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Surface Modification of Polyfluoroolefin Films by Glow Discharge

A. B. Gilman, M. S. Piskarev, M. Yu. Yablokov, and A. A. Kuznetsov

Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences,
ul. Profsoyuznaya 70, Moscow, 117393 Russia
e-mail: plasma@ispm.ru

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Abstract—Effect of dc discharge treatment on the surface properties of polyfluoroolefin films was studied. It is found that modification leads to significant improvement of contact properties. It is shown that the efficiency of treatment on the anode and cathode depends on the chemical structure of polymers. Changes in the composition and structure of polymer films were studied by X-ray photoelectron and Fourier transform IR spectroscopy, and the formation of new oxygen-containing groups was found. A procedure for quantitative assessment of the adhesion characteristics of polyfluoroolefin polymer films modified by plasma was developed.

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INTRODUCTION

Fluorine-containing polymers have unique chemical and physical properties, and, at the same time, they have low surface energies, poor wettability and binding power, poor adhesion to sputtered metals, etc. To improve the contact properties of the polyfluoroolefin surface is a practically important task for many applications.

At present the contact properties of the polyfluoroolefin surface are improved by means of chemical etching [1] and by treatment by plasma of various discharges: corona [2], dielectric barrier [3], high-frequency (13.56 MHz) [1, 4], radiofrequency (2.45 GHz) [5], or low-frequency (50 Hz) [6]. There methods allow one to improve the contact properties of the polymer surface, but the water contact angle (θ) for, specifically, poly(tetrafluoroethylene) (PTFE) still remains fairly large (≥55°). As the discharge power increases, the etching rate of the PTFE surface increases, and its contact properties are not improved [1]. For the contact properties to be improved by high-energy chemistry methods, treatment parameters should be optimized so that the surface is largely functionalized rather than etched. What process is preferred depends not only on the nature of the working gas and the type, power, and other parameters of the discharge, but also on the chemical nature and structure of the polymer. For example, treatment of PTFE in the afterglow of a high-frequency discharge in oxygen did not appreciably decrease the contact angle; moreover, the θ value increased to 160° with increasing discharge power [7]. This result is probably explained by the fact that the surface roughness enhanced due to etching, whereas its chemical composition remained almost the same. At the same time, treatment of poly(vinylidene fluoride) (PVDF) films in the afterglow of an oxygen plasma [8], as well as their bombardment with argon ions [9] decreased the contact angle from 90° to 71° and 31°, respectively.

In the present paper we summarized the results of our research on the effect of dc glow discharge treatment on the surface properties and chemical structure of a series of polyfluoroolefin films. The advantage of the dc glow discharge that it allows separate exposure of films to be modified to positively and negatively charged reactive plasma species by treatment on the cathode or anode.

EXPERIMENTAL

Commercial films of PTFE (thickness of 40 μm), copolymers of tetrafuoroethylene with hexafluoropropylene (F4MB, 80 μm), ethylene (F40, 50 μm), and perfluoro(propyl vinyl ether) (80 μm), as well as copolymer of vinylidene fluoride with hexafluoropropylene (F62, 50 μm), produced by Plastpolymer (St. Petersburg, Russia), were used. Thus, the polymers

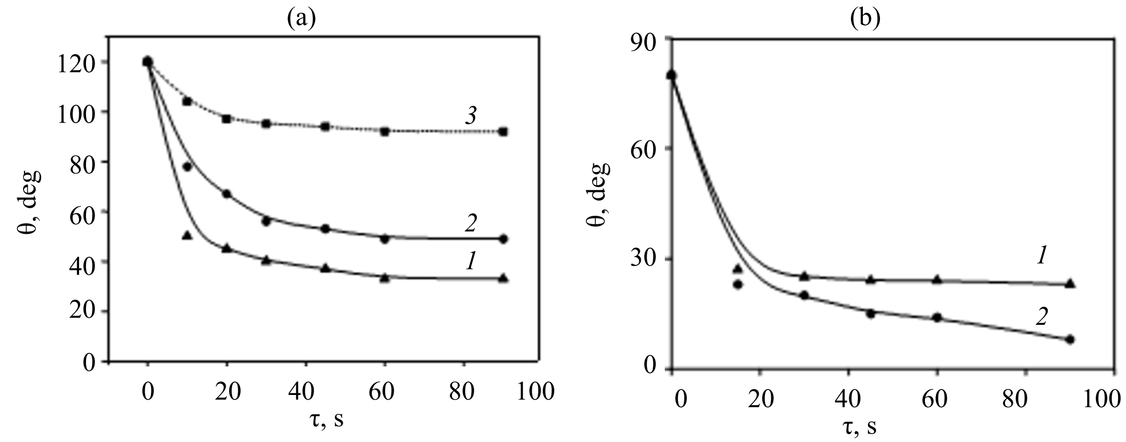

Fig. 1. Dependences of the water contact angles of the (a) PTFE and (b) PVDF films on the time of dc discharge treatment (discharge current of 50 mA) on the (*1*) anode and (*2*) cathode. For comparison: (*3*) Dependence for the PTFE film modified by a low frequency glow discharge (50 Hz).

studied in this work included both perfluorinated polymers [PTFE, F4MB, F50] and polymers containing hydrogen atoms along with fluorines [PVDF, F40, F62].

The procedure of dc discharge film modification was detailed in [10]. The samples were mounted on the cathode or anode, treatment was performed in the flow mode at the working gas (air) pressure of 10–20 Pa and discharge current of 10–50 mA for 10–90 s.

The changes in surface properties were characterized by the contact angles measured on an Easy Drop DSA100 instrument (KRUSS, Germany) with a Drop Shape Analysis V.1.90.0.14 software, using two test liquids (deionized water and glycerol), with an error of ±1°. The measurement results were used to calculate, by the procedure described in [11], the work of adhesion, as well as the total surface energy (γ) and its polar (γ^p) and dispersion (γ^d) terms.

Surface analysis of films was performed by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy.

The XPS spectra were registered on a Riber LAS-3000 instrument equipped with an OPX-150 hemispherical retarding-field analyzer using an AlK_α X-ray source (1486.6 eV), at an accelerating voltage of 12 kV and emission current of 20 mA. The C1s level (284.6 eV) was used as reference [13, 14]. The atomic element concentrations were calculated by standard formulas from the XPS peak areas and corresponding element sensitivity factors [15].

The reflection spectra were measured on a Bruker Equinox 50S FTIR spectrometer with a MIRacle single reflection horizontal ATR accessory, using a ZnSe crystal, over the range of 400–4000 cm^{-1}; data of 500 scans were collected with a scanning step size of 2 cm^{-1}. Band assignment was performed according to [16, 17].

Adhesive properties of films were studied by a procedure specially developed for plasma-modified thin films, using a Scotch®810 adhesive tape [18]. The T-peel test was performed on a Shimadzu Autograph AGS 10 KNG universal testing machine at a crosshead speed of 100 mm/min. As a result, a curve presenting the change in the peel resistance along the sample length was obtained.

Properties of Polyfluoroolefin Films Modified by DC Glow Discharge Treatment

The dependences of the water contact angle on the time of dc discharge treatment on the anode and cathode for PTFE [19] and PVDF films [20] (Fig. 1) are quantitatively similar to each other: The strongest changes in θ occur within the first ~20 s, after which the curves gradually flatten out, and at $\tau \geq 60$ s the θ value virtually no longer changes. With PTFE films, smaller θ values were obtained under treatment on the anode (33° vs. 49° on the cathode); similar results were obtained for the other pefluoroolefin films F4MB [21] and F50 [22]. With PVDF, by contrast, smaller θ values were obtained under treatment on the cathode (10° vs. 23° on the anode); similar results were obtained for the other pefluoroolefin films containing hydrogen atoms along with fluorines, specifically, F62 [23] and F40 [24].

Study of the dependence of the contact angle on discharge current at $\tau = 60$ s showed that lower θ values for the PTFE films are obtained on their

Table 1. Contact properties of the surface of the starting and modified polyfluoroolefin films[a]

Polymer	Contact angle, deg		Work of adhesion W_a, mJ/m^2		Surface energy, mJ/m^2		
	water	glycerol	water	glycerol	γ	γ^p	γ^d
PTFE	120[b]	106	36.4	45.9	13.18	0.03	13.15
	33[c]	26	133.9	120.4	61.50	42.0	19.50
	49[d]	40	120.6	112.0	50.70	29.3	21.40
F4MB	108	94	50.3	59.0	18.00	0.6	17.50
	20	17	141.2	124.0	68.70	51.8	16.90
	49	44	120.6	109.0	50.00	33.3	16.70
F50	112	95	45.5	57.8	21.34	0.03	21.31
	54	48	115.6	105.8	46.20	28.9	17.30
	70	63	97.7	92.2	33.90	17.7	16.20
Poly(vinylidene fluoride)	80	70	85.4	85.0	17.70	8.9	8.80
	23	17	139.8	124.0	67.20	48.7	18.50
	10	8	144.5	126.2	72.10	55.5	16.60
F40	89	85	74.1	68.9	19.20	11.0	8.20
	15.5	18	143.0	123.7	71.00	56.4	14.60
	8	11	144.9	125.6	72.80	57.4	15.40
F62	81	75	84.2	79.8	25.30	12.8	12.50
	7	8	145.0	126.1	72.90	56.8	16.10
	6	7	145.2	126.3	73.10	57.0	16.10

[a] Treatment by dc discharge, I = 50 mA, τ = 60 s. [b, c, d] Estimates for the starting polymer, treated on the anode and on the cathode, respectively.

treatment on the anode [9]; similar results were also obtained with F4MB and F50. With PVDF films lower θ values were obtained on their treatment on the cathode [20]; the same was the case with F62 and F40. These results suggest that bombardment of polyfluoroolefin films containing hydrogen atoms with positive ions of dc discharge plasma, an additional reaction channel involving hydrogen abstraction is realized. It should be noted that if the PTFE films are treated simultaneously by negatively and positively charged components of plasma generated by low-frequency glow discharge with a frequency of 50 Hz (Fig. 1a, curve *3*), the contact angle much increases up to θ = 85° [25].

Thus, modification of polyfluoroolefin films results in much smaller water contact angles if the films are separately treated by dc discharge on the anode or cathode and thus exposed to either positively and negatively charged plasma components.

Table 1 presents the surface characteristics of polyfluoroolefin films before and after treatment in a dc discharge on the cathode and anode. As seen, discharge treatment renders the film surface hydrophilic; the surface energy much increases, and this change is mostly contributed by the polar component.

In terms of the response to treatment, the studied polymers can be divided into two groups: perfluorinated polyfluoroolefins (PTFE, F4MB, F50) which are more responsive to treatment on the anode and polyfluoroolefins containing hydrogen atoms (PVDF, F40, F62) which are more responsive to treatment on the cathode. It should be noted that dc discharge treatment results in smaller contact angles and higher adhesion works and surface energies than other known methods of polyfluoroolefin modifications [1–9, 25].

It is important for practical applications of modified films that the films have low contact angles not only immediately after plasma treatment, but also that they should retain a good wettability for a long time. As seen from the dependences in Fig. 2, the contact angles in the films treated both on the anode and on the cathode tends to gradually increase, and the strongest changes occure within the first three days. On further storage the contant angles virtually no longer changes: the curves flatten out, and the θ values reached after 14 days remain the same for a few months. The contact angles of the polyfluoroolefin films modified on the anode (Fig. 2, curves *1a* and *2a*), whatever the chemical composition of the polymer, increases to a lesser extent. Even if lower θ values were obtained for films treated on the cathode, for example, for the PVDF film (curve *2c*), a day after treatment the θ angle was higher compared with that for the same film modified on the anode (curve *2a*) [12, 20].

We also studied the effect of the temperature on the contact angle of the dc discharge-modified PTFE and F40 films [12] (Fig. 3). As the temperature is increased, the θ value for both films increases and their wettability is deteriorated. The contact angle of the PTFE film treated on the cathode much stronger increases with temperature compared to that treated on the anode. After a certain temperature point the curves flatten out. Similar temperature dependences were also observed for the F40 film. Generally the temperature changes in the polyfluoroolefin films modified both on the cathode and on the anode are similar to the changes that occur as these films are stored in air, but in the first case the contact angle increases to a greater extent.

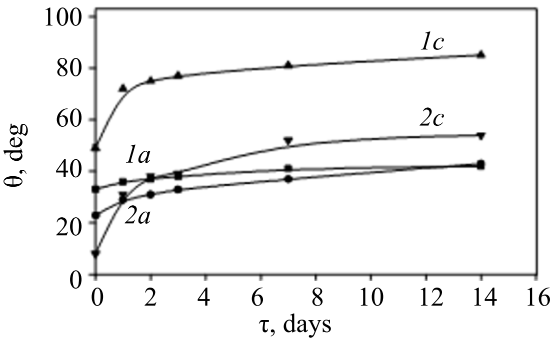

Fig. 2. Dependences of the water contact angles of the (*1*) PTFE and (*2*) PVDF films treated by dc discharge on the (*1a, 2a*) anode and (*1c, 2c*) on the time of their storage in air.

The XPS spectra of the polyfluoroolefin films before and after dc discharge treatment on the anode and cathode (Table 2) showed that the atomic concentration of fluorine in the exposed films appreciably decreases, the carbon concentration increases, and new oxygen-containing groups appear.

According to the FTIR data [10, 12, 19–24], the spectra of the modified polyfluoroolefin films differ from those of the starting films by increased intensity of bands at 1650–1900 cm^{-1} belonging to oxygen-containing groups and multiple bonds, as well as at 3500–3600 cm^{-1} assignable to the water adsorbed by the polymer film [16, 17]. At 1600–1900 cm^{-1}, there are three well-defined bands (1880, 1720, and 1650 cm^{-1}). The first two bands are likely to belong to stretching vibrations of C=O groups, including –C(O)–F– (1880 cm^{-1}) [16, 25, 26]. The bands at 1885 and 1775 cm^{-1} are probably associated with the per-

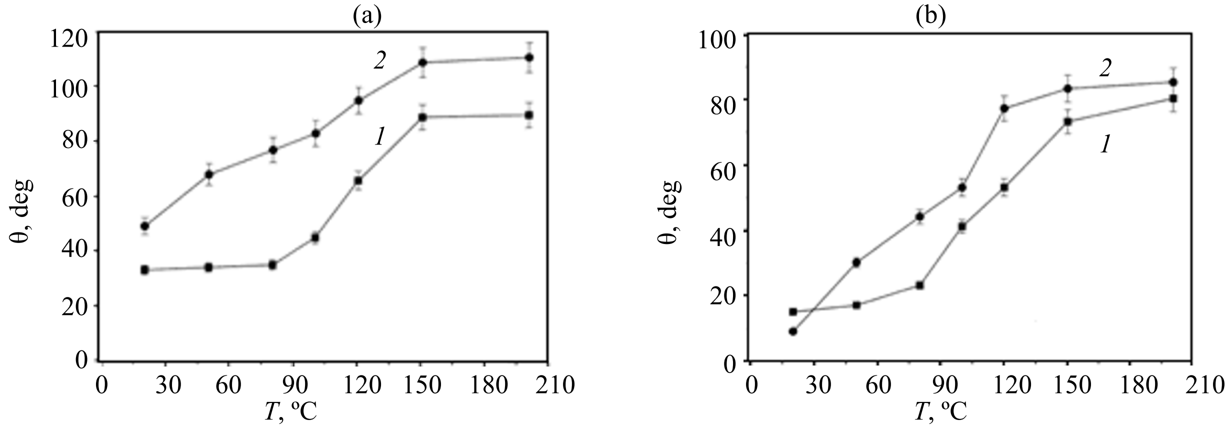

Fig. 3. Temperature dependences of the water contact angles of the (a) PTFE and (b) F40 films treated by dc discharge on the (*1*) anode and (*2*) cathode.

Table 2. XPS data for the starting and modified polyfluoroolefin films[a]

Polymer	Atomic ratio	
	F/C	O/C
PTFE	1.89[b]	–
	1.15[c]	0.32
	1.79[d]	0.36
F4MB	1.86	–
	1	0.41
	1.72	0.23
F50	1.96	0.02
	1.05	0.27
	1.23	0.34
Poly(vinylidene fluoride)	0.98	0.02
	0.91	0.09
	0.89	0.11
F40	1	–
	0.39	0.32
	0.58	0.31
F62	1.31	0.09
	0.32	0.47
	1.1	0.38

[a] Treatment by dc discharge, $I = 50$ mA, $\tau = 60$ s. [b, c, d] Estimates for the starting polymer, treated on the anode and on the cathode, respectively.

fluoroketone groups formed by fragmentation of tertiary perfluoroalkoxide radicals [29, 30]. The absorption band at 1650 cm^{-1} can be assigned to the C=C bonds formed by both fluorine and hydrogen abstraction from the polymer chain [27, 29, 30].

The XPS spectra of the PTFE films [12] allowed us to find out how the composition and structure of the films vary depending on their treatment conditions and on environmental factors. The spectrum of the starting film (Fig. 4a) has a peak at 292.2 eV due to CF_2 groups and a small peak at 281 eV assignable to some admixtures in the polymer [19, 25–27]. The F/C ratio in the starting polymer is 1.89. Treatment of the film by dc discharge on the anode strongly affects the C1s spectrum (Fig. 4b). The spectrum was resolved into five peaks: *1,* 284.6 eV (C–C, C=C); *2*, 286.5 eV (C–O–C, C–O, C–N, C–CF); *3*, 289.5 eV (C–F, O–C=O, CF–CF_2); *4*, 292,4 eV [$–(CF_2–CF_2)_n–$], and *5*, 293.6 eV (CF_2–O, CF_3).

The F/C ratio in the polymer treated on the anode decreased to 1.15. Thus, the film surface becomes hydrophilic both due to the formation of polar groups with different structures and due to decreased number of fluorine-containing groups.

In the C1s spectra of the modified films stored in air (Fig. 4c), the intensity of peaks *4* and *5* associated with fluorine-containing groups is increased and the intensity of peak *2* which is the principal peak of oxygen-containing and other polar groups is decreased. These results are consistent with the fact that the contact angles increase with time of storage. It is a common opinion that the increase in the θ angle of plasma-modified polymers as they are stored or heated is associated with thermodynamic relaxation processes, specifically, surface-to-bulk transfer of functional groups [10, 12, 19–28].

The pattern of the C1s spectra of the films heated after modification (Fig. 4d) differs from the spectrum obtained immediately after plasma treatment by slightly increased relative intensities of peaks *4* and *5* (with respect to peak *1*), which relate to the number of surface fluorine-containing groups, and increased intensity of peak *1* (with respect to the total height of the C1s peak), which is associated with the polymer carbon backbone (C–C, C=C). The latter fact points to increased number of unsaturated bonds [10, 26, 27]. A slight change in peak *2* belonging to polar groups should also be mentioned. Apparently, polar fragments of the polymer chain can be linked to both “long” and “short” chains formed by plasma-induced destruction of the polymer. Such fragments differ in the relaxation behavior. If the “short” chains can undergo surface-to-bulk transfer at room temperature, the relaxation of “long” chains occurs exclusively as a change in the conformation of the chain containing polar end groups which turn out to be inside the coil and cannot relax into the bulk of the sample. The fact that the atomic concentration of oxygen, as evidenced by the XPS spectrum of the modified polymer heated in air to 200°C, can be explained by the plasma-induced reaction of radicals with oxygen which more actively diffuses into the polymer [27]. The XPS analysis of the surface layer (≤ 10 nm) showed that the surface contains sufficient number of polar groups which do not affect its contact properties.

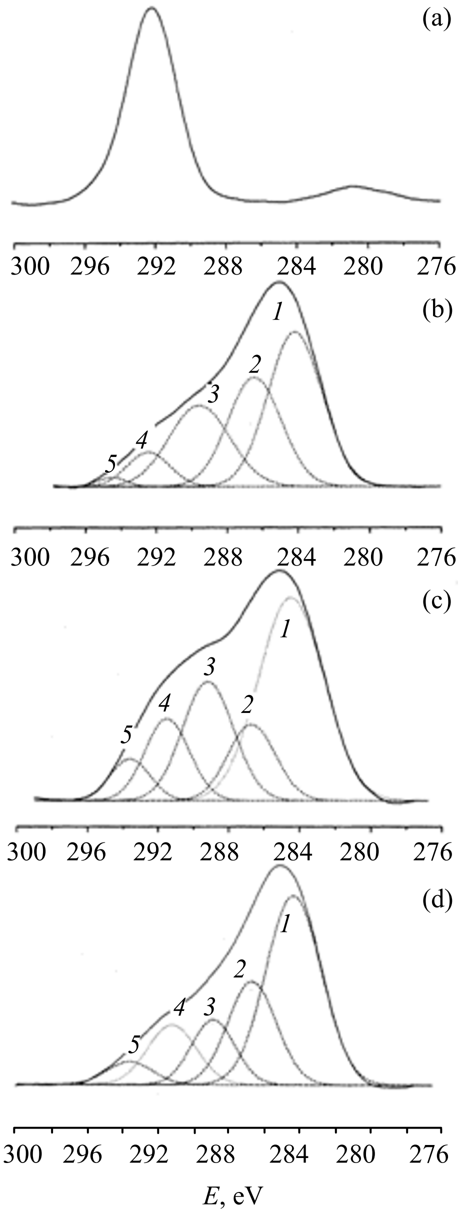

Fig. 4. XPS C1s spectra of the PTFE films: (a) starting film, (b) modified on the anode, (c) modified on the anode and stored for 14 days, and (d) modified on the anode and heated at 200°C.

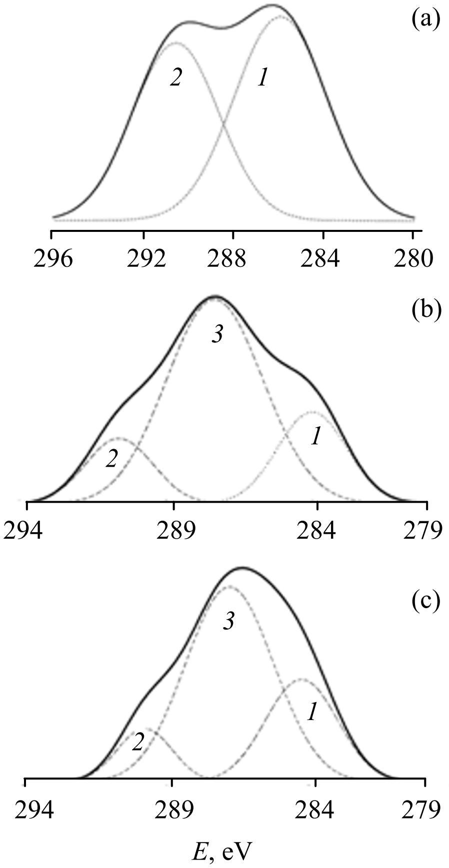

Fig. 5. XPS C1s spectra of the F40 films: (a) starting film, (b) modified on the cathoe, and (c) modified on the anode.

The results of the XPS study of the F40 film are as follows (Fig. 5). The spectrum of the starting films shows two peaks of carbons linked to hydrogen (286 eV, peak *1*) and fluorine (290 eV, peak *2*). The spectrum of the film treated on the cathode contains three peaks: *1*, 284 eV, *2*, 291 eV, and a new peak *3,* 288 eV (carbon linked to oxygen). The same peaks are observed in the spectrum of the film modified on the anode. However, the surface concentration of oxygen in the film modified on the cathode is 18.7 at %, whereas the respective value for the film treated on the anode is 12 at %. The changes in the surface structure of the F40 film, induced by discharge treatment, suggest formation of fragments like C(O)F and C(O)H [24, 29, 30].

It is presently commonly accepted that plasma modification involves exclusively the surface of a polymer and a thin subsurface layer whose thickness, according to different estimates, varies from a few tens of nanometers to a few microns; however, no published experimental evidence for these estimates is available [28]. In [31, 32] we attempted to estimate the thickness of the plasma-modified PTFE layer by means of IR spectral ellipsometry. It was found that the modified layer of the PTFE sample (10-mm thick plate fabricated by mechanical cutting) obtained by dc discharge treatment is 732±37 nm, and the thickness of the rough layer is 353±16 nm. However, this method does not provide direct experimental evidence, because it includes constructing models and fitting

Table 3. Peel resistances of the starting and modified polyfluoroolefin films[a]

Polymer	Peel resistance, N/m		
	after treatment	after storage	after heating
PTFE	–[b]	30±6	–
	200±10[c]	189±9	168±9
	134±4[d]	78±5	81±8
F4MB	–	33±4	–
	162±14	177±14	63±7
	153±8	154±15	75±8
F50	–	34±5	–
	202±12	179±9	132±9
	144±9	120±8	104±9
Poly(vinylidene fluoride)	–	95±4	–
	133±8	143±8	113±9
	166±12	167±17	93±8
F40	–	61±4	–
	188±5	140±10	121±7
	212±17	166±12	94±7
Scotch®810/Scotch®810	–	396±5	–

[a] Data for the films treated by dc discharge (50 mA, 60 s) on the anode and cathode, stored for 14 days after treatment of the anode and cathode, and heated at 150°C after treatment of the anode and cathode. [b, c, d] Estimates for the starting polymer, treated on the anode, and treated on the cathode, respectively.

experimental parameters using the Bruggeman equation for a two component material [33], and the instrument design does not allow measurements on thin films because of reflection from their reverse side.

In our experiments on the estimation of the thickness of the modified layer of the PTFE films (50 μm) we used a combination of XPS and atomic force microscopy (AFM) [34]. Ion etching of the modified polymer films was performed directly in the spectrometer. The XPS spectra were taken at certain intervals over the course of etching; as a result, dependences of the atomic concentrations of elements, including oxygen, on the time of etching were performed. To determine the etching rate, the ion etching was performed with a mask covering half of the etching area. Atomic force microscopy was used to determine the depth of the etching crater, and the etching rate was calculated as the ratio of crater depth to etching time. These values were used to recalculate the dependence of the atomic concentration of oxygen on the etching time into the dependence on the atomic concentration of oxygen on the crater depth. For the PTFE films treated by dc discharge on the anode (I = 50 mA, τ = 60 s), the thickness of the modified layer is 40–50 nm. The most essential changes in film structure are observed at a depth of < 10 nm [34].

One of the main advantages of low-temperature plasma modification of polymers is that it affects exclusively the contact properties of the polymer: wettability, adhesion to other materials, and binding power, whereas its bulk properties remain invariable [2, 10, 28]. In the literature we could find only qualitative estimates for the adhesive properties of films, including fluorine-containing polymer films.

Park et al. [4] estimated the peel resistance of a ~30-μm copper layer from a RF discharge-modified film of a tetrafluoroethylene/hexafluoropropylene copolymer 50 μm in thickness. The copper layer was deposited in two stages: first by chemical vapor deposition (~0.2 μm) and then by electrochemical deposition until the layer thickness reaches 30 μm. This approach is fairly complicated and labor-consuming: two-stage “wet” copper deposition with the use of acids (H_2SO_4 and HCl), tin–palladium catalyst, copper sulfate, and special polishing reagent, followed by washing of the sample and its drying for 12 h at 80ºC.

Wade et al. [35] in their adhesion tests used the polymer films with a 100–150-Å aluminum layer deposited by vacuum thermal evaporation. The adhesion strength at the metal–modified surface interface was determined by the ASTM D3359-02 standard, according to which the Scotch®810 adhesive tape was applied on the Al layer and then peeled off, and the quantity of Al removed from the film surface was estimated. The adhesion strength was measured by the ratio of the portion of the Scotch®810 tape area occupied by Al to the total tape area and, depending on the resulting ration, characterized quantitatively as “very good,” “good,” and “poor.”

For adhesion tests on polyfluoroolefin films we developed a special Scotch®810 tape test [18]. Using this test we established that dc discharge treatment much enhances the peel resistance of the films (Table 3). Comparison with the Scotch®810/Scotch®810 autoadhesion contact shows that the adhesion characteristics of the modified polyfluoroolefin films are much improved.

The resulting adhesion data allowed us to solve a practically important task, specifically, to create a multilayer laminated material comprising metal nanolayers and PTFE thin films [36]. The films were mounted on the anode and subjected to plasma treatment on both sides in alternation, after which 100 nm thick aluminum layers were deposited by vacuum thermal evaporation. By our estimates, the average peel resistances were ≤308 ± 12 N/m. Consequently, thus prepared multilayer material possesses quite a high interlaminar adhesion.

A practically important result was also obtained in the study of the properties of dc discharge-modified F50 films [22]. This polymer has the operating temperature range from –196 to +250°C, it combines elasticity and a high relative breaking elongation with chemical resistance to aggressive media, and is transparent in the visible range [37].

We studied the light transmission of the F50 films modified by dc discharge treatment. The absorption and transmission spectra of the starting and modified films in the range of 200–600 nm were measured on a Shimadzu UV-2501PC spectrophotometer [22]. It was found that the light transmission of the starting film decreases from 85% at 600 nm to 23% at 200 nm. After treatment on the anode the light transmission slightly decreases, but its integral value over the entire range decreases as little as by 3.3%. Treatment on the cathode has almost no effect on the light transmission over the entire range studied. Thus, the modification of the F50 film by dc discharge scarcely affects its visible light transmission, whereas the adhesion characteristics of the film are much improved [22]. Such films can find application as a stable and transparent coatings.

CONCLUSIONS

The modification of polyfluoroolefin films in a dc glow discharge on the cathode and anode considerably improves their contact properties and increases the total surface energy and its polar term. Treatment on the anode is more efficient for perfluorinated polymers, whereas polyfluoroolefins containing hydrogen atoms are better responsive to treatment on the cathode.

The improvement of contact properties is apparently associated with the formation of new oxygen-containing groups on the polymer surface.

Experimental study of the adhesion characteristics of the modified films points to a considerable increase of peel resistance.

The modification of polyfluoroolefin films by dc discharge provides an efficient approach to improve the contact properties of polymers and can be used to manufacture new materials with valuable properties.

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