Relationship of Adhesive, Contact and Electret Properties of PTFE Modified by DC Discharge

M Yablokov, M Piskarev, A Gilman¹, A Kechek’yan and A Kuznetsov
Enikolopov Institute of Synthetic Polymer Materials RAS,
ul. Profsoyuznaya 70, Moscow, 117393, Russia

E-mail: plasma@ispn.ru

Abstract. The relationship between the contact, adhesive and electret properties of PTFE films modified by direct current glow discharge has been studied. The film samples of 40 μm thickness were placed at the anode and cathode and treated in the air as a working gas. The contact properties of polymer surface were characterized by the values of deionized water contact angle. The peel strength was determined using T-peel test for the Scotch®810/PTFE film contact. The electret potential was measured by the compensation technique using dynamic capacitor, and from the measured potential value the effective surface charge density was calculated. It has been found that there is an undoubted correlation between the change in the value of water contact angle, the peel strength of the DC discharge-treated film, and the magnitude of the effective surface charge.

1. Introduction

It is well known, that the improvement of the contact and adhesive properties of polymers by low-temperature plasma treatment is usually associated with the formation of polar groups of different chemical nature, mainly, oxygen-containing, and also with structural and morphological changes due to plasma induced partial degradation of the surface layer [1–6]. However, no direct correlation between the values of the contact angle and quantitative data on the adhesion of plasma-modified polymers of different chemical nature has been revealed. Meanwhile, it has been shown that the enhancement of the contact properties of polymers may be connected with the formation of electret states in the surface layers of polymer films [7, 8]. It was found that the formation of oxygen-containing groups and the decrease in the amount of fluorine atoms on the surface of PTFE films treated by DC discharge leads to a multifold increase in the polar component of the surface energy and a marked improvement in the thermal stability of the positive charge generated by corona treatment of the plasma-processed films, probably as a result of the emergence of new deep traps on the modified surface [9]. It was established also that the stability of the positive charge significantly increases after the treatment of tetrafluoropropylene–hexafluoropropylene copolymer films by DC discharge [10]. But despite the fact that the appearance of plasma-induced electret states in polymers has been known for a long time, there is no data connecting the value of the effective surface charge to experimentally determined values of the adhesion characteristics and the contact properties of the films modified by low-temperature plasma.

For experimental measurements of the adhesion characteristics of plasma-modified films we developed a special procedure [2]. It was shown that PTFE modification by DC discharge leads to a multifold increase in the peel strength and there is an undoubted correlation between the contact properties of the polymer and the peel strength [2]. The existing electric theory of adhesion states that
the adhesive properties of materials and electric charges are interrelated, and the formation of adhesive contact is represented as the contact electrification of the substrate and the adhesive [11]. The substrate and the adhesive are treated as capacitor plates, and the degradation of the adhesive contact is considered to be their separation process. However, the formation and degradation of the adhesive contact involving a charged substrate remains an open question [12].

The goal of this study is the research of the relationship of the change in the adhesion and contact properties of the surface of DC discharge-modified PTFE films with the plasma-induced formation of electret states in the polymer.

2. Experimental

Samples of the PTFE film of 40 μm thickness (“Plastpolymer”, St. Petersburg, Russia) were used in the study. Before plasma treatment, they were conditioned by heating at 150°C in air for 30 min. The procedure for film modification by DC discharge is described in [9]. The samples were placed on the anode or cathode and treated at the air as a working plasma gas, pressure of 10–15 Pa and a discharge current of 50 mA for 60 s.

The surface properties were characterized by values of the contact angle (θ) of deionized water measured using an Easy Drop DSA100 instrument (KRUSS, Germany) with the software Drop Shape Analysis V.1.90.0.14 (error ±1°).

The electret potential was measured by the compensation technique using a dynamic capacitor [13]. The experimental setup and the procedure of measurement are detailed in [14]. From the measured value of electret potential (U), the effective density of the surface charge (σ) was calculated by the equation σ = ε₀εU/L. In this equation, ε₀ is the electric constant and L is the thickness of the polymer film. The dielectric permittivity of the samples was taken to be ε = 2.

The adhesive properties of the films were investigated according to the procedure described in [2]. The peel strength (A) was determined using the T-peel test for the Scotch® 810/PTFE film contact.

Values of θ, A, and U were measured immediately after DC discharge treatment, during the storage of the films in air at room temperature and atmospheric pressure for 30 days, and after heating at 150°C for 30 min. The thermal treatment was carried out in the isothermal mode in an SNOL 58/350 oven in air at atmospheric pressure.

3. Results and discussion

Figure 1 (a) and (b) present data on changes in contact angle of water θ and peel resistance A, respectively, for (1) the initial PTFE film and (2 A, C) PTFE films modified at the anode (A) and cathode (C) under the above conditions, (3 A, C) for the films after storage in air for 14 days under ambient conditions and (4 A, C) for the films after heat treatment under isothermal conditions at 150°C in air for 30 min. It can be seen that the treatment of the films at the anode is more effective than at the cathode, and the values of θ for water measured either immediately after the discharge treatment or after 14 day storage or 30 min heat treatment are lower. The films modified at the anode acquire hydrophilicity and retain this property after heat treatment or storage (θ < 60°). These films also possess better adhesion properties: the values of A measured immediately after the plasma treatment and after thermal treatment or storage were higher. These results indicate the existence of an inverse correlation between the contact angle and the peel strength: the less the value of θ, the greater the value of A. This relationship is characteristic of the both types of films modified at the anode or the cathode.

Experimentally determined values of effective surface charge density (σ) for the PTFE films modified at the anode or cathode are shown in Fig. (c). There are data given for (1) the initial film and the films (2 A, C) immediately after plasma treatment at the anode and cathode, (3 A, C) after 14 day of storage and (4 A, C) after heat treatment. Note that the initial film had a small negative surface potential and the effective charge density of this film is σ = −15 μC/m². The presence of this potential is apparently due to the sample prehistory.
After modifying the film at the anode, the effective density of negative charge increases to $-36 \, \mu\text{C/m}^2$, whereas the film treated at the cathode acquires a positive surface potential.

It is seen that as the storage time increases to 14 days, the contact angle increases, the peel strength decreases, and the effective surface charge density is reduced. Note that there is the undoubted correlation between the effective surface charge density and $\theta$, as well as between $\sigma$ and $A$. These data show also that the parameters for the films treated at the anode undergo substantially smaller changes than those for the films modified at the cathode.

Thus, these data suggest that the rise of the effective density of negative surface charge in the films after their modification at the anode correlates with the increment in the peel strength, and its fall during storage of the films or after heat treatment correlates with the decrement in $\sigma$. After the treatment at the cathode, the films acquire a positive effective surface charge, and the peel strength increases as compared with the initial value, although to a lesser extent than in the case of the treatment at the anode.

It is known [13, 14] that the experimentally determined value of the effective surface charge density is an integral characteristic of the electret state and is the sum of homo- and heterocharges. During dc discharge treatment of a polymer, the homocharge is induced by injection of electrons or ions from the plasma, depending on the treatment conditions and the position of the polymer film relative to the electrodes. The heterocharge can be generated as a result of the formation of polarized states of polar groups oriented in the electric field induced in the discharge gap. These polar groups are formed in the surface layer of the polymer by chemical reactions occurring during its plasma modification. Thus, the nature of the DC discharge-induced electret state in the polymer film may be
associated not only with the charges as such, but also with oriented dipoles occurring on the surface [13]. We have shown that the thickness of the PTFE layer chemically modified by plasma at the anode is 40–50 nm [15]. It is at this distance from the polymer surface that the concentration of oxygen atoms is reduced from ~10% to zero. At the same time, it is known that the homocharge is built up in a layer of ~0.1–0.01 μm in thickness [16], which corresponds to the aforementioned thickness of the modified polymer layer. The determining role in the buildup of the homocharge is played by the traps, which are associated with various defects such as terminal groups of macromolecules, long-lived free radicals, crystallite defects, the interface between the polymer crystalline and amorphous phases, and polar groups on the surface. The depth and concentration of traps in a plasma-treated polymer substantially depend on the mode of treatment [13]. Based on our experimental data, we can suggest that the treatment at the cathode gives rise to a variety of shallow traps in the surface layer of PTFE film, which are rather quickly depopulated by thermal motion. On the other hand, the PTFE film treated at the anode has a substantially larger number of polar groups on the surface [2], thereby greatly facilitating the formation of deep traps. Calculations for model systems showed [17] that polar impurities localized near structural defects can cause the formation of traps in the vicinity of the defect, themselves not being the traps. It is due to the formation of deep traps in the case of treatment at the anode that the surface potential relaxation rate for the PTFE film is lower.

In summary, the results of this study show that there is an undoubted correlation between the adhesion characteristics, the change in the contact angle, and the magnitude of effective surface charge of the PTFE film treated in DC glow discharge.

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