and industrial applications. The effect of trapped charges on dielectric properties of the polymer electrets is important for more intelligent utilization of these materials. The electret properties of polymer dielectrics have been investigated in many literary sources [1-4].

In the recent years, the interest in the fundamental and the applied aspects of dielectric spectroscopy of polymer material has increased considerably since dielectric properties of the materials provide information on how the substance interact with electromagnetic energy. Detailed information of the basic aspects of the dielectric behavior of a polymeric materials can be found in many articles, books and reviews [5-9]. The information of these articles, however, refers almost exclusively to systems that do not change over time or are valid under certain conditions. The systematic studies with dielectric spectroscopy of systems with a time evolution of the structure have a more recent origin. The enormous potential of the dielectric spectroscopy of polymer materials is extensively motivated by G. Williams in [10]. The examples include testing systems that are chemically or physical changed as a result of chemical reaction, crystallization, phase separation, time, temperature and others.
The rapid development of modern technologies requires the research of new materials, polymer mixtures (blends) and composites based on polymer materials, design of dielectric materials and its modification at different voltages and temperatures.

The aim of the present paper is to investigate the lyophilization effect on electret and dielectric properties of different polymer films.

2. Experimental

2.1. Materials and samples preparation
Polystyrene (PS), polyactic acid (PDLA) and poly-ε-caprolactone (PeC) purchased from Lactel Absorbable Polymers (USA) were used for the preparation of different films. The two film types (non-lyophilized and lyophilized) were prepared in the following way: 1) non-lyophilized films of PS, PDLA and PeC – by 1 g polymer in 50 ml dioxane. The solution was poured in petri dishes and dried until the solvent evaporation; 2) lyophilized films of PS, PDLA and PeC – by dissolving of 1 g polymer in 50 ml dioxane. The solution was placed in a vacuum dryer at temperature -50 °C and dried until the total solvent evaporation. After that the obtained films were kept in an exicator at room temperatures and 0 % relative humidity (RH). After that two types samples of 30 mm diameter were cut from obtained films.

2.2. Corona charging and surface potential measurement
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 ground plate electrode and a grid placed between them. The distance between the corona electrode and the grid was 10 mm and the distance between the grid and the grounded plate electrode was 3 mm. The experimental setup is shown on figure 1. The samples were charged under room conditions (T = 21-23 °C and RH = 50-60 %) for 1 minute. Positive or negative 5 kV voltage was applied to the corona electrode. Voltage of 600 V of the same polarity as that of the corona electrode were applied to the grid. Introducing a grid between the corona electrode and sample limits the electret surface potential to that of the grid and produces a more uniform distribution of charge on the electret surface. 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 normalized surface potentials $V/V_0$ were calculated, as the value $V_0$ was the initial surface potential measured about 1 minute just after charging the electrets.

![Figure 1. Conventional three electrode system:](image)

1 – corona electrode (needle); 
2 – high voltage power supply; 
3 – voltage divider; 
4 – grid; 
5 – sample; 
6 – ground plate electrode.

2.3. Dielectric spectroscopy
The measurement of the impedance spectra – impedance magnitude and phase angle in the frequency range from 20 Hz up to 1 MHz was done using QuadTech 1910 Inductance Analyzer. The magnitude of the test signal was 1 V. The tested sample was placed between two flat electrodes fixed to a Teflon holder. A spring was used to ensure good contact between the electrodes and the sample and to
provide constant tension force. The system of the sample and the electrodes was placed in an insulated chamber.

3. Results and discussion

3.1. Time storage influence on electrets surface potential decay
The dependences of the normalized surface potentials on the storage time for positively and negatively charged PS, PDLA and PεC non-lyophilized and lyophilized films have been studied for 360 minutes. The surface potential was measured once for 2 minutes except for the first 10 minutes because the change was rapidly decaying. After the period of 360 minutes steady state values of the surface potential were established for all investigated samples. Time dependences of the normalized surface potential for positively and negatively charged PS, PDLA and PεC non-lyophilized films are presented in figure 2a and figure 2b respectively. Such dependences for positively and negatively charged PS, PDLA and PεC lyophilized films are presented in figure 3a and figure 3b, respectively. In figure 4 the steady state values (after 360 minutes) of the normalized surface potential for all investigated samples is presented. Each point in the figure is a mean value from 4 samples. The calculated standard deviation was better than 5 % from the mean value with confidence level 0.95.

Figure 2. Time dependences of the normalized surface potential for PS, PDLA and PεC non-lyophilized films.
The results presented in figure 2-4 show that:

- For all investigated samples the values of the normalized surface potential are initially decaying exponentially for the first 50 minutes and then are slowly decreasing and are practically stabilized to the 360th minute.

The values of the surface potential of electrets depends on the amount of trapped charges in the different localized surface states of the samples. In the initial period of time after the corona charging, the surface potential rapidly decreases due to the release of the weakly captured charges from the shallow energy states. Then the surface potential stabilizes to a steady state value caused by the tightly captured charges in the deep energy traps. A similar behavior of exponential decay in electrets is observed in [10].

- 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.

It was established in [11-13] that during the corona discharge in the air, at atmospheric pressure, different types of ions are deposited on a sample, since charging in a corona discharge depending on the corona polarity. In the case of a positive corona the ions are mainly $\text{H}^+ (\text{H}_2\text{O})_n$ and the ones for the negative corona – $\text{CO}_3^-$. Those ions are bound in traps of various depths and are released from them depending on the surrounding conditions.

- The values of the normalized surface potential of non-lyophilized films decay faster than those of the lyophilized independently of the corona polarity and the material type.

- The highest steady state values of the normalized surface potential and the best stability were observed for all investigated lyophilized films.

We assume that the lyophilization leads to the formation of porous structure and this significantly improves the ability to store charge and to a better stability with time. This was explained by investigating the morphology with scanning electron microscopy (SEM) in [14].

3.2. Dielectric spectroscopy

In figure 5, the frequency dependences of impedance magnitude $Z$ for one biopolymer PeC and one synthetic polymer PS samples are presented. In figure 5, the frequency dependences of phase angle $\phi$...
for the same two PeC and PS samples are presented. Since the uncertainty did not exceed 4 %, the confidence intervals are not presented in the figures.

Figure 5. Impedance magnitude dependences on frequencies of investigated polymers.

As it can be seen in figure 5 and figure 6, the impedance magnitude values $Z$ and phase angle $\phi$ for lyophilized samples show considerable differences in the low frequency interval and the curves merge in the high frequency interval. This is supposed to be related to the porous structure of lyophilized samples. According of these results, frequency dependences of magnitude values $Z$ and phase angle $\phi$ are the dielectric spectroscopy parameters, sensitive to the uniformity of the film structure. Since the main differences were observed in the low frequency interval (up to 400 Hz) one may choose to monitor the behavior of $Z$ and $\phi$ at this low frequency range.

Figure 6. Phase angle dependences on frequencies of investigated polymers.

4. Conclusion
In this paper the lyophilization effect on electret and dielectric properties of different polymer films was investigated. The experimental results showed that the lyophilization influences on electret and dielectric properties of all investigated polymer films (biopolymer and synthetic polymer). The highest steady state values of the normalized surface potential and the best stability were observed for all investigated lyophilized polymer films. Therefore, the lyophilization effect lead to significantly improvement of the ability to store electrical charges and obtaining a stable electrets, which could be used in various applications. It was found that the frequency dependences of the dielectric spectroscopy parameters (magnitude values and phase angle) for lyophilized samples show considerable
difference in the low frequency interval (up to 400 Hz). In this interval they were more sensitive to the uniformity of the film structure.

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