CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 10, No. 2, 2016 Chemical Technology

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STRUCTURAL CONFORMATION OF POLYTETRAFLUOROETHYLENE COMPOSITE MATRIX

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Received: December 12, 2014 / Revised: March 03, 2015 / Accepted: August 28, 2015

Abstract. Enhancement of physical and mechanical properties and structuring activity of polytetrafluoroethylene as matrix of composites by means of mechanical activation is shown. Operating modes of mechanical activation equipment are defined, in which the service properties of PTFE are maximized. The effect of mechanical activation technology on restructuring and change of morphology and supramolecular structure of PTFE is detected for the first time.

Keywords: polytetrafluoroethylene, structure, properties, mechanical activation, composites.

1. Introduction

To create reliable modern machinery and technological equipment it is necessary to design and develop highly efficient wear-resistant materials to ensure reliable operation of friction joints of mechanisms operated in a wide range of loads, speeds and temperatures, and able to work in aggressive environments, as well as in vacuum. Use of polymers as structural materials for tribotechnical needs is due to many factors, including the possibility to form composites with desired properties [1].

Review of the literature, patent and commercial sources [2-5] reveals a low potential of traditional technological approaches in obtaining polymeric composite materials (PCM) based on polytetrafluoroethylene (PTFE). However, various advanced technological methods may be performed to allow obtaining composite materials and products from them with the properties required by customers. In particular, it is the synthesis of polymeric matrices of different composition and structure [6, 7]; formation of mixtures by joining polymers and oligomers with different levels of interaction [6]; modification of matrices of various origins by means of directed restructuring and structural interaction by energy impact [2, 8-10]; matrix modifying with the help of activating additives of various sizes, shapes and properties [11-14]; creation of nanophase matrices with significantly different characteristics [5, 15].

It should be noted that the industrial implementation of these technologies is associated with significant energy, material and labor costs and requires managerial study in terms of “quality–price” trend.

The technology of energy impact on the structure and properties by means of mechanical activation (mechanical effect) presents itself as the most acceptable in the case of PCM with PTFE matrix [9].

A distinction is made between two cases of mechanical activation: in the first one the time of mechanical effect and formation of stress field and its relaxation is longer than the time of chemical reaction (such processes are usually called mechanochemical); in the second one, on the contrary, the time of mechanical effect and stress field formation is less than the time of chemical reaction, or these processes are actually separated in time. In the latter case there mechanical activation takes place [16].

Since the chemical, petrochemical, oil and gas, nuclear, aerospace, transportation, ore mining, and many other branches of engineering for the purposes of efficient, reliable and safety operation of equipment require the use of PTFE-based PCM in critical friction joints that determine performance and durability of manufactured equipment and competitiveness of manufactured products, the studies performed and the work results obtained are topical and relevant.

2. Experimental

2.1. Objects of Research

The object of the research is PTFE of F-4-PN brand. Activation of PTFE powder was performed on MRP-1M mill with various rotation speed of working members in the interval of $n = (5–9)\cdot10^3$ min^{-1} and during experimentally determined time interval of $\tau = 3–8$ min.

Activated powder was obtained by dry milling in MRP-1M high speed blade mixer.

Test samples were obtained by cold molding technology (molding pressure $P_{mold} = 50.0–70.0$ MPa), followed by free sintering of tablet blanks in air at 638 ± 5 K at a speed of heating–cooling of 40 K/h.

2.2. Research Methodology

Methodology of studying the composite properties included determining the density ρ (kg/m^3), rupture strength σ_r (MPa), relative elongation at break δ (%) and wear rate $I\cdot10^{-6}$ (mm^3/N·m) as basic necessary data about the material for designers, production engineers and operating staff.

Tests of rupture strength and relative elongation at break were performed on ring samples of 50x40 diameters and 10 mm height using rigid half-discs at R-1 disruptive installation at the motion speed of sliding member of 0.25 cm/min.

The density ρ of the samples was determined by hydrostatic weighing.

The study of the wear rate was carried out on SMT-1 serial friction machine according to “partial insertion-shaft” scheme and on UTM-1 friction machine according to “disc-finger” scheme with the purpose of control comparison.

The set of samples was tested in the friction mode without external lubrication at the sliding speed $V = 1$ m/s and pressure $P = 1$ MPa. Counterbody was the roller of ø48 mm made of steel 45 (HRC 25, Ra – 0.38 micron). Partial insertion was manufactured of PTFE and was a sector with the width of 16 mm from the ring ø80 on ø60 mm and the height of 9 mm.

The rate of mass wear was assessed by mass loss of samples per time unit. The magnitude of wear of the samples was determined gravimetrically on an analytical balance within the accuracy of 10^{-5} g and transferred to the intensity of wear by known methodologies. The moment of friction was recorded using Termodat 17E3 device.

The temperature in the “PCM–steel counterbody” contact zone was determined with a thermocouple fixed in the polymer sleeve at the distance of 1 mm from the friction surface, and the measurement was duplicated with CEM DT-8867H professional infrared thermometer (pyrometer). Investigation of the structure of composites before and after friction was performed on TESCAN MIRA 3 LMU scanning electron microscope of high resolution.

The study of physical and chemical structure of activated PTFE powder was performed by the methods of electron microscopy, X-ray diffraction and thermal analysis.

The study of supramolecular structure of activated PTFE powder was carried out using TESCAN MIRA 3 LMU scanning electron microscope of high resolution.

The degree of crystallinity and crystal lattice parameters were determined using X-ray diffraction method (DRON-4-07 diffractometer) using filtered CuKα radiation (wavelength was 0.154 nm), Bragg-Brentano focusing of θ–2θ (2θ is Bragg angle). The values of current and voltage on X-ray tube were 20 mA and 40 kV. Surveying of the samples was carried out in incremental registration mode (exposure is 3 s), range of angles 2θ was from 16 to 20°.

IR spectra of surfaces of PTFE and wear products were registered on FT-IR Nicolet 5700 spectrometer in display mode. Wear products had been previously tableted at room temperature at the pressure of 50 MPa. Absorption band of CF_2 groups of PTFE was used as comparison band at 1206 cm^{-1}. The relative error of optical density definition in a series of three measurements was ~20 %.

Thermographic studies of activated PTFE were performed on Q-1500 derivatograph at temperatures ranging from room temperature to that which is above the melting point of the crystallites by 60–70 K (approximately up to 700 K), in the linear heating mode in air at the speed of 5–10 K/min or cooling of the samples together with the furnace at the speed of approximately 5 K/min.

Planning and processing of experimental data was performed by the methods of mathematical design of experiments and mathematical statistics.

3. Results and Discussion

Polytetrafluoroethylene has a number of unique properties and is actively studied by various methods. Recently, the works on creation of new forms of polytetrafluoroethylene, which are free of flaws of the base polymer, has successfully progressed. Structure and properties of modified forms, and therefore, opportunities and fields of their application largely depend on the technology for their production [17-21]. Therefore, a need arises for careful study of each product obtained in a novel way [8, 22].

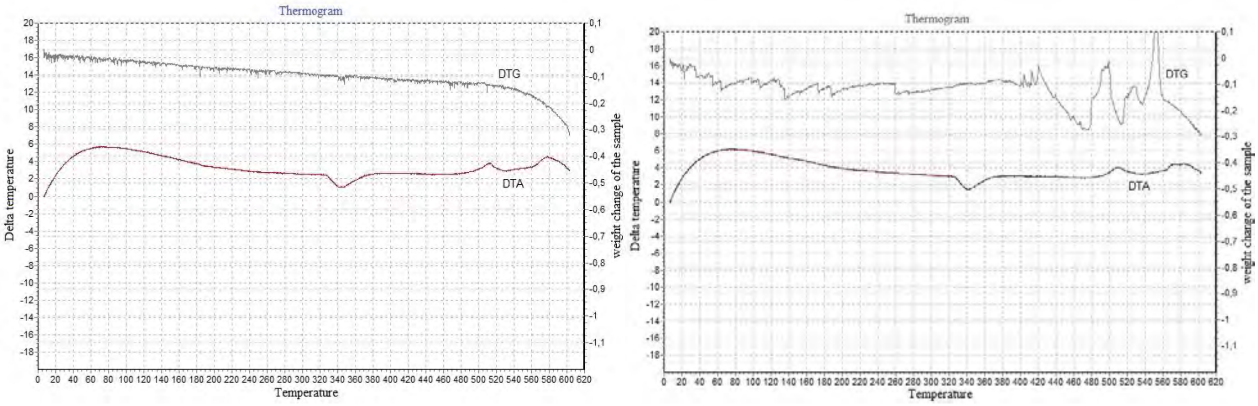
The difference between the structure of activated and non-activated PTFE leads to differences in physical and mechanical properties (Table 1).

Derivatographic studies have shown that the highest rate of weight loss of the industrial PTFE sample of F-4 brand occurs in the temperature range of 773–853 K. Thermal behavior of activated PTFE is different: interval of polymer decomposition is 853–873 K (regions of slow (473–493 K) and rapid (493–793 K) thermal decomposition are apparent (Fig. 1).

Table 1

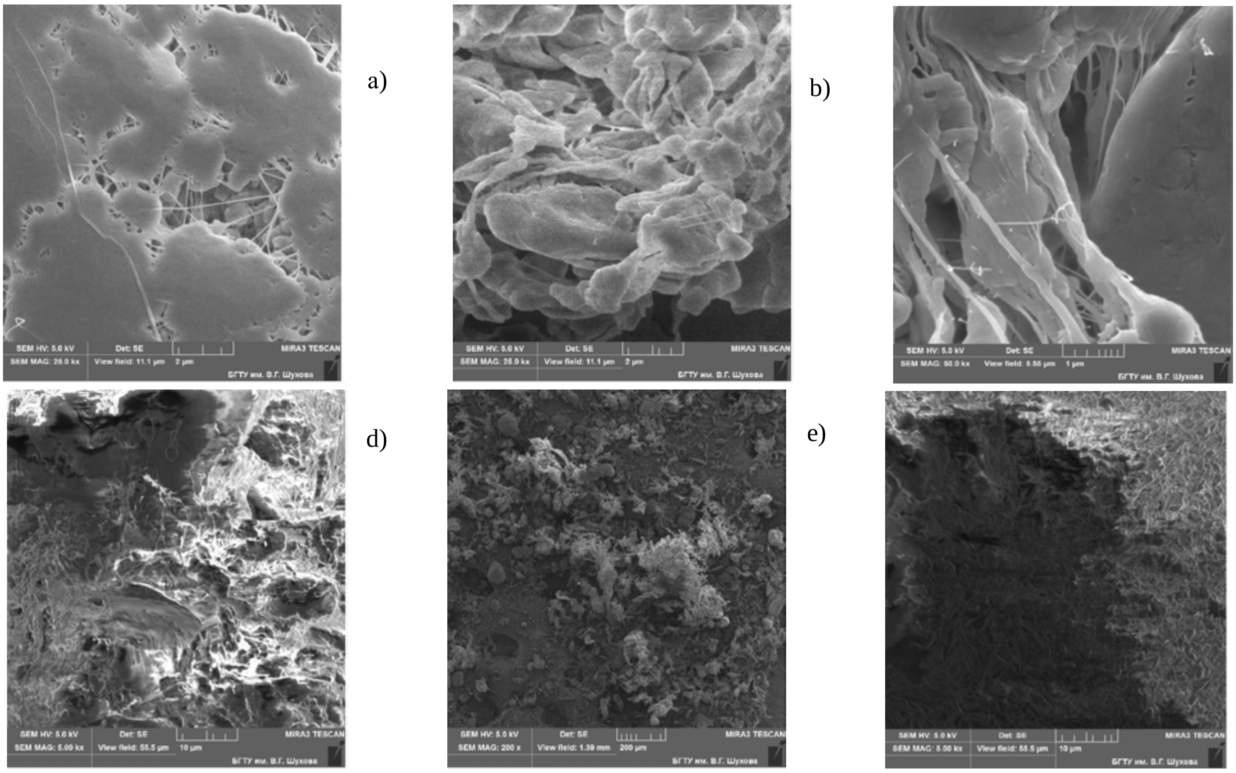
Effect of PTFE mechanical activation on mechanical and tribotechnical properties

No. of sample	Technology of obtaining	Density ρ, g/cm^3	Breaking strength rupture limit σ_r, MPa	Relative elongation δ, %	Wear intensity I$\cdot 10^{-6}$, mm³/N·m
1	non-activated	2.269	9.5	96	1133
2	τ = 5 min, n = 5000 min^{-1}	2.211	21.6	416	930
3	τ = 8 min, n = 5000 min^{-1}	2.175	17.3	280	800
4	τ = 5 min, n = 7000 min^{-1}	2.205	23.5	423	820
5	τ = 8 min, n = 7000 min^{-1}	2.211	18.2	358	717
6	τ = 3 min, n = 9000 min^{-1}	2.203	19.6	290	890
7	τ = 5 min, n = 9000 min^{-1}	2.214	24.8	415	610
8	τ = 8 min, n = 9000 min^{-1}	2.213	18.0	340	720



a) b)

Fig. 1. Thermograms of industrial PTFE samples (a) and its activated form (b) in activation mode $n = 9\cdot 10^3$ min^{-1}and τ = 5 min



a) b) c) d) e) f)

Fig. 2. Structure of PTFE before (a) and after (b-f) mechanical activation

Results of thermographic analysis of the samples of materials show that PTFE mechanical activation increases macromolecule rigidity, leading to an increase in the thermal resistance of a modified polymer by 20–80 degrees. This is due to the presence of phases with different thermal resistance due to their different molecular weight [10].

In the structure of PTFE samples after mechanical activation, lentil-like formations are observed in the form of granules with micron scale dimensions in area and thickness (Fig. 2b), threadlike strands of fibers with the length of 10 to 50 microns and diameter from 10 to 100 nm (Fig. 2c) and other formations ("cobweb", "frost flowers", "lace" and "branch" structures, *etc*.) (Figs. 2d, e, f), which are absent in non-activated PTFE structure (Fig. 2a).

Difference between particle morphology of factions is due to the fact that the products obtained at different thermobaric effects have different ratio of molecular components, and each of them is intended to construction of certain morphological formations.

Study results given in Fig. 2 show that division into nano- and microscale objects in case of fluoropolymers is conditional. Basically, the first ones are parts that form microobjects.

The difference is also found in X-ray diffractograms of non-activated and activated polymer (Fig. 3).

Fig. 3 (*curve* 1) shows that the PTFE F-4 amorphous ring is located at $2\theta = 18.10$ deg. Intensive mechanical activation shifts it to the region of lower Wulff-Bragg angles ($2\theta = 17.82–17.98$ deg.), simultaneously reducing the intensity (Fig. 3, *curves* 2-8). The significant decrease in the intensity of diffracted radiation (3.1 times) is observed in the samples (sample 7) manufactured after PTFE activation at $n = 9\,000$ min^{-1} during $\tau = 5$ min. At that condition, both the cell parameters and crystallite sizes in the plane (100) undergo changes (Table 2), which provides optimal-reacting structure of PTFE with maximum in physical and mechanical properties.

Physical and mechanical properties of PTFE show maximal values at that condition and in terms of breaking strength rupture limit (σ_r) are 2.6 times more than in case of non-activated PTFE, in terms of relative elongation at brake (δ) 4.3 times, and the wear rate of the material is 54 % less.

Therefore, it is logical to conclude that the intense energy impact in the form of mechanical activation has a significant influence on the formation of a special supramolecular structure of PTFE, which from the standpoint of mechanics of polymers has a positive effect on physical and mechanical properties of the polymer.

The study of molecular and supramolecular structure of polytetrafluoroethylene in this paper is performed by IR spectroscopy method.

In carrying out theoretical analysis of the vibrational spectra of polytetrafluoroethylene, structural model is usually accepted in which the unit cell contains one molecular chain C_nF_{2n+2} [23].

Fig. 4 shows a typical IR spectrum of industrial polytetrafluoroethylene of fluoroplastic-4 (F-4) brand [23].

As it is seen from Fig. 4, the most intense bands refer to the valence vibrations of CF_2 groups (1211 and 1154 cm^{-1}) and vibration ν (CC), which manifests itself in the form of a band at ~1233 cm^{-1}. The region below 650 cm^{-1}contains deformation and out-of-plane vibrations of CF_2 groups: wagging vibrations $\gamma\omega$ (CF_2) appear at 639 cm^{-1}, bands 555 and 516 cm^{-1} characterize the deformation and pendular oscillations of CF_2-groups, respectively [23, 24].

When modifying polytetrafluoroethylene by mechanical activation treatment, a transition of polymer into dispersed, ultradispersed and another state (threads, granules, cobweb, *etc*.) occurs (Fig. 2).

Usually, in the IR spectra of these formations, bands that characterize the valence vibrations of C–F and C–C, deformation vibrations of C–C–C and CF_2-groups, out-of-plane vibrations of CF_2-groups, individual fragments and whole chain [23-27] even with intense energy impact are preserved. This allows to assume that external influence does not lead to noticeable destruction of polytetrafluoroethylene molecular chain.

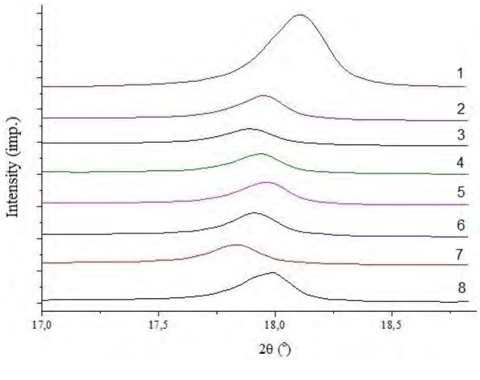


Fig. 3. Diffraction curves of industrial PTFE (1) and its structural modifications (2-8)

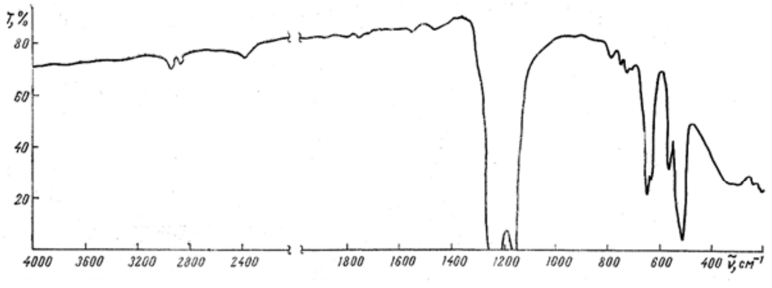


Fig. 4. IR absorption spectrum of industrial polytetrafluoroethylene of F-4 brand

Table 2

X-ray structure analysis

No. of sample	Size of crystallites in the plane (100), nm	Parameters of unit cell $a = b$, nm	Parameter of cell c, nm
1	29	0.566	0.972
2	28	0.57	0.949
3	26	0.572	0.949
4	29	0.57	0.921
5	29	0.57	0.921
6	29	0.571	0.959
7	27	0.574	0.965
8	31	0.57	0.965

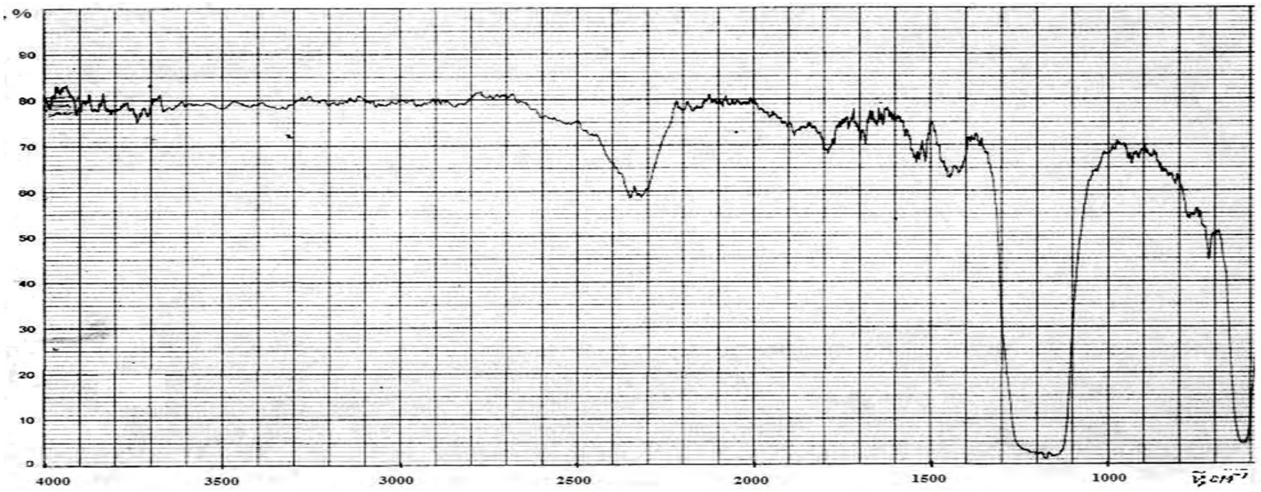


Fig. 5. IR spectra of industrial PTFE ofF-4 brand after mechanical activation in mode $n = 9{\cdot}10^3$ min^{-1} and $\tau = 5$ min

However, there is an assumption that certain changes that lead to changes in the polymer properties are taking place at the molecular level.

Analysis of the research conducted indicates the changes in morphology and supramolecular structure of polytetrafluoroethylene after treatment, even while maintaining the chemical structure of the polymer [27, 28]. IR spectra are sensitive to such changes and provide information about the structure of the modified polymer forms.

Fig. 5 shows the absorption spectrum of industrial PTFE of F-4 brand after energy impact by means of mechanical activation.

As one would expect, in case of PTFE mechanical activation the change in shape and intensity ratio of most bands is observed.

Since the interpretations of bands of IR spectra of PTFE absorption made by various authors disagree in some detail we adhered to the interpretation of bands in IR spectrum of polytetrafluoroethylene made in [28].

Studies have shown that the optical density of band at 780 cm^{-1} observed in IR spectra of PTFE increases linearly with decreasing degree of crystallinity of sample. This band is used to determine the degree of ordering in polytetrafluoroethylene structure [23]. We refer it and several other bands observed in 700–800 cm^{-1} region to the vibrations of molecular chains in the amorphous phase. The bands at 640, 625 and 516 cm^{-1}are considered as ordering bands [25]. They are also considered as the crystallinity bands.

When comparing the IR spectra of non-activated and activated PTFE, some differences are observed. They consist in the increase in intensity of the bands in 700–800, 620, 575, and 490 cm^{-1} region. In IR spectrum of PTFE, the most intense bands are 1211 and 1154 cm^{-1}, corresponding to valence vibrations of CF_2 groups. In activated PTFE, shift of these bands and increase in their intensity (1175 cm^{-1}) is observed. Bending vibration ν (CC) at 1233 cm^{-1} in PTFE is shifted into high-frequency region of the spectrum in activated PTFE (1350 cm^{-1}). In 800–1100 and 1350–2230 cm^{-1} region, a number of additional bands, which are absent in non-activated PTFE spectrum, is observed, which can be attributed to vibrations of finite groups and groups of the offshoot of structural factions. The band at 2390 cm^{-1} in non-activated PTFE is shifted to the low-frequency region of activated PTFE spectrum (2330 cm^{-1}), significantly expanding and intensifying. It should be also noted that the vibrations in activated PTFE spectrum in 2900–4000 cm^{-1}region in non-activated polymer are absent at all.

Expanding of the band in IR spectrum at maximum absorption, in our opinion, is due to the formation of many powdered crystallites in the polymer structure, which do not affect the degree of crystallinity in a dominating way, but form a structure that most effectively resists breaking of bonds, and therefore wear (54 %).

Thus, in case of the PTFE modification as a result of mechanical activation, a transition of the polymer into dispersed, nanodispersed and other structural states occurs. In the IR spectra of these formations the bands that characterize the vibrations of individual fragments and whole chain even under intense energy impact are preserved. This allows to assume that the external mechanical influence does not result in noticeable destruction of polytetrafluoroethylene molecular chain, but in some cases, certain changes occur at the molecular level, which leads to enhanced physical, mechanical and service properties of the polymer.

4. Conclusions

The undertaken studies reveal the possibility to use activated PTFE as a matrix of fluoropolymer composites in order to obtain a composite material with high physical and mechanical properties intended for friction joints of machinery and equipment for various purposes. As a result of the work performed, the best modes of technological equipment operation for activated PTFE treatment were defined allowing for most efficient obtaining of composites on its basis.

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СТРУКТУРНА КОНФОРМАЦІЯ МАТРИЦІ ПОЛІТЕТРАФЛУОРЕТИЛЕНОВИХ КОМПОЗИТІВ

Анотація. *Показано підвищення фізико-механічних властивостей та структуруючої активності політетрафлуоретилену як матриці композитів внаслідок механічної активації. Визначено режими роботи механоактиваційного обладнання, за яких експлуатаційні властивості ПТФЕ є максимальні. Вперше виявлено вплив технології механічної активації на структурну перебудову та зміну морфології і надмолекулярної структури ПТФЕ.*

Ключові слова: *політетрафлуоретилен, структура, властивості, механічна активація, композити.*