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Electret properties and wettability of polymer materials treated by DC glow discharge

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Abstract. We studied the influence of electret charge on the hydrophilicity of polytetrafluoroethylene (PTFE) films treated by direct-current (DC) glow discharge. DC discharge treatment of polymers leads to significant hydrophilization and appearance of surface charges on initially hydrophobic polymer surfaces. It was shown that the storage of plasma-treated PTFE films in environments with different relative humidity leads to an increased water contact angle along with a decreased surface potential. The process of hydrophobic recovery of plasma-treated PTFE films is considered as a consequence of charge relaxation in a humid atmosphere. It was established that surface charging of plasma-treated polymers makes a significant contribution to their hydrophilicity.

Keywords: direct-current glow discharge, plasma treatment, wettability, polymer electrets, hydrophobic recovery

Introduction

Surface modification by low-temperature plasma is a very efficient tool for a significant improvement of surface properties of polymer materials. It is known that plasma treatment results in a considerable change in the chemical composition of the surface caused by chemical reactions leading to an increase in oxygen-containing groups (Cvelbar et al. 2019). Hydrophobic polymer surfaces become hydrophilic after plasma treatment; however, this hydrophilicity is partially lost with time. This process is called ‘hydrophobic recovery’ (Primc, Mozetič 2022). The nature of this process is not yet understood. Hydrophilicity of plasma-treated polymer surfaces is usually interpreted as a result of the increase in the content of oxygen-containing polar groups on the surface. We consider this interpretation too simplified as it does not take into account the charging of polymers during their plasma treatment. Earlier, we observed correlations between surface charging, wettability and adhesion properties of PTFE films treated by direct-current (DC) glow discharge (Yablokov et al. 2015). Electret charges were measured after the corona discharge treatment of fluorocarbon polymers, and the role of high humidity in surface charge relaxation was underlined (Shuvayev et al. 1977).

The aim of the present work is to study the influence of electret charges arising in PTFE films treated by DC glow discharge on the hydrophilicity of these films.

Materials and methods

PTFE film samples with a thickness of 40 μm (‘Plastpolymer’, Saint Petersburg, Russia) were used in this study. The procedure for film modification by DC glow discharge is outlined in detail in (Rychkov et al. 2012). Polymer samples were placed on the bottom electrode of a two-electrode system (anode or cathode) and treated in the air as a working plasma gas, at a pressure of 10–15 Pa and a discharge current of 50 mA for 30 s. Electret measurements were performed using Ultra Stable Surface DC Voltmeter Model USSVM2 (AlphaLab, Inc.). Surface properties were characterized by the contact angle values measured with an Easy Drop DSA100 instrument (KRUSS) using distilled water as a test liquid. Plasma treated samples were stored in plastic boxes at room temperature in the air with different relative humidity (RH). Different RH of air was obtained above saturated aqueous solutions of salts. Air with RH = 75% was obtained over the saturated aqueous solution of NaCl. Air with RH ≤ 1% was obtained in a plastic box with a desiccant.

Results

The water contact angle (WCA) and the electret properties of DC glow-discharge-treated PTFE films were measured simultaneously. After treatment, polymer films were stored at different relative humidity at room temperature. The experimental data on changes in the contact angle by water (θ) with time for polymer films treated at the anode and at the cathode are shown in Fig. 1. The surface potential of PTFE films treated at the anode and at the cathode is shown in Fig. 2. The decay curves are normalized by the value measured just after the plasma treatment. The highest hydrophilicity (the lowest WCA value) can be seen (Fig. 1) in the film treated at the anode. The film treated at the cathode has the lowest hydrophilicity (highest WCA). A significant difference is observed for the hydrophobic recovery of films stored in dry (RH ≤ 1%) and humid (RH = 75%) atmosphere. Hydrophobic recovery, or increase of the WCA of films stored in humid atmosphere, is larger. This difference is observed both for films treated at the anode and at the cathode. Storage in humid atmosphere leads to a significant decrease in the normalized surface potential. This result corresponds to the well-known effect of the influence of ambient air humidity on the stability of the electret charge. Slower relaxation of the normalized surface potential is observed for the films treated at the anode (electrons and negative ions are active agents during plasma treatment) compared to the treatment at the cathode.

Surface potential decay of the polymer film in humid atmosphere is the result of the increased surface conductivity (Shuvayev et al. 1977). Electret charges on the polymer surface attract polar water molecules, thus increasing water droplet–surface interaction during WCA measurement.

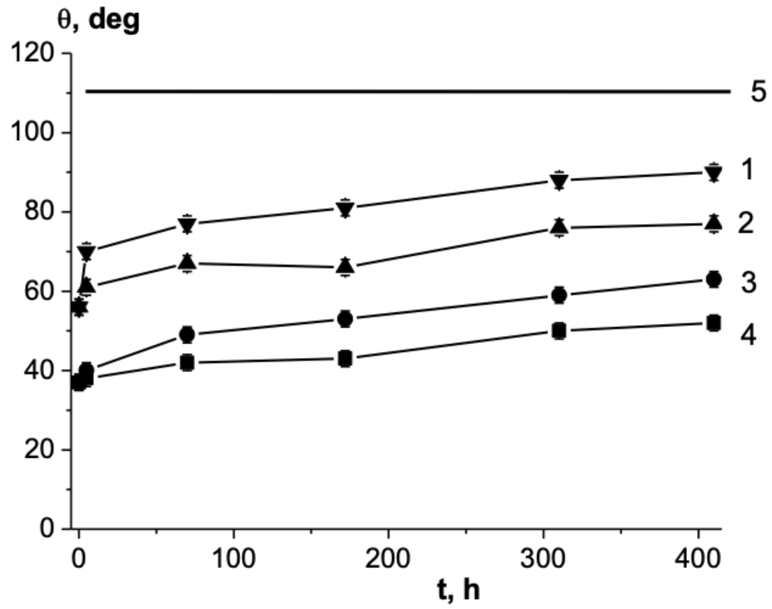

Fig. 1. Water contact angle temporal evolution of direct-current glow-discharge-treated PTFE films, stored at different relative humidity: 1 — film treated at the cathode, stored at RH = 75%; 2 — film treated at the cathode, stored in dry (less than RH = 1%) atmosphere; 3 — film treated at the anode, stored at RH = 75%; 4 — film treated at the anode, stored in dry (less than RH = 1%) atmosphere; 5 — contact angle of the pristine PTFE film

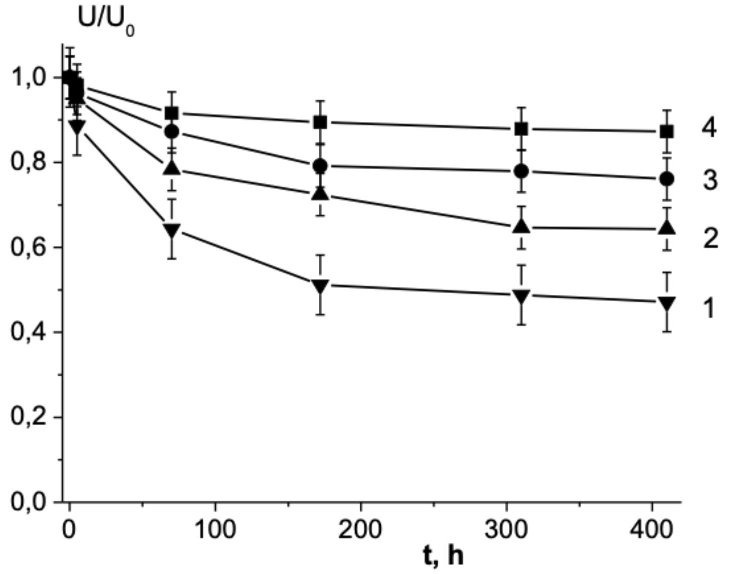

Fig. 2. Normalized surface-potential decay of direct-current glow-discharge — treated PTFE films, stored at different relative humidity: 1 — film treated at the cathode, stored at RH = 75%; 2 — film treated at the cathode, stored in dry (less than RH = 1%) atmosphere; 3 — film treated at the anode, stored at RH = 75%; 4 — film treated at the anode, stored in dry (less than RH = 1%) atmosphere

Conclusions

The results of the study of wettability degradation and charge relaxation of PTFE films after treatment by direct-current glow discharge are presented here. The water contact angle was shown to increase during the storage of polymers at room temperature in environments with different relative humidity. It was also demonstrated that surface potential decreases in time in humid atmosphere faster than in dry air. Hydrophobic recovery of plasma-treated polymer films may be considered as a consequence of electret charge relaxation. It means that surface charging in the process of plasma treatment contributes to the effect of polymer surface hydrophilicity improvement.

Conflict of Interest

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

Author Contributions

All the authors discussed the final work and took part in writing the article.

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