

**SURFACE MODIFICATION OF POLYETHYLENE TEREPHTHALATE SUBSTRATES BY
HIGH FREQUENCY AIR DISCHARGE PLASMA. STRUCTURE, MORFOLOGY,
ADHESION PERFORMANCE**

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Abstract

Effect of high frequency air discharge plasma on the surface and adhesion performance of polyethylene terephthalate (PET) substrates of different thickness was investigated. Based upon X-ray photoelectron spectroscopy, contact angle measurements and ATF FTIR was shown that chemical composition of thin surface layer changes even after first 5 minutes of plasma treatment in spite of mild conditions of etching. Structure changes were estimated by AFM and TEM. It was shown that plasma treatment reveals phase structure organization of PET, but total surface relief changes insignificantly. Dramatic change in surface energy after treatment was revealed by contact angle measurements. At the same time, it was shown that surface energy relaxation occurs during storage of substrate in room conditions. These results are in good agreement with adhesion performance of PET substrate to model silicon scotch estimated by 180° Peel Test.

Key words: surface energy, adhesion properties, plasma etching of PET surface

1. INTRODUCTION

Plasma treatment is now widely used method of surface modification of polymeric and inorganic surfaces. Many authors have published fundamental and practically important results during the last two decades. For surface modification, different researchers have used various types of plasma discharges, from weak corona discharge to hard – arc-plasma discharge that modeling the effect of atomic oxygen within the upper atmosphere on polymeric protect coverings. Of course, low-energy plasma of different gas discharges, for example, air, nitrogen, oxygen, ammonia, hydrogen, noble gases, etc is used for surface modification without some dramatic changes such as carbonization of polymer surface.

Surface treatment of polymer films and substrates in plasma discharges of different gases atmosphere is widely used for alteration of the following parameters: (i) increase of surface energy and hydrophily of the surface (Morra, Occhiello and Garbassi, 1993; Youxian, et al. 1991); (ii) increase of surface hydrophobicity (Iriyama, et al. 1991); (iii) control of adhesive performance (Wu, et al. 1995; Guezenoc, et al. 1993; Qiu, Deflon and Schwartz, 1993; Noha, et al., 2007). Plasma surface treatment of polymeric biomaterials and inorganic implants is used for the purpose of increase the bio- or blood-compatibility (Huang, et al. 2004; Chu, 2007; Tamada and Ikada, 1993), cleaning of metals from oxide films (Noha, et al., 2007), increase of biodegradation of polymers (Matsunaga and Whitney, 2000).

Covalent immobilization of polar groups (Sheu, et al. 1993) and polymer chains (Gong, et al. 2000; Kang, et al. 1996) onto polymeric substrates is also utilized for further chemo-sorption of specific chemical preparations and medicines.

The comparison analysis of some results of polymer surface plasma modification in different gases have shown that oxygen plasma discharge treatment leads to functionalization of surface and formation of new oxygen-containing groups; but, for example, argon plasma treatment improves surface wettability (Guruvenketa, et al. 2004).

It's well known that low-energy plasma treatment of polymer films and compositions is widely used as a preparation stage for reveal phase structure of the system. It becomes possible due to difference in etching rates of crystalline and amorphous phases of polymer.

Plasma etching of polymer surface accompanies with all above mentioned processes, and also there are several processes, for example, local temperature increase on a polymer surface that leads to surface amorphization, net-work formation within thin top layer, polymer destruction, carbonization, material erosion, and etc. And these surface changes are directly connected with plasma type and treatment conditions.

From fundamental point of view, it was interesting for us to change just one parameter of polymer surface during surface modification to control the surface energy and, as the result, to estimate the adhesion performance of initial and modified PET substrate. So, based upon the previous experience we decided to use low-energy plasma treatment where the effect of all negative parameters was minimized.

In our recent work (Chalykh, et al. 2009) we showed that strength of adhesive joint can be described by the following correlation:

$$A \sim k(W_0 \cdot S + \psi) , \quad (1)$$

where A is a peel strength of an adhesive joint; W_0 is thermodynamic work of adhesion that can be calculated based upon the surface energy of adhesive and substrate; S is area of contact between adhesive and substrate surfaces that relating to substrate surface relief; ψ connects with deformation work of adhesive within the destruction zone, and it is the mechanical response of the system on external deformation action.

The contribution of the deformation work of adhesive in the A value was investigated successfully and presented in our recent work (Gladkikh, et al. 2011). We changed the mechanical characteristics of adhesive due to formation of chemical net-work during expose to high-energy electrons and at the same time the other parameters of Equation 1 stays invariant.

Thus, in the present paper, the effect of surface modification of polymeric substrate by high-frequency air discharge plasma on its structure, chemical composition and adhesive performance to standard adhesive was investigated. Stability of the surface characteristics after plasma treatment was also estimated during room conditions storage.

2. EXPERIMENTALS

Commercial PET films (Polyplast, Russia) were used as polymer substrates with different thickness: 5 and 20 μm . These films are two-axial oriented. Melting point of PET is 250-260°C, glass transition point T_g is 70°C. Crystallinity degree of such PET was not higher than 10%.

High frequency air discharge plasma treatment was carried out in vacuum chamber of Coating System E306A, Edwards (Fig. 1) under air pressure of 0.09 mm Hg. Frequency of the generator was 10 MHz; the amplitude voltage was 1.2 kV. Such plasma is well known as low-temperature plasma, the energy of electrons was not higher as 4-6 eV.

PET substrate was set on specimen stage as shown in the Fig. 1. Duration of plasma treatment was varied from 0 to 60 minutes.

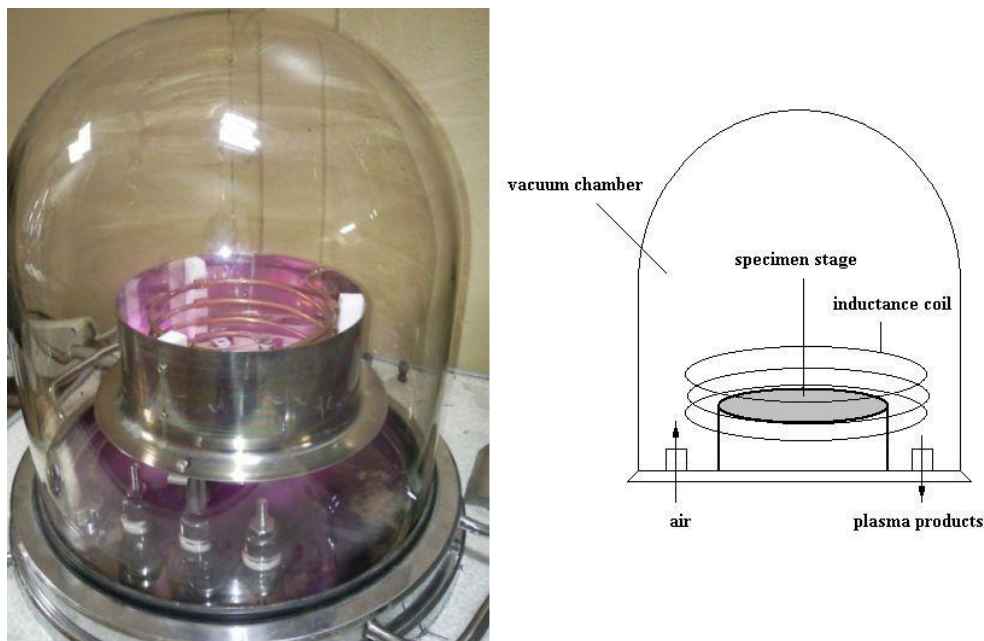


Fig. 1. Schema of plasma treatment chamber.

Surface structure before and after treatment was estimated using Transmitting Electron Microscope (TEM) EM-301, Philips. Specimens were prepared by the use of method of two-stage surface replica with platinum shadowing.

The relief change of PET surface after plasma treatment was investigated by Atomic Force Microscopy (AFM) (Centaur, NanoScan Tech.) in tapping mode. Probe diameter was 2 nm.

Chemical composition of the surface layer of PET after plasma treatment was used by Attenuated Total Reflection Fourier Infrared spectroscopy (ATF FTIR) using FTIR-Microscope HYPERION 2000 Bruker, associated with IFS-66 v/s Fourier spectrometer, and X-ray photoelectron spectroscopy (XPS) (XSAM-800, Kratos Analytical Ltd.).

Surface energy was estimated by contact angle measurements with standard test liquids on FM40 EasyDrop, Kruss GmbH. Value of surface energy, and its polar and disperse parts were calculated by Owens-Wendt equation (Owens and Wendt, 1969).

Adhesion performance of plasma modified PET substrates in model adhesive joints with standard scotch (silicone scotch on PET backing, 3M) was determined by 180° Peel Test on Instron Tensile Tester 1121 at peeling rate of 10 mm/min. Adhesive join formation (lamination) and debonding (peeling) were carried out at room temperature $23 \pm 1^\circ\text{C}$.

3. RESULTS AND DISCUSSION

3.1. Phase structure and relief of PET surface

Typical TEM micrographs of PET before and after plasma treatment are shown in the Fig. 2-4. Initial PET is characterized by practically smooth and homogeneous surface without any sharp phases. And it's obvious that plasma etching reveals phase organization of polymer (Fig. 3 and 4). After the first 10 min of plasma etching the micro-domain structure becomes visible. Probably, commercial PET film is characterized by sufficiently high content of crystalline phase because of the way of orientation during production; and efficient crystallinity degree of 5 μm thick PET is much higher that of 20 μm thick one. After 35 min of plasma treatment the surface state stays invariant but phase structure reveals sharply. It should be emphasized that PET surface structure, which formed after plasma treatment, remains stable and unchanged during long-term storage in room conditions (more than 1 month).



Fig. 2. TEM micrograph of initial PET film surface (5 μm thickness).

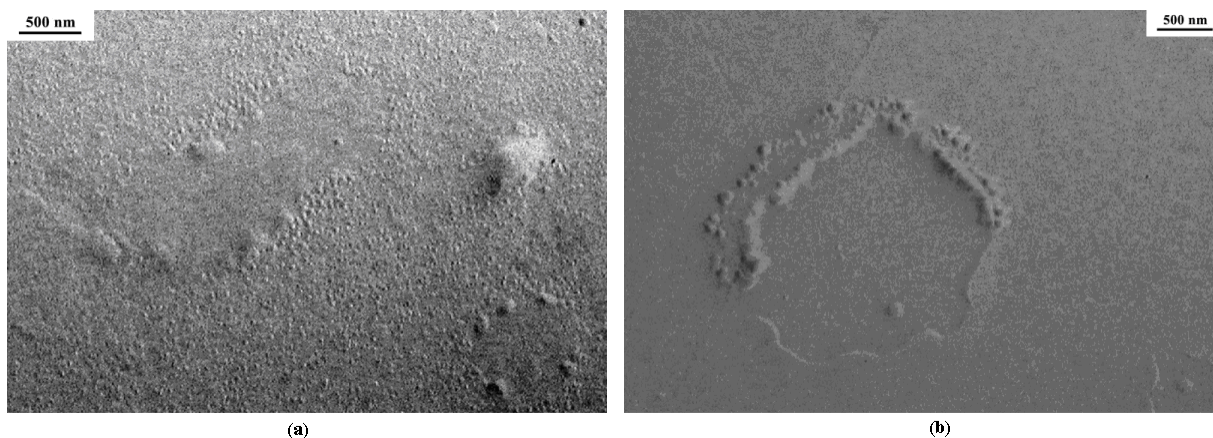


Fig. 3. TEM micrographs of PET film (5 μm thickness) surface after plasma treatment during 10 (a) and 35 min (b).

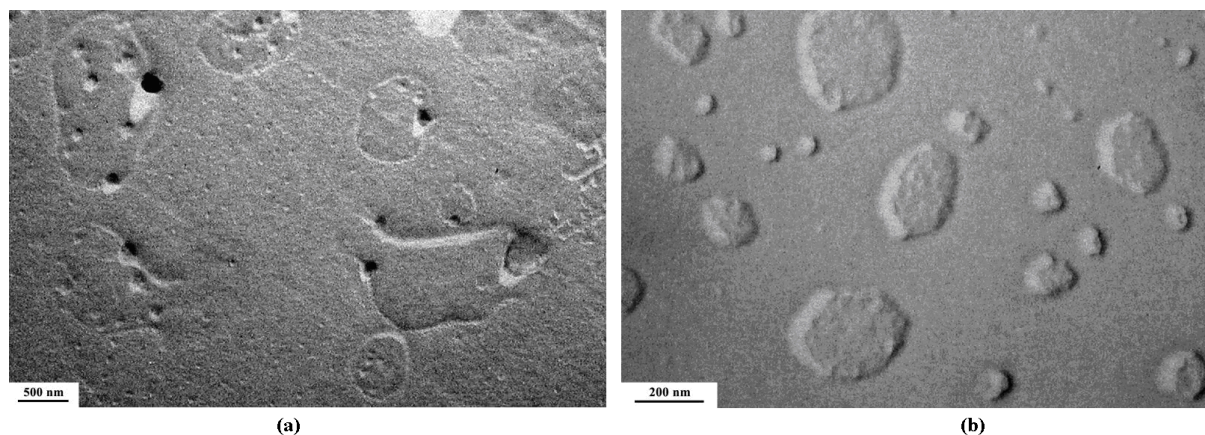


Fig. 4. TEM micrographs of PET film (20 μm thickness) surface after plasma treatment during 10 (a) and 35 min (b).

Changing the surface relief after plasma treatment that was estimated by AFM is presented in Fig. 5-7. Figure 5 shows that the initial relief of untreated PET substrate is not ideally smooth, but the altitude of these wrinkles is not higher than 10 nm.

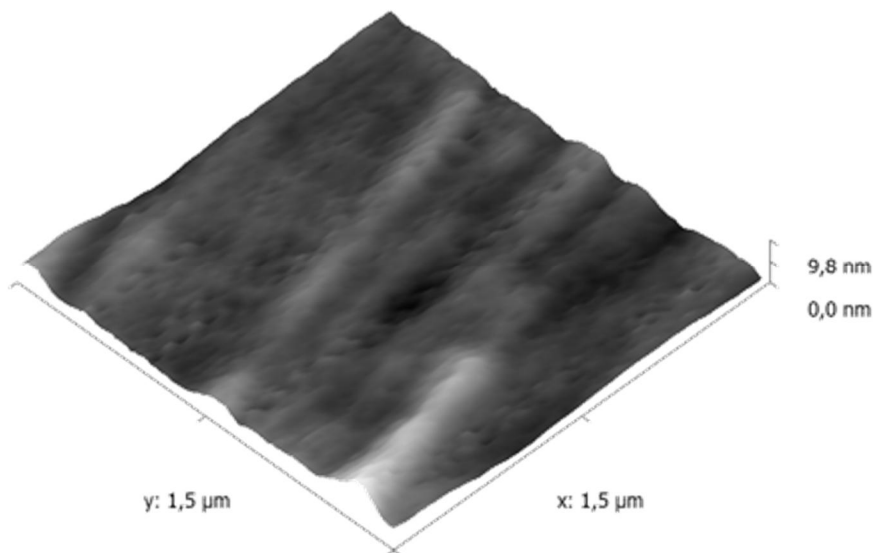


Fig. 5. AFM picture of untreated PET substrate (5 μm thick).

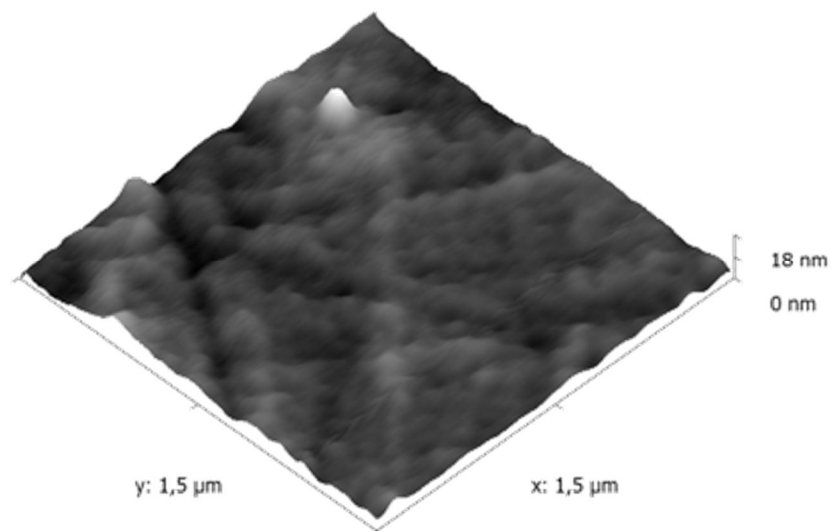


Fig. 6. AFM picture of PET substrate (5 μm thick) after 20 min plasma treatment.

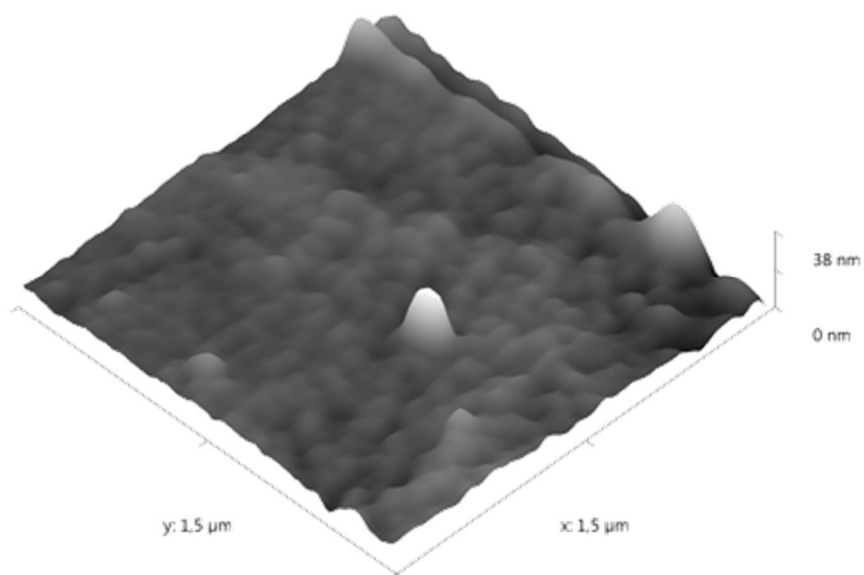


Fig. 7. AFM picture of PET substrate (5 μm thick) after 60 min plasma treatment.

As a result of plasma etching, and even under very mild treatment conditions, the developed surface relief is formed. Protuberances and hills can be determined as crystalline phase, and concave spaces and cavities can be defined as amorphous areas.

After first 15-20 min of plasma treatment, the height of crystalline areas reaches 18 nm. It appears that increase of etching time up to 40-60 min doesn't affect the surface relief dramatically, but separate protuberances become 35-38 nm in height.

It's clearly that surface modification of PET substrate in high-frequency air discharge plasma leads to slightly growth in specific surface area at approximately 17-21% in comparison with initial one. These estimations were done by means of AFM-equipment software. Nevertheless, such nanoscale changes don't effect on total value of adhesive strength via Equation 1.

3.2. Chemical composition of PET surface

Chemical composition and its alteration after plasma treatment were estimated due to two methods. It should be noted that IR analysis was done just after treatment, but XPS was done 12 hours later.

The first analysis – ATF FTIR showed that after plasma etching a chemical composition changes dramatically, but it's necessary to point out that these changes can be detected during the first 30 min after treatment only. Among these spectral changes it should be noted the formation of oxygen-containing groups and peroxide groups; also the appearance of new spectral bonds that can characterize the accession of heteroatom to polymer chain.

More detailed analysis was done by XPS, and the results are shown in Fig. 8 and 9. Plasma treatment leads to formation of new nitrogen-containing functional groups (pear 1s N), and the total content of nitrogen after 20 min treatment was detected as 4.66 at. % (see Table 1). Intensity of oxygen peak (1s C) also increases after plasma etching. Probably the concentration of oxygen-containing groups was higher in the first moment, as it was shown by ATF FTIR measurements, but storage in contact with air results in rearrangement of surface structure, so the sum amount of oxygen after 12-hours storage increased lightly. Chemical composition of PET surface and its alteration after plasma modification is shown in the Table 1. Equal results were obtained for both 5 and 20 μ m PET substrates.

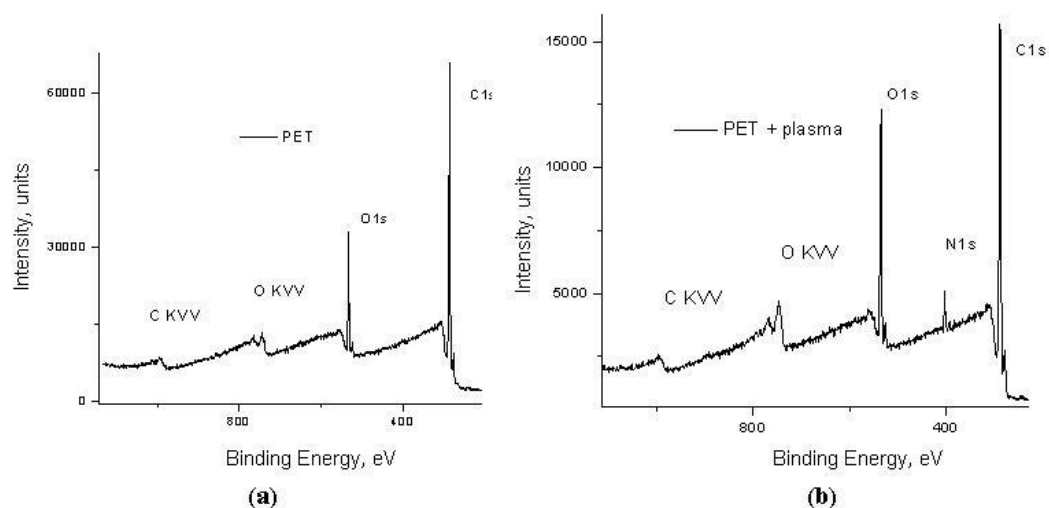


Fig. 8. XPS spectra of initial PET surface (a) and after its plasma modification (b). PET thickness was 20 μ m, treatment time – 20 min.

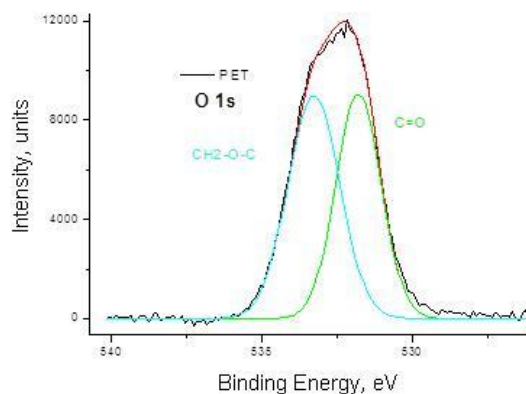


Fig. 9. XPS spectra of surface after plasma modification: the detail analysis of 1s Carbon peak.

Table 1. Chemical composition of initial PET surface and after plasma modification.

<i>Chemical Element</i>	<i>Initial PET</i>	<i>PET after plasma</i>
<i>C, at. %</i>	78.59	69.52
<i>O, at. %</i>	21.41	25.82
<i>N, at. %</i>	-	4.66

3.3. Surface energy and adhesion performance

It was obtained that surface modification by low-energy plasma etching leads to considerable increase of surface energy, especially its polar part. This phenomenon is widely used for surface modification to control and improvement of wettability, printability and adhesive properties. In our case, the duration of plasma treatment effects on total value of surface energy, but the most significant changes were detected during the first thirty minutes of treatment. The further etching (above 30 min) doesn't influence the surface energy. All these results are summed in Table 2.

Table 2. Surface energy (γ) and its polar (γ^p) and disperse (γ^D) parts of PET substrate (20 μ m thick).

<i>Duration of plasma etching, min</i>	<i>γ, mJ/m²</i>	<i>γ^p, mJ/m²</i>	<i>γ^D, mJ/m²</i>
<i>0</i>	38.6	4.2	34.4
<i>1</i>	42.5	21.4	21.1
<i>30</i>	64.1	41.1	23.0
<i>60</i>	64.6	43.0	21.6

There is a correlation between alteration of surface energy and adhesion properties of PET substrate after plasma treatment. Plasma modification of substrate also increases peel strength to model scotch as it's shown in the Table 3.

In spite of plasma treatment can remove loosely bonded surface contamination (Liston, Martinu and Wertheimer, 1993) and some authors relate this effect with increase of surface adhesion performance, we believe that the increase of adhesive bond also connects with increase of polar part of surface energy and formation of new polar functional groups. This assumption was proved by long-term storage experiments, and these results are described in the next paragraph.

Table 3. Adhesion performance (Peel Strength – A, N/m) of PET substrate to model scotch.

<i>Duration of plasma etching</i>	<i>0 min</i>	<i>5 min</i>	<i>20 min</i>
A, N/m	130	170	210

Relaxation of surface energy

Relaxation of surface energy was observed during long-term storage of modified PET substrate in room conditions. It was determined that the first high value of surface energy (just after treatment) decreases during storage in contact with air. The same results were obtained in our team recently for the other system: ethylene and vinyl acetate copolymers (Chalykh, et al. 2009). In this case, we observed the decrease of surface energy, and the rate of such surface reorganization was very high. Practically total relaxation of surface characteristics occurred during 160-180 min (Fig. 10). Further observations showed that slowly phase of relaxation of surface energy to some low magnitude can takes several days, but anyhow the initial value of surface energy (for untreated PET) doesn't achieve.

Total recession of surface energy is due to decrease of the polar part, as long as the disperse part doesn't change during storage. Regardless of the fact that T_g of PET is significantly high and at room temperature it is in glass state, the surface is devitrified and the mobility of side groups remains. As it was shown recently (Chalykh, et al. 2009) relaxation of surface energy is related with rotational displacement of new-formed surface polar groups into a PET bulk (under the surface), because air is less energy-favorable media for them existence.

Interesting, that adhesion performance of modified PET to model scotch changes the same way (Fig. 11). Since polar groups turns under the surface during storage in contact with air the adhesive strength decreases. So it's obvious for us that the first growth of adhesion performance is related to functionalization of PET surface due to plasma treatment.

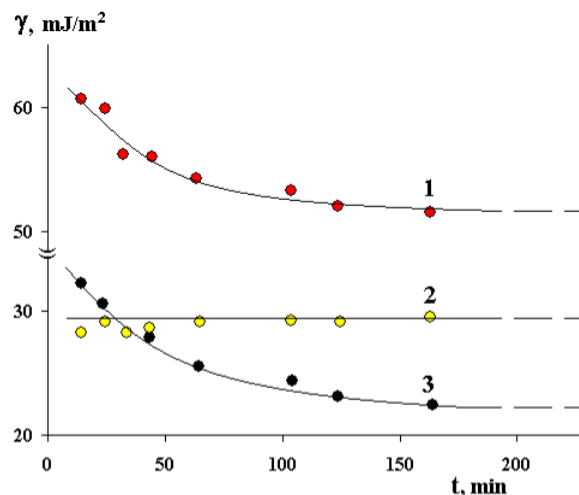


Fig. 10. Relaxation of surface energy (1) and its disperse (2) and polar (3) parts during 200 min storage in room conditions.

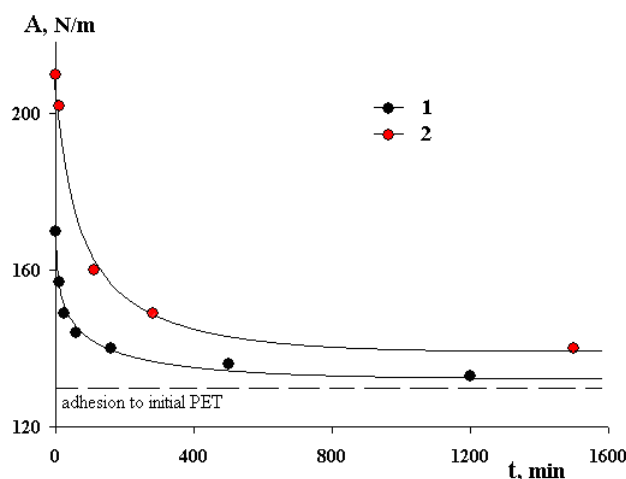


Fig. 11. Alteration of adhesion properties (Peel Strength) of plasma modified PET during storage in room conditions. Treatment duration was 5 min (1) and 20 min (2). Dotted line shows the adhesive strength of untreated PET to the same model scotch.

Turning back to Equation 1, we should note that surface modification in high-frequency air discharge plasma doesn't lead to change the mechanical response of the system (ψ), but strongly effect on the first component W_0S . At that, nanoscale changes of surface relief and contact area don't effect on total value of adhesive strength. Peel strength of adhesive joints with model scotch dramatically increase because of surface functionalization of PET after plasma treatment. Relaxation of surface energy and its adhesive performance can be related to rotational displacement of new-formed surface polar groups into PET bulk.

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