PHYSICOCHEMICAL PROCESSES
AT THE INTERFACES

Plasma Chemical Modification of Polymer Surface. Polyethylene Terephthalate

A. A. Shcherbina and A. E. Chalykh

Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences,
Leninskii pr. 31, bldg 4, Moscow, 119071 Russia
e-mail: aachalykh@mail.ru
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Abstract—Methods of electron microscopy, atomic force microscopy, contact angles, multiple attenuated total internal reflection IR spectroscopy, and X-ray photoelectron spectroscopy were used to study the molecular-chemical, structural and morphological, and energy characteristics of polyethyleneterephthalate (PET) surfaces before and after treatment in plasma of high-frequency air discharge. It is shown that modification of PET surface results in a change in the structural-morphological surface properties and the formation of oxidized near-surface layers. The peel test was used to determine the adhesion characteristics of the substrate with respect to a standard adhesive. It is shown that the decisive role in providing high strength of adhesive joints in the course of plasma chemical modification is played by a significant increase in the surface energy of the substrate, namely its polar component. The kinetics of relaxation of surface characteristics of the substrate are studied in the case of long-term storage under laboratory conditions.

INTRODUCTION

Modification of the surface of polymer materials in order to give them required functional properties is at present used in various fields of polymer materials science. In the literature, different methods are described used to actively affect the molecular-chemical and structural-morphological characteristics of surface layers of polymer fibers, films, membranes, coatings, cloths. etc. A special place among these methods is occupied by the methods of plasma treatment of a polymer surface [1], which are widely used, in particular, to change the surface energy and increase the hydrophilicity of polymers [2−5]; regulate their adhesion properties [6−9]; and provide bio- and blood-compatibility of material [10−12], covalent grafting of polar groups and polymer chains into the polymer surface [13−15], and improvement of biodegradability of polymer materials [16]. Nevertheless, issues regarding the stability of structural and physicochemical surface parameters after plasma chemical modification remain open.

The aim of this work was to perform a complex study of the surface of a PET polymer substrate after plasma chemical modification and monitor variation of characteristics in the course of long-term storage.

EXPERIMENTAL

The polymer substrate used in the work represented industrial biaxially−oriented films of polyethylene-terephthalate (PET) of different thicknesses (5 and 20 μm) (NPO Plastmassy, Russia) that are used for industrial production of bi- and trilayer protective films and coatings.

Thermochemical characteristics of the initial films $T_{melt} = 250-260°C$, $T_{Tg} = 80°C$ were determined using the differential scanning calorimetry (DSC) technique. The crystallinity degree of PET did not exceed ~10%.

The PET surface was treated by plasma of high-frequency (HF) air discharge in an Edwards E306A vacuum chamber (Fig. 1) at a pressure of 0.09 mm Hg. The generator frequency was 10 MHz, and the voltage
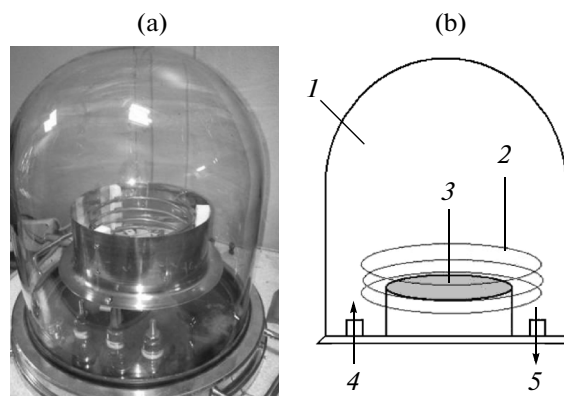

Fig. 1. (a) Vacuum chamber with burning plasma of HF air discharge and (b) scheme of the etching node of the setup. (*1*) Vacuum chamber, (*2*) reactive coil, (*3*) sample stage, (*4*) air, and (*5*) plasma products.
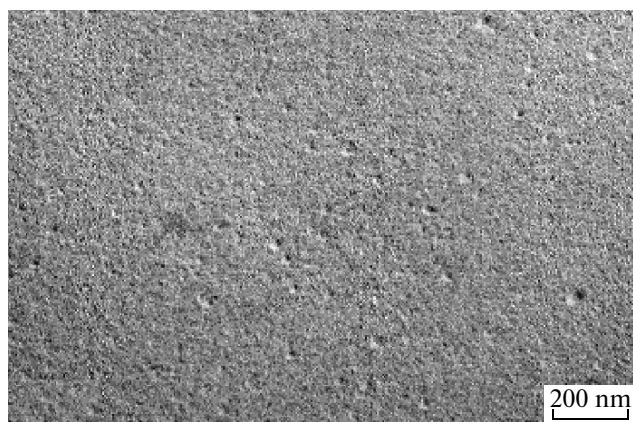
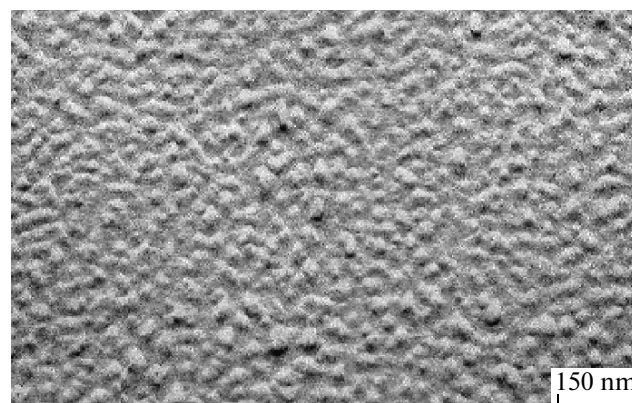**Fig. 2.** Microphotograph of PET surface before etching.

Fig. 3. Microphotograph of surface morphology of PET after etching for 30 min.

amplitude was 1.2 kV. The energy of electrons in the etching region did not exceed 2–4 eV according to the data of a double electric probe; i.e., the "soft" etching mode was used, as opposed to in [17, 18]. The etching duration was varied from 1 to 60 min. The PET film was set on an object stage inside a reactive coil (Fig. 1b). Preliminary studies show that the position of the sample within the reactive coil does not affect the etching kinetics and etched surface morphology. This is one of the specific features of plasma of HF gas discharge.

The morphology of the PET surface before and after treatment in plasma of HF discharge was studied with the help of two-stage carbon-platinum replicas using the transmission electron microscopy technique on an EM-301 microscope (Philips).

The surface topography of PET samples was found on a Centaur atomic probe microscope (NanoScan Tech) in the semicontact regime. The probe diameter was ~2 nm.

The chemical composition of the PET surface was studied using the methods of Fourier-transform IR spectroscopy in the attenuated total internal reflection regime and X-ray photoelectron spectroscopy (XPS). IR spectra were recorded in the static and dynamic modes on a HYPERION 2000 Fourier-transform IR microscope (Bruker) (Ge crystal) combined with an IFS-66 v/s Fourier-transform spectrometer (Bruker). Electronic spectra of etched PET surfaces were recorded on an XSAM-800 spectroscope (Kratos Analytical Ltd). The spectra were obtained 12 h after plasma chemical treatment of the substrate surface.

Surface energy of the objects and its variation after plasma chemical modification, as well as after long-term storage of films in air at a temperature of $22 \pm 1°C$ was determined using the contact angle technique with the help of a number of test liquids (polyethylene glycol, water, glycerol, tricresyl phosphate, diiodomethane) on an FM40 EasyDrop automatic setup (Kruss GmbH). Surface energy γ and its polar γ^P and dispersion γ^D components were calculated within the Owens–

Wendt approach using the software package provided with the device.

Adhesion properties of the initial and plasma-modified films were studied using 180° peel test on a Z010 Tensile Tester (Zwick/Roell) at the rate of 10 mm/min. For this purpose, adhesive joints of PET with model industrial scotch tape (3M, United States) based on partially cross-linked silicon adhesive were prepared. The time of contact between the scotch tape and PET did not exceed 5 min. A standard roller (450 g) was used to bond the joint components; lamination was carried out in the absence of additional pressure.

RESULTS AND DISCUSSION

Preliminary gravimetric measurements on an ME235P, SARTORIUS analytical balance with a sensitivity of 10^{-5} g were used to determine the kinetics of etching of model PET film samples in the HF discharge plasma. It was found that there was a linear dependence of the sample mass loss on the treatment duration. The mass rate of PET etching is determined, which is 0.19–0.20 mg/(cm² h) and is independent of the polyether film thickness. Thus, one can state that the etching front penetrates to the depth of ~2.5 nm in 1 min to ~150 nm in 60 min in the course of plasma chemical modification of the PET film surface.

Typical microphotographs of PET surface before and after treatment in HF air discharge plasma are shown in Figs. 2–4. One can see that the surface of the initial PET is not characterized by any noticeable profile. Etching for 10–40 min reveals the domain structure typical for amorphous glassy polymers [19, 20]. The average domain diameter is ~15–17 nm, which correlated with the diameter of inhomogeneity estimated on the basis of the data of small angle X-ray scattering [20]. When the etching is more prolonged (etching depth up to 200 nm), inhomogeneity of the structural-morphological film organization are revealed (Fig. 4) with a size of ~60 nm, which is probably related to the
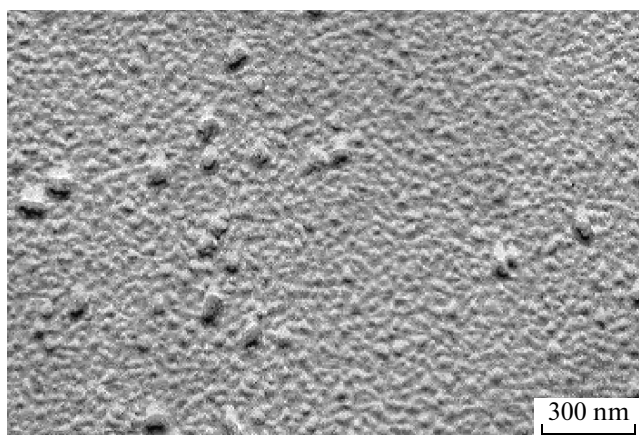
Fig. 4. Microphotograph of surface morphology of PET after etching for 65 min.

Fig. 5. Dependence of (1) PET surface energy (*1*) and its (*2*) polar and (*3*) dispersion components on the etching time in HF air plasma.

specifics of the molecular-mass substrate characteristics.

Variation of the surface profile in the course of PET etching is also observed in measurements on the atomic force microscope. Herewith, if the profile height was only 2−3 nm for the initial substrate, etching for 35−40 min leads to a profile height of 6−8 nm. It is of interest to point out that, according to the data of electronic microscopy and atomic force microscopy, the surface profile and domain structure parameters reached a certain steady-state value at the PET etching times of 35−40 min and further remained practically unchanged within the measurement accuracy. Let us note that, under the chosen conditions, no etching of a structural-morphological carpetlike type formation appearing under PET erosion is observed in the atomic oxygen flow and under electronic bombardment with the energy of 15−30 eV [21, 22].

The process of the "soft" etching of PET films is accompanied by polymer destruction and variation of the molecular−chemical surface composition [19]. This effect is illustrated in Fig. 5, where kinetics curves of variation of surface energy (γ) and its dispersion (γ^D) and polar (γ^P) components vs. etching time are shown. One can see that the γ value for the initial films was 38.6 mJ/m^2. At an increase in the etching time, surface energy of PET increases and asymptotically approaches the steady-state value of ~64.6 mJ/m^2. Meanwhile, considerable surface activation to 61−62 mJ/m^2 occurs already in the first 20 min of etching. The further increase in the etching time to 60 min introduces no significant corrections into the surface characteristics of PET.

The main contribution to variation of surface energy is introduced by its polar component γ^P changing from 4.2 to 43.0 mJ/m^2. Dispersion component γ^D of surface energy related to the packing density of macromolecular fragments in the surface layer decreases from 30 to 25 mJ/m^2. This change is, however, not critical. When one compares the obtained
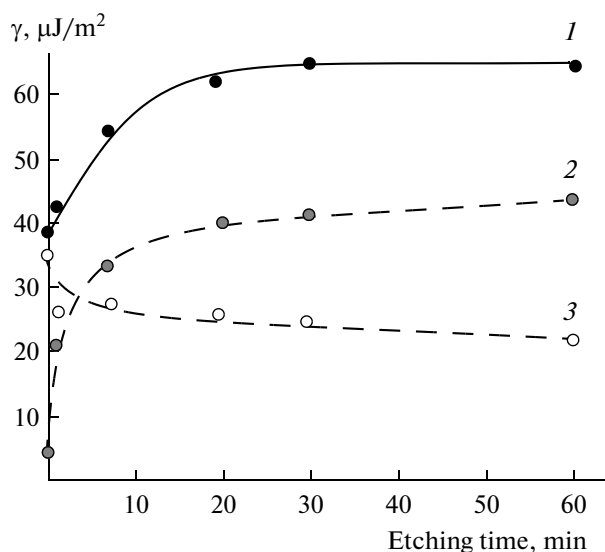
data with the energy characteristics of the test liquid surface [23], it is obvious that they are close to the values of γ, γ^D, and γ^P of polar liquids: glycerol ($\gamma^P = 30$, $\gamma^D = 34$, and $\gamma = 64$ mJ/m^2) and ethylene glycol ($\gamma^P = 19.0$, $\gamma^D = 29.3$, and $\gamma = 48.3$ mJ/m^2). This result allows us to suggest that formation occurs of polar groups, e.g., hydroxyl, on the surface of modified PET.

The data of the X-ray photoelectron spectroscopy shown in Fig. 6 and in Table 1 demonstrate unambiguously that PET treatment in HF air discharge plasma results in formation on its surface of nitrogen- and oxygen-containing functional groups (internal levels of N1*s* and O1*s*). The overall amount of nitrogen incorporated into the surface PET layer for 20−35 min of etching is 4.7 at % (Table 1).

The intensity of the O1*s* peak increases at an increase in the etching time, which correlated with the data of IR spectroscopy. It is found that plasma treatment leads to a change in the intensity of the absorption bands in the ranges of 3500 and 1760−1540 cm^{-1}, which points to formation in the surface layer of samples of hydroxyl, carboxyl, and carbonyl groups, respectively [24]. It is worth noting that the data of XPS and IR spectroscopy are independent of the

Table 1. Elemental composition of PET surface before and after its modification in high-frequency air discharge plasma

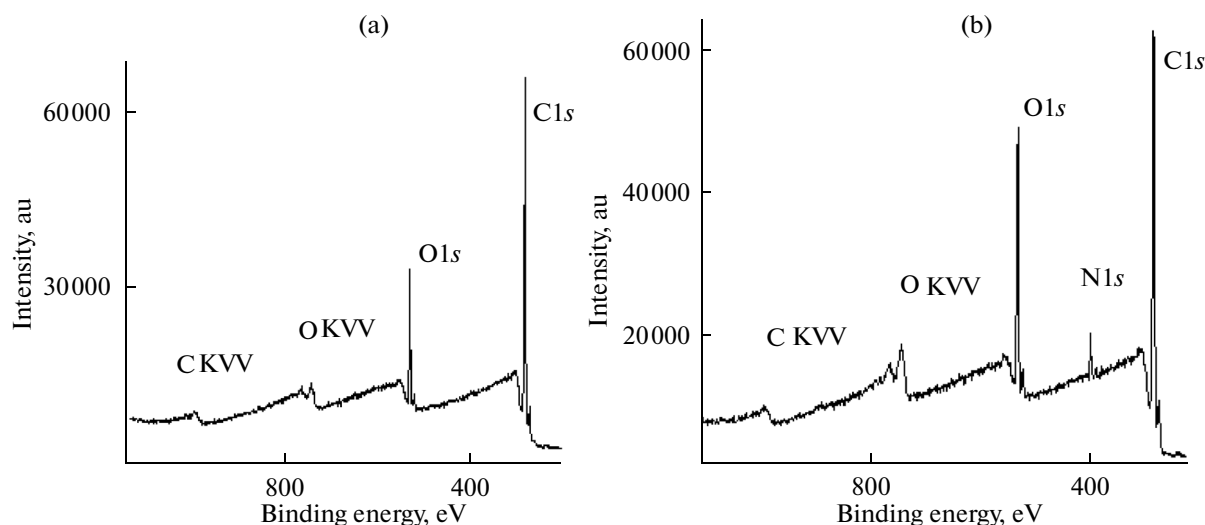| PET	Element content, at %		
	carbon	oxygen	nitrogen
Initial	78.6	21.4	−
Modified	69.5	25.8	4.7

Fig. 6. Electronic spectra of the surface of (a) the initial and (b) plasma-modified PET. The substrate thickness is 20 μm; the etching time is 20 min.
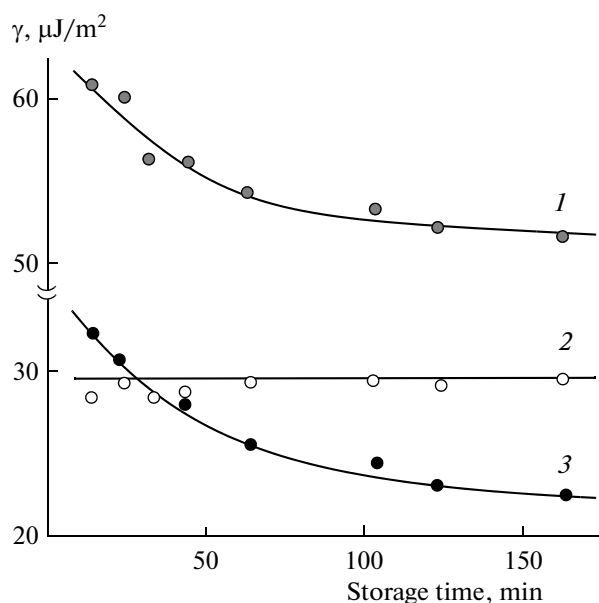

Fig. 7. Relaxation of (*1*) surface energy and its (*2*) dispersion and (*3*) polar components in 200 min of storage at room temperature and pressure.
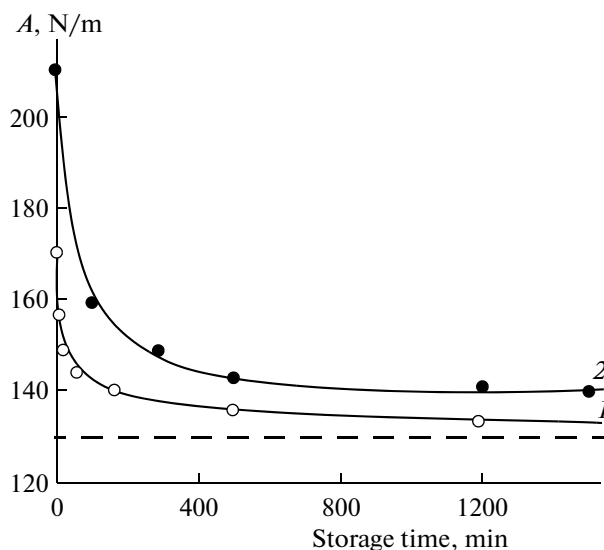

Fig. 8. Kinetics of variation of adhesion strength of plasma-modified PET to model scotch tape in the course of storage of the modified substrate at the room temperature. The etching time is (*1*) 5 and (*2*) 30 min. The dashed line corresponds to the adhesion strength between untreated PET and model scotch tape.

thickness of PET films, as are the results of measurement of surface energy of etched polyether samples.

The strength of the adhesion contact between PET modified in HF discharge plasma and the model scotch tape increases symbatically to the increase in surface energy (Table 2). Despite the fact that some authors [24, 25] relate the effect of an increase in peel resistance after plasmochemical exposure to removal of thin, "weakly bound" layers of surface impurities, we believe that an increase in adhesion strength of the contact is primarily related to an increase in adsorp-tion interaction of polar groups of the modified substrate and adhesive.

It is found that the molecular-chemical organization of the PET surface formed in the course of etching is unstable in the absence of gas discharge plasma. This result is also illustrated in Figs. 7 and 8, where kinetic curves of spontaneous variation of surface energy of etched samples and their adhesion characteristics in the course of long-term storage at room temperature (23 ± 1°C and relative humidity of 48 ± 2%) are shown. One can see that the initially high values of surface energy and peel resistance immediately after PET
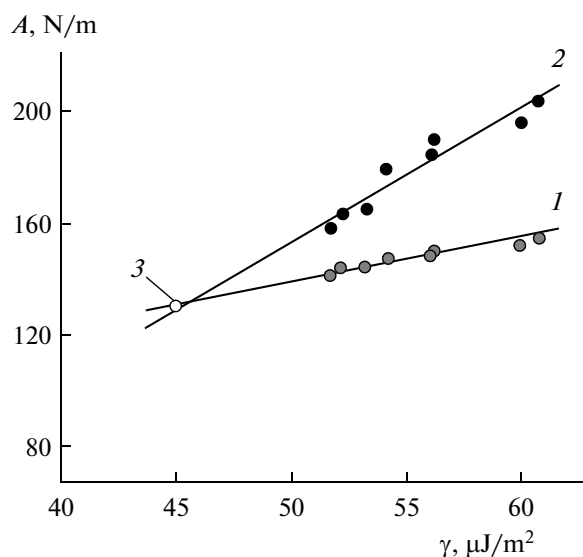
Fig. 9. Correlation dependence in the Deboer coordinates of peel resistance of the PET-model scotch tape adhesion contact on surface energy of PET for different storage times of the modified substrate. The etching time of PET is (*1*) 5 and (*2*) 20 min. (*3*) Initial unmodified PET.

treatment decrease and approach asymptotically the value of $\gamma = 45$ mJ/m^2 close to the surface energy of PET [26] and peel resistance of the initial system. Let us point out that we obtained similar results earlier [27] for copolymers of ethylene and vinyl acetate.

The rate of a decrease in the γ and A values is rather high, especially in the first ~40 min of storage. Practically complete relaxation of surface energy γ is observed in ~180 min of storage. The overall surface energy decrease in the course of storage occurred due to a decrease in the polar component, while the dispersion mode remained practically unchanged in the whole course of observation. These results agree with the data of morphology studies that showed that the surface profile remained unchanged in the course of storage of modified samples.

It is of interest to note that a linear correlation dependence between surface energy and peel resistance is observed in Deboer coordinates at all stages of aging of film modified PET samples (Fig. 9). One can see, first, that the slope of these dependences is determined by the chosen value of the point in the kinetic

Table 2. Peel resistance (*A*, N/m) of the adhesion contact of PET−model scotch tape at different etching times in high-frequency discharge plasma

Etching time, min	0	5	20
A, N/m	130	170	210
γ, mJ/m^2	38.8	50.1	63.0

curve of the start of the aging process and, second, that linear correlation dependences intersect each other in the point corresponding to the values of γ and A of the initial PET sample. This points to a long-term trend toward modified polyether storage.

Thus, one can state that etching even under comparatively soft conditions results in formation of a specific domain profile on the surface of PET film samples, which is related to supramolecular polyether organization. Simultaneously, variation of the molecular-chemical surface composition is observed due to formation of nitrogen- and oxygen-containing functional groups on the etched surface. It is shown that the structural-morphological organization of the PET surface formed in the course of etching is unstable in the absence of gas discharge plasma. Spontaneous variation of the surface energy of etched samples and their adhesion characteristics is observed in the course of storage due to recombination of functional groups and conformation reorganization of macromolecules in surface layers. It is suggested that the adhesion properties of air discharge plasma-modified PET substrates are determined by adsorption interactions of surface functional groups.

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