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Characteristics of the structure and properties of the low temperature fraction of nanodispersed polytetrafluoroethylene

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ABSTRACT

The low-temperature fraction is separated from the nanodispersed modification of polytetrafluoroethylene, FORUM™. The results of studies of the morphology, thermal properties, composition and structure of the fraction separated at a temperature of 70ºÑ are summarized in this paper. Some possibilities of practical application of this new material are shown.

KEYWORDS

Low-molecular
polytetrafluoroethylene;
Structure;
Morphology;
Thermal properties;
Coating.

INTRODUCTION

Modified forms of polytetrafluoroethylene (PTFE) having the properties different from those of its commercially available forms are of special interest for a number of state-of-the-art technologies. The above forms include the nanodispersed polytetrafluorethylene (NPTFE) produced by the thermal gas-dynamic method (under the trademark FORUM™)[1]. Complex physical-chemical studies of the material have revealed some characteristics of its structure and properties[2-5]. The material unique properties gave rise to different possibilities of its practical application[6,7]. One of the FORUM™ material characteristics consists in its destruction in a wide temperature range: from 50 up to 500ºÑ[2]. Such a behavior is related to the presence of phases of different thermal stabilities in the powder composition, which results from the powder polymolecular nature, i.e. various molecular weights of macromolecules forming these phases. The above characteristic enabled us to separate from the FORUM™ material both high- and low-temperature phases, which, as was shown in[4], differ in structure and, therefore, could find different fields of application.

The present paper summarizes the results of studies of the morphology, thermal properties, composition, structure and possibilities of practical application of one of the fractions of the FORUM™ material, namely, the fraction separated at a temperature of 70ºC.

EXPERIMENTAL

The fraction under study was produced by the sublimation of the FORUM™ powder under isothermal conditions at 70ºC. The installation for the fraction production consisted of the thermostat, reaction flask with the initial powder and cooling collector for the condensed polymer product. The separation process was performed until the point when the polymer product stops to emerge on the collector surface and reaction flask neck. The process was rather slow. The mass of the FORUM™ sample put into the flask was equal to 100-115 g. The latter amount yielded ~2 g of the low-molecular fraction at 70ºC. The process was completed after 13 days. The product comprised small luminous platelets of a yellowish color.

The fraction morphology was studied on a scanning electron microscope (SEM) of high resolution Hitachi S5500 (Japan). The sample was fixed on a sticky carbon adhesive tape and sputtered with gold. Also, the samples microphotographs were obtained using an atomic force microscope (AFM) SOLVER manufactured by the JSC NT-MDT (Zelenograd, Moscow Oblast, Russia). The powder sample was spread over an adhesive tape, then shaken off and blown over from a rubber bulb. The particles that remained adhered to the tape were investigated by the microscope. The shooting was performed under semi-contact conditions with recording the topography height (amplitude image) and cantilever side deviations (phase contrast mode). The amplitude image shows only the surface topography in relation to the height, while the phase contrast mode does not reflect the real topographical height but provides much more contrasting image in the XY plane without distortion of shapes and sizes.

The thermal studies were performed on the derivatographs DTG-60H (Shimadzu Corporation, Japan) on air with the heating rate 2.5 degrees/min and STA 449C (NETZSCH, Germany) in the argon atmosphere with the heating rate 10 degrees/min. Corundum crucibles with lids served as the sample holders. The calcined alumina was used as a reference sample. The activation energy of the low-temperature fraction sublimation was calculated by the least-squares method.

The chromatography-mass spectrometry analysis was performed on a gas chromatograph-mass spectrometer Shimadzu GCMS QP-2010 (Shimadzu, Japan). The separation was performed on a column DB-5ms (30 m × 0.25 mm, phase film thickness 0.25 micrometers) at the temperature programming from 50 up to 300ºC; the heating rate 25 degrees/min, carrier gas – helium (1 ml/min). The sample of ~0.1 mg was put into a microtube, which was then placed into a multifunctional injector Optic-3 (ATAS GL, Netherlands), initial temperature 35°C (10 s), and heated up to 300°C with the rate 300°C/min, flow divider 1:200. The components identification in the sample was conducted using the mass spectra libraries NIST 05 and Wiley 8.

The X-ray pictures of the low-molecular fraction under study and the FORUM™ powder were recorded on diffractometers D8 ADVANCE in accordance with the Bragg-Brentano method without the sample rotation under CuKα-irradiation. The samples were not crumbled prior to recording.

The Raman scattering spectra were obtained in the range 100-3500 cm^{-1} in the reverse scattering geometry on a Raman-spectrometer RFS 100/S (Bruker, Germany) with the resolution 4 cm^{-1}. Irradiation from the Nd: YAG-laser with the wavelength 1.06 μm and the power 600 mW was used as an excitation source.

The ^{19}F NMR spectra were recorded on a solid state NMR spectrometer BRUKER AVANCE AV-300 (field power 7.04 T). The single-impulse sequence was used. In the experiments with the sample rotation at a "magic angle", the spin echo synchronized with the sample rotation frequency (15 kHz) was applied. Hexafluorobenzene (C_6F_6) was used as a reference for the chemical shift calculations.

The quantum chemistry calculations of vibration and NMR spectra of model molecules were performed using the software GAUSSIAN 03[8]. The calculations were made within the scopes of the methods HF (basis 6-31G) and DFT (B3LYP, basis 6-311+G(d))[9]. Justification of the technique for the selection of the calculation procedure for the vibration spectra is presented in[10,11]. To check the optimal character of the calculation procedure for the NMR spectra, the spectra were calculated for a series of model fluorocarbon molecules, including hexafluorobenzene, the reference system for the chemical shift values in the experimental spectra.

RESULTS AND DISCUSSION

Morphology

According to the scanning electron microscopy data, the fraction separated at 70ºC (Figure 1) consists of flat formless films of a size ~10 μm. The film thickness was equal to 30±5 nm. It was estimated from the bent edge which is shown in a square in figure 1a and presented in an enlarged form in figure 1b. Besides, the

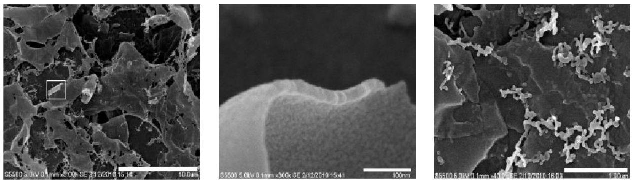
(a) (b) (c)

Figure 1 : SEM-images of the FORUM™ fraction separated at 70°Ñ: (a), (c) different parts of the sample surface; mark lengths: (à) 10 µm, (b) 100 nm, (c) 1 µm

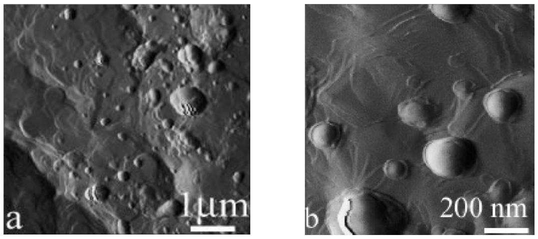

Figure 2 : AFM images of the surface of the FORUM™ fraction separated at 70°Ñ

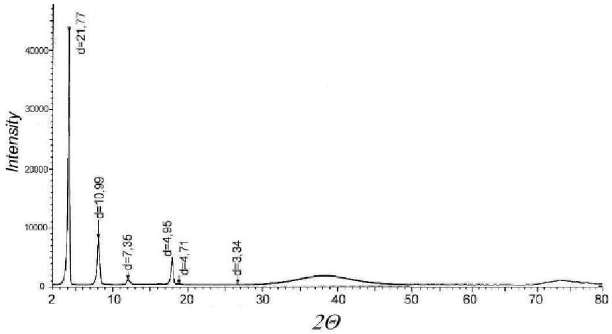

Figure 3 : X-ray picture of the FORUM™ fraction separated at 70°C

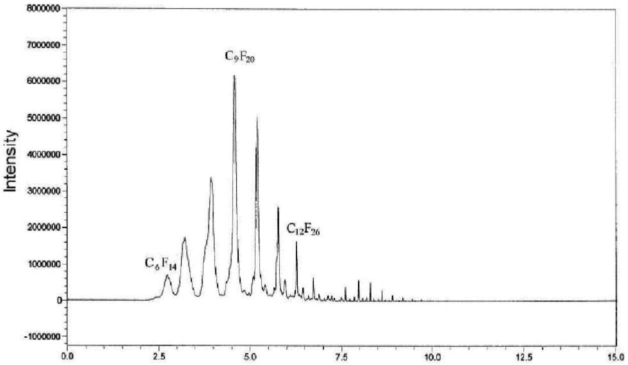

Figure 4 : Chromatogram of the low-temperature fraction

samples include some formations with the fiber-like shapes, as seen in figure 1c. The "diameter" of these "fibers" is about ~50 nm. One may assume that they comprise some PTFE supramolecular structures[12].

During the sample study by the SEM method, the fraction material could evaporate by the microscope beam, especially at prolonged studying process for a selected surface part. Since the latter creates some difficulties in producing quality SEM images at large magnification values, we additionally used the atomic force microscopy (AFM) method which does not pose the above difficulties and, at the same time, does not require the sample sputtering by a conduction material, which could create the situation of an artifact emerging. The AFM studies also showed that the fraction under study was condensed as layered molten film structures. Among the films, one can distinguish flattened spherical particles and particles whose shape can be considered spherical with a good approximation (Figure 2). The particles diameters were in the range ~0.1-0.4 µm. In some cases the particles stick together or protrude from the film bulk, thus disrupting it (Figure 2b). The layer thickness estimated from the disruption image, directly from the value of the AF microscope deviation cantilever, is equal to ~20 nm, which is in good agreement with the result obtained by the SEM method.

Thermal properties

The thermal behavior of the FORUM™ sample and the difference of its thermal properties from those of the commercially available polytetrafluoroethylene are described in detail in[2]. The low-molecular fraction of the FORUM was investigated in[13]. It was established during the above studies that the fraction mass loss occurred in the temperature range 50-150ºC. At 150ºC the sample mass loss is about 99.7%. As regards the FORUM™ sample, the mass loss occurs at a temperature above 500ºC, while at 150ºC only 3-4% is lost, which fact allows assuming that the fraction under study constitutes ~3-4 % in the initial product composition.

X-ray study

The X-ray picture of the low-temperature fraction powder (Figure 3) indicates to the presence of a crystal phase in the structure of the sample under study. Its comparison with the diffractogram of the initial FORUM™ product demonstrates substantial differences. Aside from the peak with the value 2Θ=18º characteristic for FORUM™, in the range of small angles one can observe a set of distinct reflections: a narrow low-intensity peak at 11.5ºC, more intensive one at 8ºÑ and the most intensive one at 4ºC are seen clearly. Two diffusion halos can be detected around 40 and 72º. The presence of diffusion areas in the X-ray picture indicates directly to a loss of orientation in the structure of the sample under study. One should mention that the X-ray picture of FORUM™ also contains two halos in the same ranges[6]. The earlier studies[14] demonstrated that FORUM™ was an essentially crystalline material and belongs to the hexagonal syngony. Analysis of the diffraction data and the structure simulation enabled us to conclude that FORUM™ comprises the form of PTFE with a complete angle disordering of the spiral. The angle disordering is accompanied by the shift disordering of the adjacent molecules of the hexagonal axis relatively to each other.

Low molecular weight of macromolecules forming the sample under study (fraction 70ºC), which results from the analysis of the fraction thermal behavior, must inevitably affect its crystal structure as well. Analysis of the low-temperature fraction X-ray picture showed that the system had a typical layered paraffin-like structure[15] with an expressed layer periodicity (four orders of reflection are resolved unambiguously). The reflections at relatively low diffraction angles correspond to the layered packing of perfluorinated paraffins (in particular, the peak at $2\Theta=4.0^{\circ}$ corresponds to the periodicity 22 Å of the perfluorinated n-alkane n-$C_{10}F_{22}$). The X-ray picture of the low-temperature fraction under study is close to that of the n-alkane n-$C_{16}F_{34}$. The structure of molecules inside the layer is 2D-hexagonal, which is typical for odd n-alkanes[15]. There is no correlation between the chains in the transverse direction (random rotation shift of a molecule relatively to its own axis characteristic of axisymmetric bodies having the cylindrical symmetry).

Besides the layered packing, an intralayer crystallization can be observed in the system. The attempt to identify the above complex crystal lattice gave rise to the conclusion that the lattice had a monoclinic syngony with the following parameters: a=25.103 Å, b=12.464 Å, c=5.712Å, β=96.23, V=1776.4 Å^3, FM=34.7.

The system has two phases. Aside from the well-shaped crystalline phase, it contains the mixture of linear and discotic fractions of different geometric sizes built from CF_2-groups. The crystalline/amorphous phase ratio is 70/30, respectively.

TABLE 1 : Fluorocarbons contents in the low-temperature fraction

Carbon atoms number	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}
Component content (relative %)	4,36	13,97	25,15	28,50	16,65	6,26	2,42	0,68

Chromatography-mass spectrometry analysis

The composition of the FORUM™ low-temperature fraction under study was investigated by the method of gas chromatography-mass spectrometry. It was found that the main components of the fraction comprise fluorocarbons with the carbon atom numbers from 6 up to 13. (TABLE 1). In the chromatogram (Figure 4) every peak corresponds to the fluorocarbon with a specific carbon atoms number. The fluorocarbons with compositions C_nF_{2n+2} and C_nF_{2n} leave the column as one poorly separated peak. The conclusion on the presence of saturated and unsaturated fluorocarbons of the compositions C_nF_{2n+2} and C_nF_{2n} in the system is made from the differences in mass spectra in different points of a peak.

As seen from TABLE 1, the main components of the low-temperature fraction comprise fluorocarbons with the carbon atoms number from 7 up to 10 (their total content is about 85 %). Such molecules must be well identified by spectroscopic methods, although shorter molecules C_6F_{14} and C_6F_{12} (total content about 5%) can be found in IR, Raman and NMR spectra as well.

Molecular structure

Studies of the molecular structure of PTFE, FORUM™ material and its separation products performed using the IR-spectroscopy[4-6,16,17] unambiguously demonstrated that the fragments building the molecules of the fraction separated at 70ºC could be described as short-chain formations CF_2=CF-(CF_2)n-CF=CF_2. Besides, the presence of branched structures emerged due to formation of the side CF_3 groups was revealed in the low-molecular fractions compositions.

The results of IR- and mass-spectroscopy studies of the system are in good agreement with each other. Both methods indicate to the presence of short chains in the low-temperature fraction structure, while the fragments –CF=CF_2 appear to be the end groups. The latter is also corroborated by the presence of the band at 1785 cm^{-1} in the Raman spectrum of the fraction under study (Figure 4). The Raman spectrum of the initial FORUM™ powder does not contain such a band. The reason here consists in lower intensity of the band under discussion (in accordance with the selection criteria) in the Raman spectrum, so that it becomes visible only at high content of end groups in the structure, i.e. in the case of the system low-molecular character.

Aside from the mentioned end groups, the fluorocarbon chains can be closed by the groups CF_3. It appears difficult to identify these groups in the spectra, since the respective bands are located in the range 1200-1300 cm^{-1} and, because of their low intensity, they are masked by intensive bands characterizing the vibrations ν(C-C) and ν(C-F) building the chain from CF_2-groups. In the Raman spectra, as seen from figure 5, the bands are narrow, that is why one can observe the emerging of the bands (albeit with low intensity) at 1350 and 756 cm^{-1}, which are not detected in the structure of the initial FORUM™ material. According to the data presented in[16], the above bands are not observed in the Raman spectrum of PTFE (a chain from 15 CF_2 fragments), however, as follows from our quantum chemistry calculations, in the Raman spectrum of a shorter molecule $CF_3(CF_2)_6CF_3$ the bands around 1350 and 756 cm^{-1} become visible and correspond to valent and deformation vibrations of the end CF_3 groups.

Additional information on the molecular structure of the low-molecular fraction can be obtained from the NMR data. The experimental ^{19}F NMR spectrum of the low-molecular fraction under discussion is presented in figure 6. Figure 7 shows the calculated ^{19}F NMR spectrum for a model molecule $C_{13}A_{26}$.

In accordance with the calculation data, we have attributed the signals observed in the experimental spectrum. The presence of chains built from CF_2 in the fraction composition is corroborated by the signal (the most intensive one) with the chemical shift (CS) value 39 ppm in the ^{19}F NMR spectrum. A number of signals located nearby the latter one and having substantially lower intensities correspond to the signals of fluorine atoms in the chain CF_2 groups located close to end groups and side branches. Another intensive signal with the chemical shift value 77 ppm, which is absent in the experimental PTFE ^{19}F NMR spectrum, but present in that of FORUM™[6], was interpreted as the signal from fluorine atoms in the end groups CF_3. The signals with the chemical shift values 70 and 54 ppm characterize the end group =CF_2. The signals with the CS values -31

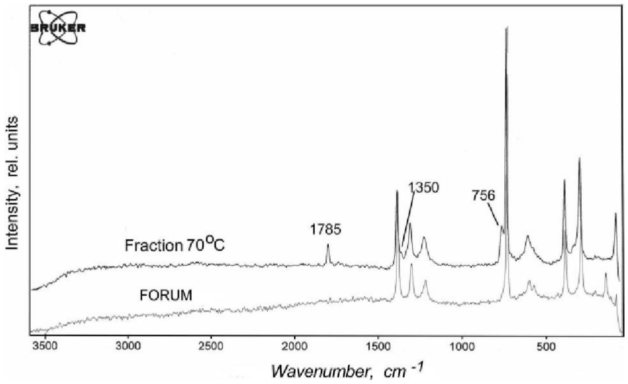

Figure 5 : Raman spectra of the low-molecular fraction (70°Ñ) and the FORUM™ powder

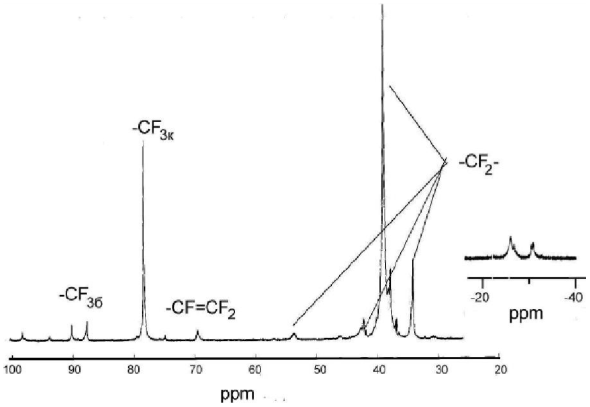

Figure 6 : Experimental ^{19}F NMR spectrum (at room temperature) of the FORUM™ fraction separated at 70°C

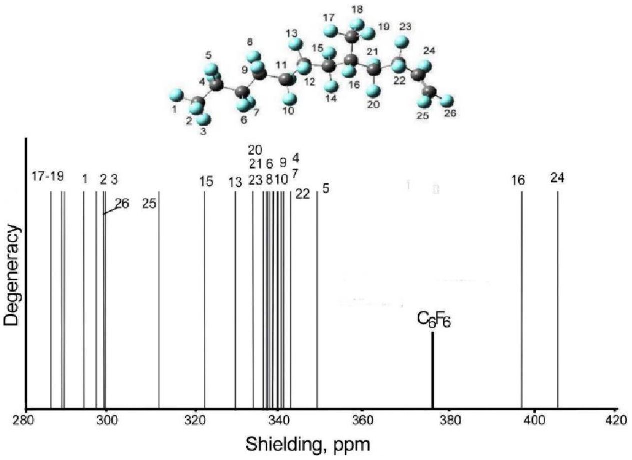

Figure 7 : Calculated ^{19}F NMR spectrum of the model molecule $C_{13}F_{28}$

and -28 ppm characterize the fluorine atoms of the groups C-F emerging in the structure at formation of the end groups –$CF=CF_2$ and side branches -CF_3. The signals with the CS values 90 and 88 ppm are attributed to the fluorine atoms in the side -CF_3 group.

To sum it up, as considered from the molecular structure point of view, the fraction under study consists of the molecules $CF_3(CF_2)_nCF_3$, $CF_3(CF_2)_n CF=CF_2$ with the n value, as obtained using the mass-spectrometry analysis, varied from 13 down to 6 as well as of the same types of molecules having the side branches CF_3.

Practical application

In conclusion, let us consider some aspects of the practical application of the obtained fraction.

The conducted studies[18,19] demonstrated that the low-temperature fraction under study was soluble in supercritical carbon dioxide. The latter enabled us to develop the technology of putting nano-thin (2-4 nm) fluoroplastic coatings on various surfaces. Deposition of such thin fluoropolymer coatings on the surface of rough substrates could impart super-hydrophobic properties to these substrates: increase the water contact angle above 150° and reduce the contact angle hysteresis value. Such surfaces are non-wettable and capable for self-purification, thus being prospective for some practical applications. We have tested various porous and rough materials as potential substrates: polymer track membranes, microporous and composite polymer structures, porous woven and nonwoven materials, nanostructured and crystalline surfaces. In all cases the suggested technology enabled us to increase the surface hydrophobicity. The technology allows putting the coatings not only on external, but also on internal surfaces of materials[20]; the latter was implemented for ceramic and metal sponges. A regular sponge absorbs water perfectly due to capillary effects, while after putting a fluoropolymer layer the sample becomes hydrophobic and ceases to absorb water. If one puts both samples into water, the initial sample rapidly drowns, while the treated one stays on the water surface.

Use of the above technology also enabled us to encapsulate hydrocarbon paraffins into fluoropolymer shells with formation of colloidosomes of a size up to 300 μm and the coating of a thickness up to 10 μm[21].

The peculiarities of thermal properties of the low-temperature fraction have made it possible to apply it in development of composite coatings on the basis of oxide layers[22,23]. The layers were formed on the titanium surface by the method of plasma electrolytic oxidation (PEO), then they were treated with the fraction under study and heated at 100ºC for 1 hour. The electrochemical studies showed that the composite coating containing the low-temperature fraction had very good protective (anti-corrosion and anti-scale) properties. Low melting point of the fraction enabled the polymer to form a homogeneous structure due to particles melting and mutual adhesion. The purposeful selection of the thermal treatment temperature allows providing maximum percolation of the polymer inside pores and produce a uniform distribution on the product surface with "sealing" the existing pores.

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