

Effect of Supramolecular Structure on the Morphology of the Surface of Carbonized Polytetrafluoroethylene

S. A. Khatipov, N. V. Sadovskaya, A. Yu. Obvintsev, and A. N. Kasatkin

Karpov Institute of Physical Chemistry, Moscow, 105064 Russia

e-mail: khatipov@nifhi.ru

Received January 16, 2014

Abstract—The morphology of the surface of polytetrafluoroethylene (PTFE), subjected to chemical etching in a sodium naphthalene solution in tetrahydrofuran, is studied by high-resolution scanning electron microscopy. It is shown that along with the molecular defluorination processes, etching of the polytetrafluoroethylene surface leads to surface fragmentation and crack formation. The emerging microstructure of the etched surface is associated with the bulk supramolecular structure and rheological properties of the polymer. The decreasing ductility of polytetrafluoroethylene after the pressing and sintering of polymerizate particles results in an increase in the number of cracks per unit area. The orientation of fibrils under uniaxial tension and the formation of spherulites, occurring upon radiation modification, is manifested in the preferred orientation of cracks. Increasing density and decreasing porosity of PTFE significantly lower the etching rate and the depth and length of cracks.

DOI: 10.1134/S1027451014050085

INTRODUCTION

Polytetrafluoroethylene (PTFE) has a unique combination of physical and chemical properties and is widely used in many industries. Recently, there has been increased interest in the study of radiation-modified PTFE, associated with the discovery of significant improvement in its practically important properties after exposure to radiation. Radiation-modified PTFE (RM PTFE) was obtained, which is characterized by an abnormally high increase in wear resistance (more than four orders of magnitude), a significant improvement in viscoelastic properties, and increased radiation resistance [1, 2].

However, to solve a number of technological problems, in particular, to create adhesive joints, an increase in the surface energy of PTFE is required. This polymer has very low adhesive properties both in the initial state and after radiation modification. One of the ways of improving the adhesion properties of PTFE is chemical etching of its surface with a solution of sodium naphthalene in tetrahydrofuran (THF) [3]. As a result of this treatment, partial or complete defluorination of sections of polymer chains occurs, accompanied by the formation of multiple (double and/or triple) carbon–carbon bonds (Fig. 1), which leads to an increase in the surface energy of PTFE.

As for partially crystalline polymers, chemical etching is also of interest from the point of research of a supramolecular structure. The method is informative due to the difference in the rates of the etching of crystalline, amorphous, and porous areas. It is known that the etching of polyethylene with fuming nitric acid can

lead to the removal of most of the amorphous regions due to degradation of the basic C–C bonds of the polymer, whereas in the crystalline regions, no change is observed [4]. In PTFE, the main carbon chain is nondegradable under the action of any reagents irrespective of the phase state, and etching in a solution of sodium naphthalene only leads to the partial defluorination of macromolecules. Therefore, the method of chemical etching was not considered for the study of the supramolecular structure of PTFE. The majority of works were devoted to the practical aspects of PTFE surface modification [3] and only a few studies clarify the chemical nature of the carbonized layer and its further functionalization [5–7].

In this paper, we investigate the morphology of the chemically etched PTFE surface before and after radiation modification by means of high-resolution electron microscopy. The emphasis is given to explaining the nature of the bulk supramolecular structure and its possibility of affecting the morphology of the etched surface.

EXPERIMENTAL

Objects

Samples of initial PTFE of slurry polymerization in the form of powder particles (polymerizate), sintered plates 5 mm in thickness, cleavages of the sintered plates, and oriented and unoriented films 50 and 150 μm in thickness were studied. Radiation-modified PTFE samples were examined in the form of sintered

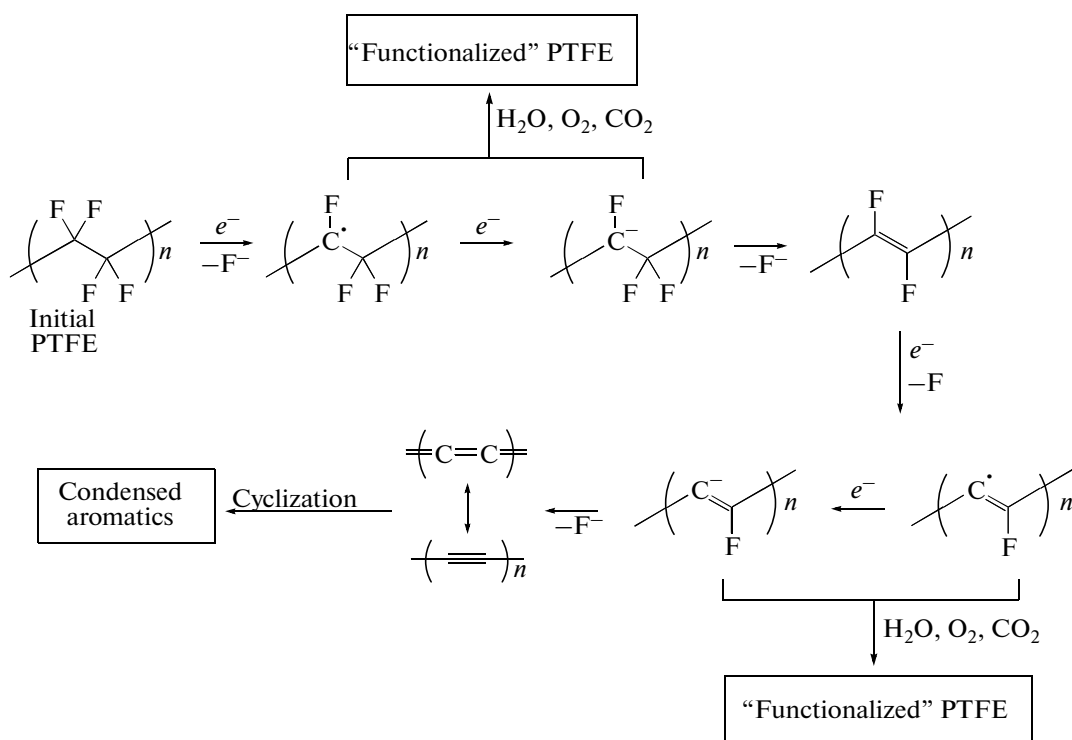


Fig. 1. Key stages of the chemical etching of PTFE: a diagram of the defluorination of sections of polymer chains during etching of the PTFE surface by a sodium-naphthalene solution in tetrahydrofuran.

plates 5 mm in thickness, cleavages of the sintered plates, and an unoriented film 150 μm in thickness.

Irradiation

Irradiation of the PTFE samples was performed at a temperature above the crystallite melting point in an inert atmosphere (argon) by ^{60}Co γ rays with an average energy of 1.25 MeV at the absorbed-dose rate of 0.25 Mrad/h. The irradiation dose was 20 Mrad.

Preparation of a One-Molar Solution of Sodium Naphthalene in THF

Sodium (23.0 g, 1.00 mol), cut into sheets $\sim 15 \times 15 \times 1$ mm in size, was slowly (for 1 h) added to a solution of naphthalene (128.0 g, 1.00 mol) in abs. THF (900 mL) while stirring with a magnetic stirrer under argon. After adding 5% of the total sodium amount, the solution becomes dark blue, almost black, in color. The mixture continued to be stirred at room temperature for 12 h; the resulting homogeneous dark-blue (almost black) solution of sodium naphthalene was stored under argon in the dark at ~ 0 – 5°C .

Chemical Etching of the PTFE Surface

One hundred milliliters of a ~ 1 -M solution of sodium naphthalene and predried PTFE samples were

placed under argon in a flask 200 mL in volume, carefully dried, flushed with argon, and equipped with a magnetic stirrer. The flask contents were stirred at room temperature in an argon atmosphere for a predetermined time; then, the solution of sodium naphthalene was poured off. After etching, the samples were washed in air with abs. THF (6×150 mL), water (6×150 mL), and alcohol (2×150 mL) and dried in a vacuum oven at 40 – 50°C for 8 h.

The key stages of the process of the chemical etching of PTFE are schematically shown in Fig. 1; they are: (a) the progressive reduction of C–F bonds with sodium naphthalene anion radicals with the formation of radical ($+1e$) and then carbanionic ($+2e$) centers in polymer PTFE chains and (b) the β -elimination of F^- anions from carbanions resulting in the formation of multiple carbon–carbon bonds. It should be noted that some actively forming intermediate (radical and/or anionic) centers, apparently, remain “live” to the water-treatment stage and yield in contact with water, oxygen, and carbon dioxide a number of oxygen-containing functional groups ($-\text{OH}$, $-\text{C}(\text{O})-$, $-\text{CO}_2\text{H}$, etc.), and C–H fragments [5–7].

High-Resolution Scanning Electron Microscopy

The surface morphology of the PTFE samples was examined by high-resolution scanning electron microscopy (HRSEM). To obtain images, a JSM-7500F scan-

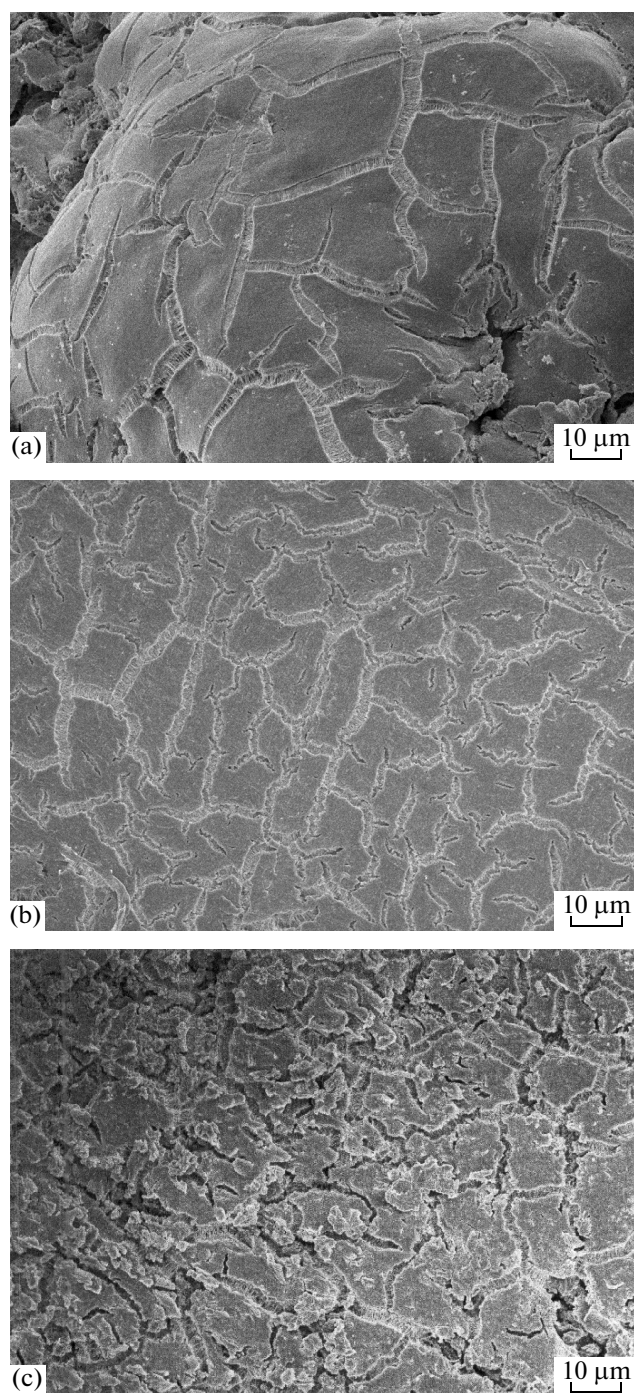


Fig. 2. Images of the carbonized PTFE surface after chemical etching in a solution of sodium naphthalene for 48 h: (a) polymerizate particle, (b) sintered plate; and (c) cleavage of the sintered plate; magnification, $\times 1000$.

ning electron microscope with a field-emission cathode (JEOL, Japan) was applied. The images were obtained in the low-energy secondary-electron mode, as this mode provides the highest resolution: at a primary-beam energy of 5 keV, the resolution was 1 nm. In order to avoid charging effects and possible destruc-

tion of the samples under the effect of the electron beam, the following methodological approaches were used: (1) studies were performed at a low electron-beam current (3×10^{-11} A), which was ensured by the presence of a field-emission cathode with cold field emission, and (2) a platinum metal film was deposited onto the sample surface, irradiated with an electron probe, by means of magnetron sputtering. During deposition of the platinum, the following parameters were set: electric current, 30 μ A; deposition time, 20 s; the distance from the target to the sample, 40 cm; and pressure, 5 Pa. Under these conditions, a platinum film of approximately 5 nm in thickness was obtained. In order to avoid artifacts related to the deposition of platinum, preliminary experiments on the application of platinum onto silicon single crystals were conducted under the same conditions. The size of the platinum particles on the single crystal faces, obtained under the given deposition mode, was 4–5 nm.

The chemical composition of the etched surface was monitored by X-ray microanalysis (XMA). For this purpose, an INCA Penta FET $\times 3$ energy dispersive X-ray microanalyzer (Oxford Instruments) was used as a set unit for the JSM-7500F scanning electron microscope. Calibration was obtained at a probe energy of 5 keV using a high-purity silicon crystal. In determining the chemical composition, the scan area was varied from 2.5×2.5 to $200 \times 150 \mu\text{m}^2$.

Measurements of the Contact Angle

To obtain data on changes in the surface energy after chemical etching, the contact angle of deionized water was measured using an EasyDrop instrument (KRÜSS). The contact angle was measured for at least five sites for each sample by the sessile drops method after the drop took a stable position. To analyze the droplet shape, we used DSA1 software provided with the instrument. The droplet volume was 4 μ L.

RESULTS AND DISCUSSION

The primary product of the polymerization of PTFE is powder particles (polymerizate), which are pressed and sintered to produce bulk products. The supramolecular structure of the polymerizate particles is characterized by the formation of highly crystalline fibrils with a cross section of 20–30 nm and a length of up to 3 μ m, consisting of macromolecules oriented along the direction of the fibrils [8–10]. At the macroscopic level, the polymerizate particles are characterized by the presence of domains of two types: loose (porous) regions, consisting of single randomly oriented fibrils, and dense regions with ordered packing of the fibrils [11]. Sintering the polymerizate particles leads to a change in the supramolecular structure. Extended lamellae 1–3 μ m in length and 100–300 nm in

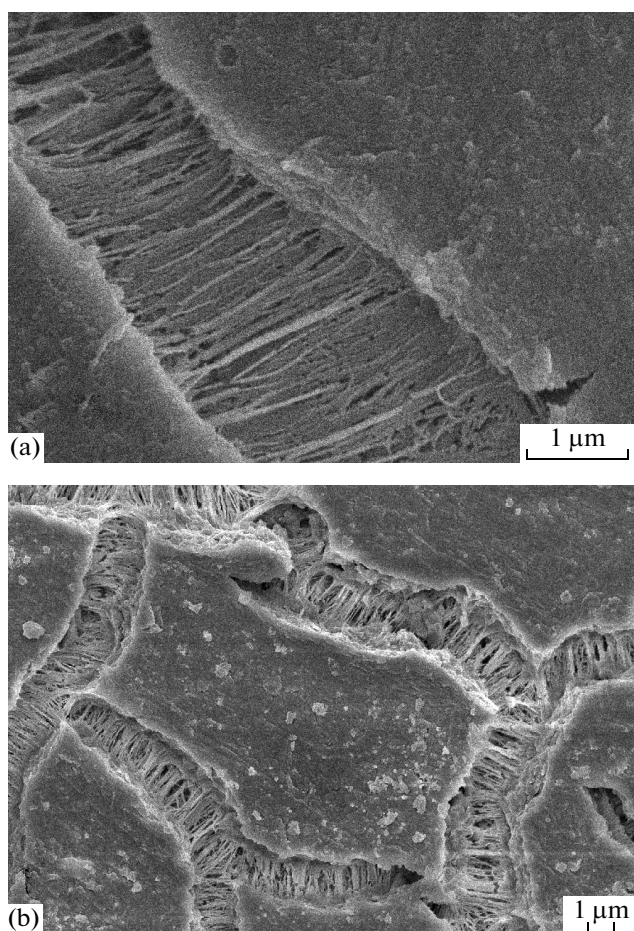


Fig. 3. Microstructure of cracks on the carbonized PTFE surface after chemical etching in a solution of sodium naphthalene for 48 h: (a) polymerizate particle (magnification, $\times 20000$) and (b) sintered plate (magnification, $\times 5000$).

width become its main elements. According to [11–13], lamellae are formed by stacking fibrils perpendicular to the long side of the lamella.

The images obtained at the same magnification for the etched surface of a polymerizate particle, a sintered plate, and a cleavage of the sintered plate are shown in Fig. 2. A common feature of the microstructure of these surfaces in all three cases is the presence of cracks. The cross-section size of the cracks is 2–3 μm . The typical size of the surface fragments separated by cracks for the polymerizate particles, sintered plate, and cleavage of the sintered plate is, respectively, 40, 20, and 10 μm . In the crack areas, fibrils are elongated and oriented predominantly perpendicular to the boundaries of the surface fragments (Fig. 3).

The character of the surface fragmentation depends on the time of etching. With increasing etching time from 0.4 to 240 h, a gradual increase in the number of cracks and their length and depth is observed on the PTFE surface. For short times within 1 h, single nonoverlapping cracks appear (Fig. 4a). At large times (240 h), the surface is fragmented into a system of overlapping deep and shallow cracks (Fig. 4b).

The occurrence of cracks during the chemical etching of PTFE can be explained by spatially inhomogeneous surface compression. Indeed, because of diffusion limitations, the penetration depth of naphthalene anion radicals into PTFE is small (less than 1 μm). Therefore, a thin surface layer undergoes defluorination; the inner surface of this layer is firmly connected to the lower layers that were not etched. The decreasing volume of the etched layer upon defluorination causes its all-around compression. However, uniform compression of the surface layer as a whole in the surface plane is much more difficult due to the

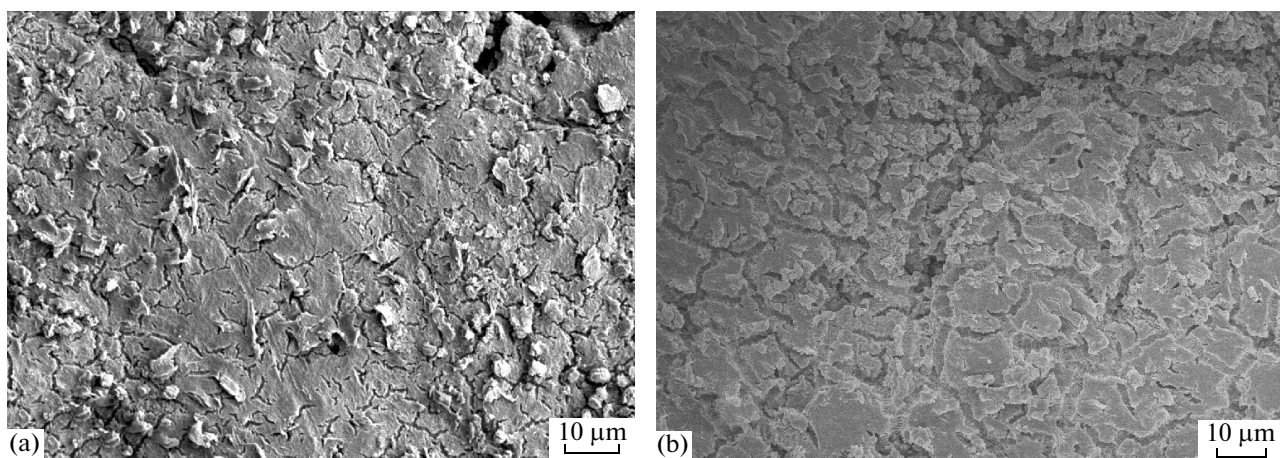


Fig. 4. Images of the sintered PTFE plate surface after chemical etching in a solution of sodium naphthalene for (a) 1 and (b) 240 h; magnification, $\times 1000$.

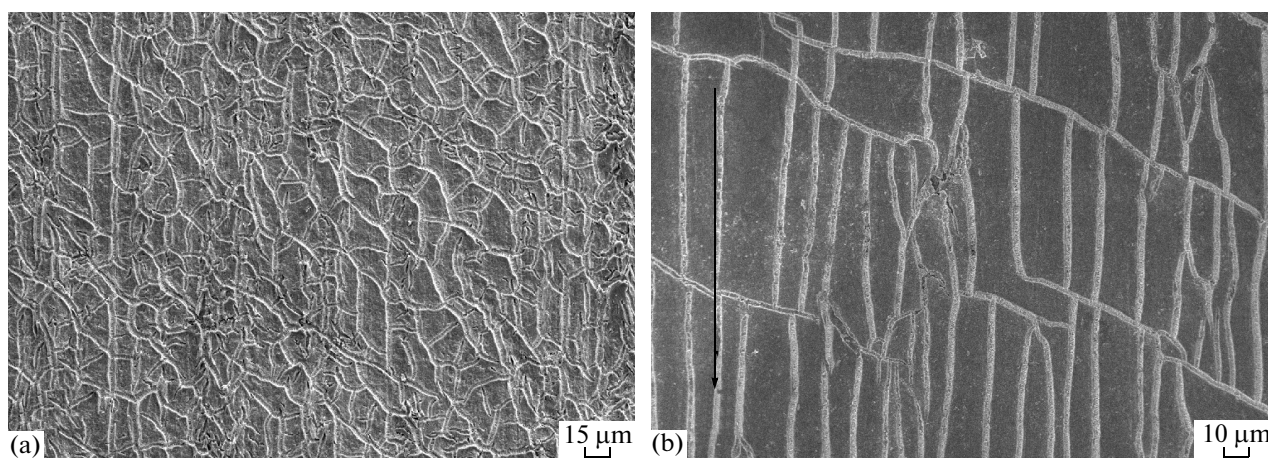


Fig. 5. Images of the carbonized PTFE surface after chemical etching in a solution of sodium naphthalene for 48 h: (a) unoriented film and (b) oriented film; magnification, $\times 500$. An arrow shows the stretching direction of the polymer.

connection to the internal layers and depends on the bulk rheological (viscoelastic) properties of the material. Depending on the hardness and ductility, the character of surface fragmentation and fracture will change.

Under all-around compression of the selected areas of the surface at their boundary, tensile deformation occurs, leading to the formation of cracks. As fragments of the surface are compressed and stretched at their boundaries, plastic deformation of the lower unetched layers develops in the field of growing cracks, followed by stretching of the fibrils (Fig. 3).

This model explains the results well. The polymerize particles have a fibrillar structure and are considerably more ductile with respect to sintered PTFE having a more rigid lamellar structure. Accordingly, the areas separated by cracks are larger and the number of cracks per unit area is smaller for the powder than for the sintered surface (Figs. 2a and 2b).

The cleavage of the sintered plate has the loosest (and porous) initial structure [11]; therefore, more cracks are formed on its surface upon etching, including deep cracks, that are not observed after the same etching time for the polymerize particles and the sintered surface (Figs. 2b and 2c).

Thus, the relationship between the morphology of the etched PTFE surface and its bulk supramolecular structure, viscoelastic properties, and the defectness of the initial surface is found.

A similar conclusion can be drawn from the study of uniaxially stretched PTFE films (Fig. 5). The preferred orientation along the axis of extraction should impede the penetration of cracks across the extraction direction and contribute to its growth along the direction of orientation of the fibrils. As seen from Fig. 5b,

this character of cracking is observed for the oriented film. On the etched surface of the unoriented film, there is no preferential direction of fragmentation (Fig. 5a). The total number of cracks for the oriented film is significantly lower.

The conclusion of [11, 14] is that the radiation modification of PTFE in melts initiates the transition from a lamellar to the centrally symmetric spherulitic packing of fibrils, decreases the overall porosity in the bulk almost to zero, and increases the density of PTFE by 1–3%. We identified spherulites on the cleavage surface by electron microscopy. However, the bulk supramolecular structure, inherent to the polymer, is distorted to some extent during the process of preparing the cleavage. Therefore, to draw a conclusion about the existence of spherulites in RM PTFE, other evidence unrelated to the process of cleavage is needed. The study of the morphology of the etched surface gives such an opportunity.

At short etching times within 1 h, radiation-modified PTFE, in contrast to the original, has a very small number of cracks (Fig. 6). It can be assumed that the etching rate of RM PTFE and, accordingly, the thickness of the etched layer at these times are considerably lower than that for the initial unirradiated sample. Indeed, the etched surface of RM PTFE visually looks much lighter in color, which is consistent with the assumption about a smaller depth of etching. Additionally, the weight loss, normalized to the unit surface for RM PTFE, is approximately twofold lower for every time of etching (table).

Increasing etching time leads to a monotonic decrease in the weight of the sample. At the same time, the dependence of the weight loss on time itself is not linear. As seen from the table, in the etching time rang-

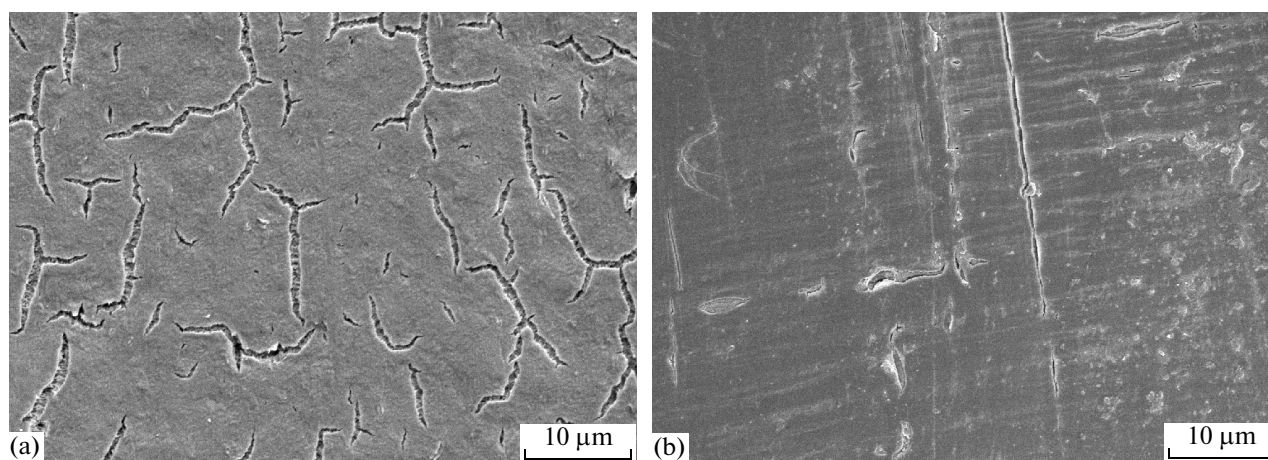


Fig. 6. Images of the carbonized surface of (a) initial and (b) radiation-modified in the melt PTFE after chemical etching in a solution of sodium naphthalene for 0.4 h; magnification, $\times 2000$.

ing from 1 to 48 h, the weight loss increases two-fold, and with a further increase in the etching time up to 240 h, the weight loss significantly decreases, especially for RM PTFE.

The contact angle is virtually independent of the etching time (table). This is consistent with the published data [3]. Major changes in the surface energy occur at short etching times of tens of seconds. The crack-formation processes, the surface fragmentation, and weight loss related, apparently, to increasing etching depth, develop over tens and hundreds of hours and have little effect on the surface energy.

At large etching times, unusual growth of cracks is observed on the RM PTFE surface (Fig. 7). In distinction to the original PTFE, the cracks have radial symmetry (Fig. 7c); the scale of the centrally symmetric structures (several tens of micrometers) is consistent with the size of spherulites in RM PTFE given in [11]. Similarly to the uniaxially oriented films of PTFE, the result for RM PTFE can be explained by the hindered growth of cracks perpendicular to the direction of orientation of the fibrils. In the case of the radial orientation of the fibrils, the growth of cracks is impeded in the tangential direction and mainly takes place in the radial direction.

Thus, chemical etching of the PTFE surface, together with molecular defluorination processes, leads to fragmentation of the surface and the formation of cracks in it. The emerging microstructure of the etched surface is coupled with the bulk supramolecular structure and rheological properties of the polymer. Decreasing ductility of PTFE after pressing and sintering of the polymerizate particles results in an increase in the number of cracks per unit area. The orientation of the fibrils under uniaxial tension and the formation of spherulites, occurring upon radiation

modification, is manifested in the preferred orientation of cracks. Increasing density and decreasing porosity of PTFE significantly lower the etching rate and the depth and length of cracks.

The contact angle and weight loss of PTFE samples as a function of the time of chemical etching in a solution of sodium naphthalene

Sample	Etching time, h	Contact angle, deg	Weight loss, $\text{mg}/\text{cm}^2, \times 10^{-4}$
PTFE, initial	0	115 ± 5	
	1	60 ± 3	5
	48	81 ± 7	9
	240	71 ± 6	11
RM PTFE	0	120 ± 5	
	1	61 ± 5	2
	48	73 ± 6	3.8
	240	60 ± 8	3.9

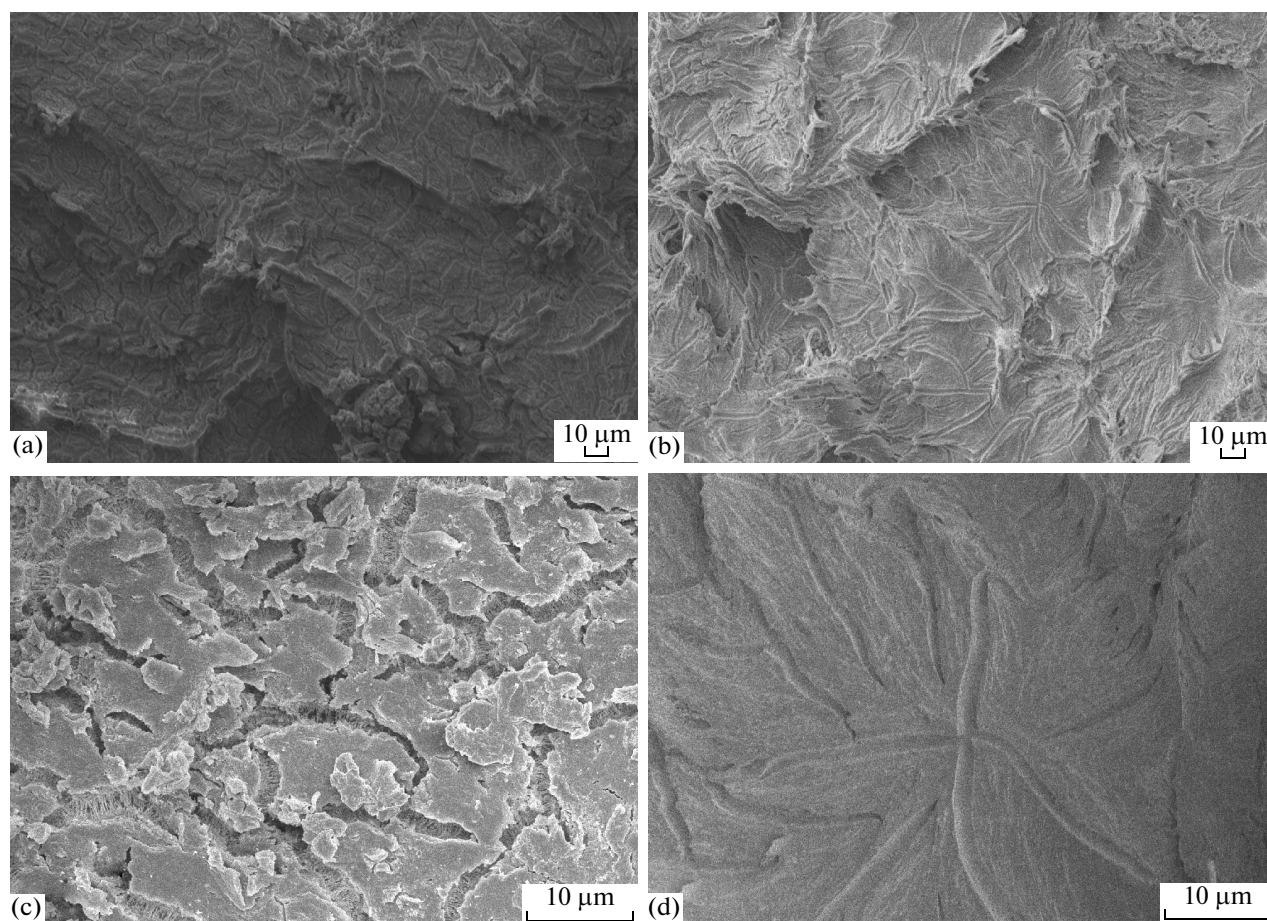


Fig. 7. Images of the carbonized surface of (a and c) the initial and (b and d) the radiation-modified PTFE after chemical etching in a solution of sodium naphthalene for 240 h; magnification: (a and b) $\times 500$ and (c and d) $\times 2000$.

ACKNOWLEDGMENTS

The work is supported by the Russian Foundation for Basic Research, project no. 13-08-12049.

REFERENCES

1. S. A. Khatipov, E. M. Konova, and N. A. Artamonov, *Ros. Khim. Zh.* **52** (5), 64 (2008).
2. S. A. Khatipov, S. A. Serov, and N. V. Sadovskaya, *Vopr. Materialoved.* **72** (4), 191 (2012).
3. D. M. Brewis and R. H. Dahm, *Rapra Rev. Rep.* **16** (3), 125 (2005).
4. S. N. Chvalun, V. S. Shirets, and N. F. Bakeev, *Vysokomol. Soedin.* **35**, 640 (1993).
5. Z. Igbal, D. M. Ivory, J. S. Szobota, R. L. Elsenbaumer, and R. H. Baughman, *Macromolecules* **19**, 2992 (1986).
6. C. A. Costello and T. J. McCarthy, *Macromolecules* **20**, 2819 (1987).
7. K. Ha, S. McClain, S. L. Siub, and A. Garton, *J. Adhesion* **33**, 169 (1991).
8. T. Davidson, R. N. Gounder, D. K. Weber, and S. M. Wecker, in *Fluoropolymers 2: Properties*, Ed. by G. Hougham et al. (Plenum Press, New York, 1999), p. 3.
9. P. H. Geil, J. Yang, R. A. Williams, K. L. Petersen, T.-C. Long, and P. Xu, *Adv. Polym. Sci.* **180**, 89 (2005).
10. L. Melillo and B. Wunderlich, *Kolloid Z.* **250**, 417 (1972).
11. S. A. Khatipov, S. A. Serov, N. V. Sadovskaya, and E. M. Konova, *Rad. Phys. Chem.* **81**, 256 (2012).
12. C. J. Speerschnneider and C. H. Li, *J. Appl. Phys.* **33**, 1871 (1962).
13. C. J. Speerschnneider and C. H. Li, *J. Appl. Phys.* **34**, 3004 (1963).
14. S. A. Khatipov, S. P. Kabanov, E. M. Konova, S. A. Ivanov, and S. A. Serov, *Rad. Phys. Chem.* **81**, 273 (2012).

Translated by O. Zhukova