

## Adhesive properties of PTFE modified by DC discharge

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**Abstract.** It is shown that low-pressure DC discharge treatment of PTFE films at both the anode and cathode leads to substantial enhancement of the contact properties of the polymer surface and alters considerably the adhesion properties of PTFE film surface. A procedure is developed for determination the adhesion characteristics of the modified surface of plasma treated thin polymer films using Scotch® 810 adhesive tape. The procedure comprises of a study of the surface coating created by means of physical vapor deposition of an aluminum layer with thickness of the order of 100 nm, an adhesive joint of the film with Scotch® 810 tape, and T-peel testing of the specimen. Using this procedure, the peel resistance of the initial and the modified PTFE film on both the anode and the cathode in DC discharge is measured.

### 1. Introduction

Polytetrafluoroethylene (PTFE) has unique chemical and physical properties: it neither swells nor dissolves in common solvents; it is resistant toward oxidants, acids, and alkalis and exhibits good dielectric properties over wide temperature and frequency ranges [1]. However, some applications concerning the use of PTFE as an engineering material demand that contact properties of the polymer surface should be improved, a task of vast practical importance. It is well known that the treatment by low-temperature plasma is a very effective method for enhancement of the polymer films contact properties such as wettability, the adhesive strength at the polymer/metal interface, the adhesive ability, the removability of applied printed matter etc. It should be noted that some changes take place on the polymer surface or within a thin surface layer with a thickness of 10 to 1000 nm as estimated by different authors. But the bulk of polymer remains intact, retaining the inherent mechanical and physicochemical properties [2, 3]. Therefore, it is of particular interest to determine experimentally the adhesion characteristics of the modified thin PTFE films.

There are various processes for surface modification of PTFE using high energy chemistry techniques: electron-beam irradiation [4], bombardment with argon ions [5, 6], treatment by means of radiofrequency (13.56 MHz) discharges in O<sub>2</sub>, Ar, N<sub>2</sub>, He, H<sub>2</sub>, etc.[6, 7], microwave (2.45 GHz) discharge [8], or the afterglow of RF discharge [9]. A combination of plasma and ozone treatment followed by grafting of chemically different substances onto the polymer surface can also be used [10]. These techniques make it possible to improve the contact properties of the PTFE surface, however they exhibit high values of the water contact angle ( $\theta$ ) (usually not less than  $\theta = 55^\circ$ ).

The most effective means of surface modification of polymers is found to be the treatment with a direct-current (DC) discharge. Such treatment allows separating the effect of the active plasma components on the polymer surface [3, 11]. Hence follows our interest to study the surface



modification of PTFE in a low-pressure direct-current discharge and to examine the adhesion characteristics of these films.

There are several investigations in literature devoted to the adhesion properties of polymers modified by low-temperature plasmas [12–15].

Wade et al. [12] studied the adhesion properties of commercial polymer films of 8–12  $\mu\text{m}$  thickness (polycarbonate, polysulfone, poly(ethylene terephthalate), polystyrene, polypropylene, poly(vinylidene fluoride)) modified in 13.56 MHz RF discharge in various gases such as oxygen, helium, and mixture of 96 %  $\text{CF}_4$  and 4 %  $\text{O}_2$ . The adhesion strength at the metal/modified surface boundary was determined by ASTM D3359-02. Scotch® 810 pressure-sensitive adhesive tape is applied on and subsequently removed from the Al layer. As a measure of the adhesion strength, the ratio of the Scotch® 810 tape area covered with Al to the total area was used. The adhesion was evaluated qualitatively as very good, good, or poor depending on the amount of removed aluminum.

The adhesion characteristics of 50  $\mu\text{m}$  FEP films modified in  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$  and Ar RF discharges were studied in [13]. In order to do this, a copper layer of  $\sim 30$   $\mu\text{m}$  thickness was applied onto the film surface in two steps. First a chemical vapor deposition was applied to create a layer of  $\sim 0.2$   $\mu\text{m}$  and then the thickness was increased to 30  $\mu\text{m}$  by electrochemical plating. The adhesion of copper to the polymer surface was measured by T-peel test with Shimadzu Instron AGS 100-A tester. The peel strength was 27–199 mN/5 mm depending of the gas nature. The disadvantage of this method is the complicated two-step wet procedure of copper deposition. In it acids (sulfuric and hydrochloric), tin-palladium catalyst, copper sulfate, and a special polishing agent are used. After that the obtained sample is subjected to washing and drying at 80 °C for 12 h.

Sandwiched specimens were prepared from plates of PET, polypropylene, poly(vinylidene fluoride), etc. treated by means of air RF discharge. The thickness of the plates was 4 mm. A two-component polyurethane resin (Betamate 7000/7050, Dow Chemicals) with a layer thickness of 0.1 mm was applied. The tests were realized on a Zwick Z030 machine [14]. The shear stress was measured with an Instron 4301 machine [15].

It should be noted however that all of the aforementioned methods allow comparing only relative values of the adhesion strength. Thus, development and application of procedure for measuring the absolute values of adhesion strength is of high interest.

## 2. Experimental

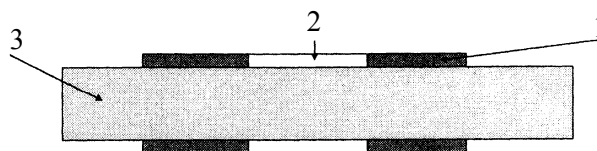
Samples of commercial PTFE film of 40  $\mu\text{m}$  thickness are used. The procedure for modification of the film surface in a DC discharge is given in details in [16]. The film samples is mounted on the anode or cathode and is treated by air discharge for 15–60 s at a gas pressure of 10–20 Pa and discharge currents of 20–100 mA.

To characterize the surface properties the value of the contact angle ( $\theta$ ) is used. It is determined with a goniometer (error  $\pm 1^\circ$ ). Two testing liquids were used – bidistilled water and glycerol. By the obtained result the work of adhesion ( $W_a$ ), the total surface energy ( $\gamma$ ), and its polar ( $\gamma^p$ ) and dispersion ( $\gamma^d$ ) terms are calculated [17].

The composition and the chemical structure of the surface of the initial and the plasma-treated PTFE films are studied by means of IR spectroscopy and ESCA. The IR reflection spectra are measured with Bruker Equinox 50S Fourier-transform IR spectrometer. It has MIRacle™ single reflection horizontal ATR attachment and uses ZnSe crystal working over the range 400–4000  $\text{cm}^{-1}$ . The data of 500 scans with a scanning step of 2  $\text{cm}^{-1}$  is collected. Band assignment is chosen according to [18]. ESCA spectra are measured on a Shimadzu ESCA 3400 spectrometer with a monochromatic  $\text{MgK}_\alpha$  source (5 kV, 20 mA). The peak positions (binding energies) were calibrated with respect to the standard  $\text{C}_{1s}$  peak (284.6 eV) [19].

A special procedure is developed to measure the adhesion characteristics of the films. An aluminum layer of  $\sim 100$  nm thickness is applied by physical vapour deposition. The layer is deposited through a mask onto the central part of the samples of the initial and the modified (at the anode or

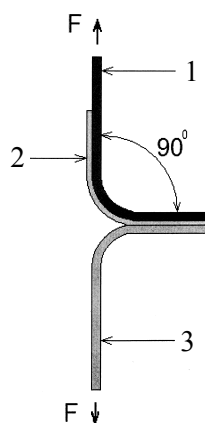
cathode) PTFE film. The layer is with 35 mm length and covering the entire width of the sample. A specimen of this type is sketched in figure 1.



**Figure 1.** Schematic top view of the specimen for the measurement of adhesion; (1) – PTFE film, (2) – aluminum layer, and (3) – Scotch® 810.

Aluminum is simultaneously deposited onto the plasma-treated and the unchanged specimens. Then, Scotch® 810 pressure-sensitive adhesive tape (19 mm width), used to measure the adhesion of paints according to ASTM D3359-02, is rolled with rubber roller of  $d = 30$  mm onto the specimen over its entire length. The force on the roller axis during rolling is 29.4 N.

T-peel test (figure 2) is performed on an Autograph AGS-10 KNG universal testing machine (Shimadzu) at a crosshead speed of 100 mm/min. As a result a curve presenting the change in the peel resistance (**A**) along the sample length is obtained. The experimental data are averaged over 20 runs. The representativeness of this procedure is established on the basis of the peel strength of two Scotch® 810 tape specimens joint by their adhesive layers (autohesion strength –  $A_a$ ). When adhesive layers (two adhesive tape layers in the given case) are brought into contact with one another, the layer thickness doubles. Since the peel resistance is proportional to the adhesive-layer thickness, the value of **A** for the Scotch® 810/ Scotch® 810 joint is  $A_a/2$ , and is equal to  $198 \pm 5$  N/m.



**Figure 2.** Schematic of the T-peel test for the modified film: (1) PTFE film, (2) Al layer, (3) Scotch® 810 tape. F denotes the applied peeling force.

### 3. Results and discussion

The experimental values of the contact angles ( $\theta$ ) of water and glycerol for PTFE films treated at the anode and cathode of a DC discharge are presented in table 1. The discharge current is 50 mA and the treating time is 60 s. The work of adhesion, the total surface energy, and its polar and dispersion terms calculated are also given. The data show that the plasma treatment leads to substantial reduction in  $\theta$ , increase in both  $W_a$  and  $\gamma$ , and manifold increase in  $\gamma^p$ . The results indicate that treatment of PTFE films in DC discharge leads to significant enhancement of the contact properties of the polymer

surface. The values of  $\theta$  are substantially lower compare to the results obtained after treatment with RF discharge. It is also seen that PTFE films modified at the anode have lower values of  $\theta$  and higher values of  $W_a$ ,  $\gamma$  and  $\gamma^p$  than those treated on the cathode.

**Table 1.** Contact angles, work of adhesion, and surface energy of PTFE films

| Polymer | DC discharge treatment | $\theta$ (deg) |             | $W_a$ (mJ/m <sup>2</sup> ) |             | $\gamma$ (mJ/m <sup>2</sup> ) |            |            |
|---------|------------------------|----------------|-------------|----------------------------|-------------|-------------------------------|------------|------------|
|         |                        | By water       | By glycerol | By water                   | By glycerol | $\gamma$                      | $\gamma^p$ | $\gamma^d$ |
| PTFE    | –                      | 120            | 106         | 36.4                       | 45.9        | 13.18                         | 0.03       | 13.15      |
|         | On the anode           | 33             | 26          | 133.9                      | 120.4       | 61.5                          | 42.0       | 19.5       |
|         | On the cathode         | 49             | 40          | 120.6                      | 112.0       | 50.7                          | 29.3       | 21.4       |

An IR spectroscopic investigation of PTFE films shows that after DC discharge treatment at the anode and cathode, the intensity of the oxygenated groups absorption bands considerably increases (stretching vibrations of the C=O group in –C–(O)–F or perfluoroketone groups; absorption band at 1885 cm<sup>-1</sup>), probably as a result of oxidation by plasma. The absorption band at 1775 cm<sup>-1</sup> is presumably due to the C=C double bonds formed as a result of fluorine atom abstraction from the polymer chain. Most likely the reason for the decrease in the amount of CF<sub>2</sub> groups is the detachment of fluorine resulting in formation of double bonds in the chain. As a confirmation of this reasoning is the appearance of the absorption band at 1775 cm<sup>-1</sup>. The intensity of the absorption bands at 3500–3600 cm<sup>-1</sup> reveals increase of water adsorption as well.

These results are confirmed by ESCA data. The spectrum of the initial PTFE film consists of a C<sub>1s</sub> peak at binding energy of 292.2 eV with width of 1.3 eV and a small peak at 286.0 eV, which is due to the presence of a certain amount of hydrocarbon impurities in the polymer [12]. The initial F<sub>1s</sub> spectrum consists of one peak at 690.2 eV with a width of 1.7 eV. After the discharge treatment of the film, a C<sub>1s</sub> peak at 287.0 eV corresponding to oxidized carbon (C=O) formations appears in the spectrum while the peak at 286.0 eV remains unchanged. The width of the F<sub>1s</sub> peak increases from 1.7 to 2.0 eV, and its shape somewhat changes. In addition, it was found that polymer contains < 4% oxygen. These results are close to those, obtained by Wade et al [12], who studies the effect of treatment of PTFE films by oxygen RF (13.56 MHz) discharge.

The adhesion characteristics were examined for the initial PTFE film and the one modified on the anode or cathode of a DC discharge. The discharge conditions are: air pressure – 10 Pa, discharge current – 50 mA and treating time – 10 and 60 s. The data in table 2, reveal that the initial PTFE film exhibits a low with respect to the deposited Al layer peel resistance (**A**) but after the modification of the film on the anode and/or cathode **A** substantially increases.

**Table 2.** Peel strength (**A**) for the initial PTFE film and the film modified in DC discharge (50 mA) with a physical-vapor deposited Al layer (Scotch® 810/Al)

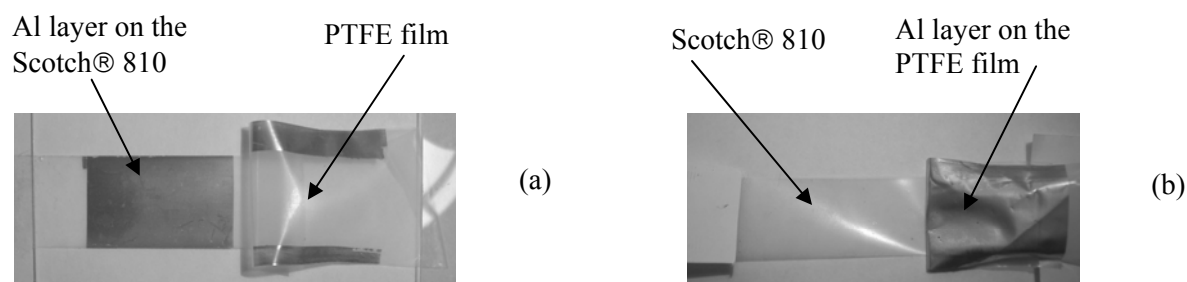
| Sample                  |      | <b>A</b> (N/m) |
|-------------------------|------|----------------|
| Initial                 |      | 78±18          |
| Treated on the cathode  | 10 s | 188±6          |
|                         | 60 s | 181±5          |
| Treated on the anode    | 10 s | 189±13         |
|                         | 60 s | 169±15         |
| Scotch® 810/Scotch® 810 |      | 198±5          |

**Table 3.** Peel strength (**A**) for the initial PTFE film and the film modified in DC discharge (50 mA) (Scotch® 810/PTFE)

| Sample                  |      | <b>A</b> , N/m |
|-------------------------|------|----------------|
| Initial                 |      | 30±6           |
| Treated on the cathode  | 10 s | 76±3           |
|                         | 60 s | 134±4          |
| Treated on the anode    | 10 s | 250±20         |
|                         | 60 s | 200±10         |
| Scotch® 810/Scotch® 810 |      | 198±5          |

Table 3 shows that the anode-treated PTFE film exhibits higher **A** values for the Scotch® 810/PTFE joint.

These results are illustrated in figure 3 by photographs of specimens of the initial and the anode-modified PTFE films after T-peel testing.



**Figure 3.** Photographs of the specimens of the (a) initial and (b) anode-modified PTFE films after T-peel testing.

It is seen at figure 3(a) that the Scotch® 810 tape pulls off completely the aluminum layer from the untreated PTFE film but it is fully retained (figure 3(b)) on the anode-modified film.

The results obtained in this work show that DC discharge treatment of PTFE films leads to substantial enhancement of the contact properties of the polymer surface. It also alters considerably the adhesion properties of PTFE film surface. The proposed procedure can be successfully used for quantitative evaluation of the adhesion characteristics of the surface of plasma-modified thin polymer films.

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