

Mechanically Activated Polytetrafluoroethylene: Morphology and Supramolecular Structure

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The nanoscale structure of polytetrafluoroethylene before and after mechanical activation was comprehensively studied by a set of modern physical research methods. The formation of a polydisperse mixture of a mechanically activated fluoropolymer with different molecular weights, the habit of single particles and arbitrary mass, size and morphology of cluster nanostructures was proved by electron microscopy. Two indicators were used to interpret the results of IR spectroscopy: the ratio of the intensities of the band maxima and the half absorption bandwidth. It was revealed that there is an increased concentration of CF₂ end groups in the composition of activated polymer, which correspond to the low molecular weight fraction and provide small sizes of its macromolecules. It was proved that filling of polytetrafluoroethylene leads to a decrease in their number, contributing to the formation of a nanostructured polymer with fewer defects. It was established that the combined use of energy exposure and dispersed filler has a positive effect on the physical and mechanical properties of the fluoropolymer. The mechanical activation increases the strength level by 2.6 times and relative elongation by 4.3 times compared to the inactivated polymer; filling the activated polymer with sodium chloride increases the strength level by 2 times and relative elongation by 3.8 times.

Keywords: Polytetrafluoroethylene, Fluoropolymer, Structural modification, Mechanical activation, Filler Energy efficiency.

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1. INTRODUCTION

The use of composite materials based on polymers is an important factor in improving the efficiency [1] and the successful development of leading industries [2]. Modern functional materials, such as multicomponent and multilayer nanoscale films [3-5] and polymer composites [6], have a potentially wide range of performance properties, provided by various technological methods of their production [7-9]. Traditional modification methods [10], effective for other polymer matrices (polyamides, polyolefins, polystyrene, etc.) [11], do not provide the expected effect for polytetrafluoroethylene (PTFE) due to low intermolecular interactions and lack of viscosity [12].

Therefore, the development of compositions and technology for the production of polymer composite materials based on PTFE requires a comprehensive approach that takes into account not only the characteristics of the original structure of the components [13], but also its transformation under the influence of technological and operational factors [14]. One of the most effective and low-cost ways to implement this approach to the formation of the structure of composites based on PTFE is the method of mechanical activation [15, 16] and the introduction of fiber or/and dispersed fillers [17, 18].

Mechanical activation is used to change the reactivity of solids, which means accelerating or increasing the efficiency of chemical or physical processes and is the most important stage of mechanochemical processes [19]. Technologies based on mechanical activation of components have found their application in the production of modern functional materials, protective polymer coatings of intermetallic powders, polymer-metal components for solid rocket propellants, etc. [20].

Although mechanochemical technologies for processing polymers have not yet passed into industrial production, promising results have been obtained from studies in the laboratory conditions [21, 22]. The relevance of further research on the influence of modes, technology, equipment of mechanical activation on the structure and properties of various materials is based on the already identified advantages in obtaining the desired structure and properties of polymer materials [23] that are not available using traditional methods of thermal or optical activation.

2. EXPERIMENTAL

The structure and properties of industrial PTFE for general-purpose products and compositions were investigated. The chemical composition and properties of PTFE meet the standards. Sodium chloride powder with spherical particles was used as a filler.

PTFE powder was mechanically activated in a dry state in a high-speed mill MRP-1M under different operating modes (the number of revolutions of the working bodies of the mill varied in the range $n = 5000-9000 \text{ min}^{-1}$ in time intervals $\tau = 3, 5, 8 \text{ min}$) [17].

Research materials were obtained by powder metallurgy. First, the initial ingredients of the polymer matrix and the filler were mixed, then the resulting mixture was pressed followed by sintering [6].

The morphology of the activated and filled PTFE powder was studied using a high-resolution scanning electron microscope TESCAN MIRA 3 LMU. The IR spectra of activated and filled PTFE were recorded on a Specord 75-IR spectrophotometer in the wavelength range $400-4000 \text{ cm}^{-1}$. The absorption band of the CF₂ groups of PTFE at 1206 cm^{-1} was used as a reference band. The relative error in determining the optical

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density in a series of three measurements was $\sim 20\%$. Phase and chemical analysis of activated PTFE was performed on an ARL 9900 WorkStation series X-ray fluorescence spectrometer with a built-in diffraction system. The method for studying the properties of the composite included the determination of density, the breaking strength, relative elongation at break, and wear rate according to standard procedures [17].

3. RESULTS AND DISCUSSION

3.1 Study of the Mechanically Activated PTFE Morphology

The presence of particles of arbitrary shape with sizes that differ by several orders of magnitude is characteristic of industrial PTFE (Fig. 1a). Large irregularly shaped particles are formed mainly due to the agglomeration of smaller fractions and create cluster structures of statically indeterminate shape and size. A PTFE particle is formed by fragments of arbitrary shape with pronounced structural differences. This leads to aggregates of a fibrillar structure with a diameter ranging from a few nanometers to 300-500 nm. Such aggregates can grow with the subsequent formation of irregularly shaped structures connected by fibrillar elements.

A characteristic feature of the industrial PTFE is its pronounced agglomeration, even when storing powder in containers in ordinary warehouses. This leads to the deformation of strong enough units, loosening, which requires special technological equipment. The agglomeration of the powder matrix prevents the formation of a homogeneous structure of the composite and the realization of contact of the same intensity throughout its volume. This effect is mainly due to the characteristic morphology of the PTFE matrix particles.

These features of the initial structure of PTFE under the influence of energy cause a high molecular weight product, which is a polydisperse mixture with different molecular weights, habit of single particles, and arbitrary mass, size and morphology of cluster nanostructures (Fig. 1b). As a result, the modified industrial PTFE determines further technologies for the formation of semi-finished products and products with specified parameters of physical, mechanical and tribotechnical characteristics.

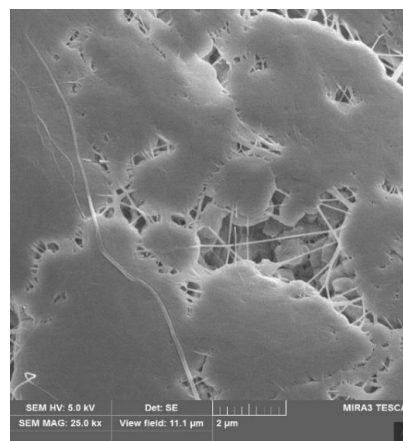
The difference in the morphology of PTFE particles of different fractions is due to the modification products under the action of different modes of mechanical activation have different ratios of molecular components. Each of them is due to the construction of morphological formations of nano- and microsized in different proportions [22].

The X-ray diffraction method revealed a decrease in the degree of crystallinity under different modes of mechanical activation, which is associated with a change in the size of crystallites (Fig. 2).

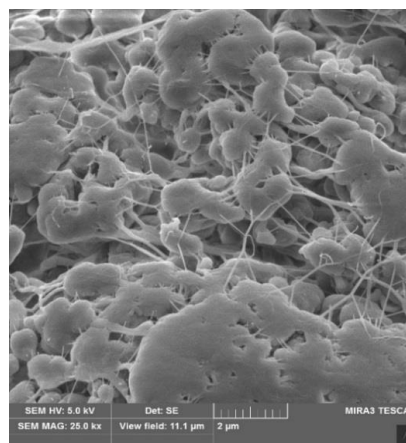
The main reflexes of industrial PTFE indicate the presence of phases with different conformation of the "fluorine-carbon" bond of macromolecular chains. The ratios of the squares of the interplanar distances in the first, second, and third crystal reflexes indicate the hexagonal structure of the crystalline phase. The radi-

ograph of activated PTFE differs from the diffraction pattern of an industrial polymer by the presence of an additional reflex, which characterizes the manifestation of CF_2 groups on the hexagonal axis of the crystalline phase, which is manifested by rotational misorientation and displacement of chain macromolecules relative to each other.

Thus, mechanical activation significantly affects the formation of a special supramolecular structure of PTFE. This leads to a positive effect on its physical and mechanical characteristics.



a



b

Fig. 1 – Microstructure of industrial PTFE (a) and mechanically activated PTFE (b) in the mode $n = 9000 \text{ min}^{-1}$, $\tau = 5 \text{ min}$, $\times 25000$

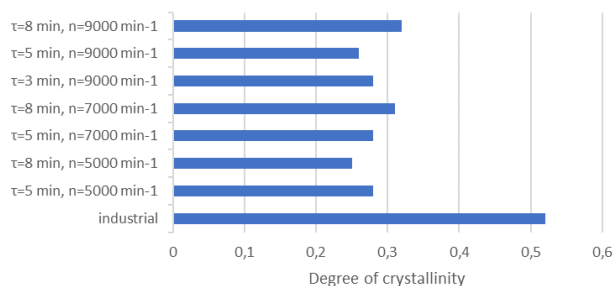


Fig. 2 – Dependence of the mode of mechanical activation of PTFE on its degree of crystallinity

3.2 Study of the PTFE Supramolecular Structure by IR Spectroscopy

Two indicators were used to interpret the IR spectroscopy data: the ratio of the intensities of the band maxima (I_0/I) and the half absorption bandwidth ($\Delta\bar{\nu}_{1/2}$).

In the industrial PTFE sample, the most intense bands are at 1240 and 1124 cm^{-1} , corresponding to the valence vibrations of CF_2 groups. After the application of mechanical activation, there is a shift of these bands and an increase in their intensity to 1350 and 1134-1196 cm^{-1} , respectively. In the absorption ranges 800-1100 and 1350-2230 cm^{-1} , a few additional bands are observed that are absent in the spectrum of inactivated PTFE. They can be interpreted as oscillations of $-\text{CF}=\text{C}<$ end groups and groups of the side branch of $\delta\text{C}-\text{H}$ structural fractions.

The band at 2370 cm^{-1} in the industrial PTFE sample is shifted to the low-frequency region of the spectrum of activated PTFE 2324-2356 cm^{-1} , significantly expanding and intensifying. The broadening of the band at 2390 cm^{-1} at maximum absorption is associated with the formation of numerous fine crystallites in the polymer structure, which form a structure that most effectively resists bond breaking and, consequently, wear.

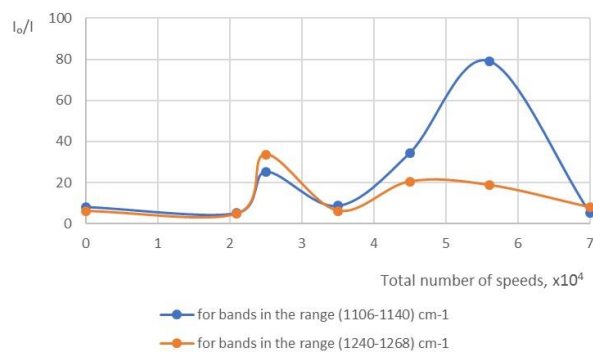
It is established that with increasing the total number of revolutions during mechanical activation, the concentration of CF_2 groups, corresponding to their valence fluctuations in the absorption ranges 1240-1268 and 1106-1140 cm^{-1} , increases (Fig. 3a). At the same time, the concentration of $-\text{CF}=\text{CF}_2$ end groups increases, the fluctuations of which are reflected in the absorption range 1778-1794 cm^{-1} (Fig. 3b), indicating an increase in the number of defects in the structure of the activated polymer.

3.3 Influence of Filler on the Nanostructure of Mechanically Activated PTFE

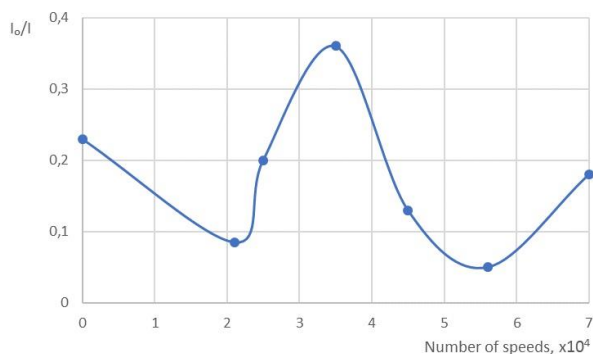
The addition of sodium chloride (NaCl) to PTFE increases the concentration of CF_2 groups, corresponding to their valence fluctuations, by 5 and 14 times at 2 and 8 wt. % filling, respectively, compared with the original polymer (Fig. 4a). An increase in the filler content increases the number of such groups by 2.8-4.8 times, as well as decreases the concentration of end groups ($-\text{CF}=\text{CF}_2$) registered in the absorption range 1783-1794 cm^{-1} , by 1.7 and 2.8 times compared with the original and activated polymers, respectively (Fig. 4b, Table 1).

It follows that, in the supramolecular structure of mechanically activated PTFE with the addition of filler, intramolecular double bonds, side branches, and end groups of different composition are formed, while the main bands characterizing oscillations of individual fragments and the entire chain are retained.

The results of electron microscopy showed that this promotes active interaction at the "matrix-filler" interface (Fig. 5). This indicates that mechanical activation does not lead to a significant destruction of the PTFE molecular chain. Nevertheless, some conformational changes consist in an increase in the concentration of valence and CF_2 end groups.

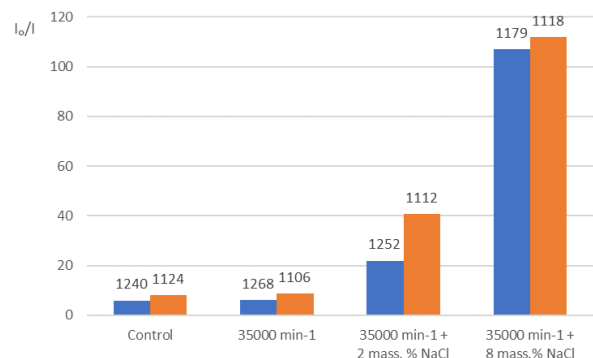


a

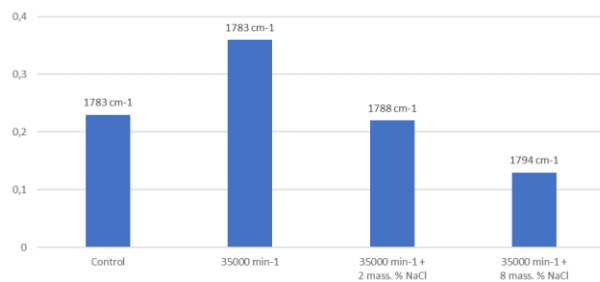


b

Fig. 3 – Dependence of I_0/I on the number of revolutions in the absorption ranges: a) 1240-1268 and 1106-1140 cm^{-1} ; b) 1778-1794 cm^{-1}



a

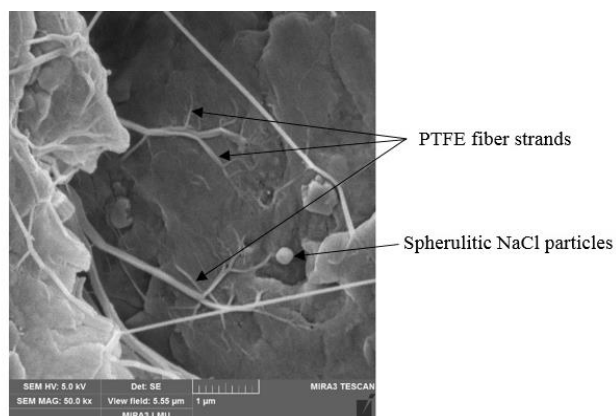


b

Fig. 4 – Influence of sodium chloride on I_0/I in the absorption range: a) 1106-1268 cm^{-1} ; b) 1783-1794 cm^{-1}

Table 1 – IR spectroscopy data of filled PTFE

Filling degree	Stripe, cm^{-1}	I_0/I	$\Delta\bar{\nu}_{1/2}$, cm^{-1}
$\tau = 5$ min, $n = 7000 \text{ min}^{-1}$, + 2 wt. % NaCl (general speed is 35000)	2370	0.77	} 233.0
	1788	0.22	
	1537	0.17	
	1441	0.26	
	1252	22.0	
	1112	40.7	
	604	124.0	
+1884 1688	470	114.0	} 220.0
$\tau = 5$ min, $n = 7000 \text{ min}^{-1}$, + 8 wt.% NaCl (general speed is 35000)	2347	1.05	} 233.3
	1929	0.13	
	1878	0.12	
	1794	0.13	
	1700	0.11	
	1542	0.15	
	1454	0.19	
	1179	107.0	
	1118	112.0	
	615	15.0	
	464	49.0	
To clarify:	Stripe, cm^{-1}	I_0/I	Assignment
	2324-2370	0.38-1.38	C–H or C≡C
	1929-1934	0.09-0.13	C=C
	1861-1878	0.12	–COOH
	1700-1721	0.11	–CF=CF–
	1531-1548	0.15-0.30	C=C
	1431-1454	0.10-0.40	$\delta\text{C–H}$

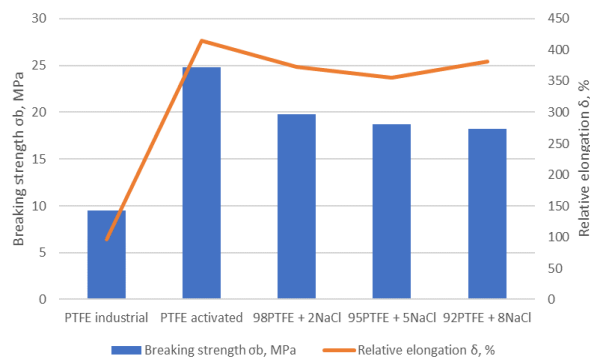
**Fig. 5** – Microstructure of nanoscale mechano-activated PTFE filled with 2 wt. % sodium chloride, $\times 50000$

The results of experimental tests showed that this leads to an increase in the performance properties of the filled polymer (Fig. 6).

Analysis of Fig. 6 showed that in comparison with industrial PTFE, mechanical activation increases the strength level by 2.6 times and relative elongation by 4.3 times. This is due to the formation of new reaction centers and an increase in the surface energy of individual fragments of macromolecules due to elastic and

plastic deformations.

Filling the industrial polymer with sodium chloride increases the tensile strength by a factor of 2 and elongation by a factor of 3.8. At the same time, the filler slightly reduces the physical and mechanical properties of activated PTFE linearly depending on the degree of filling, while increasing the wear resistance characteristics.

**Fig. 6** – Dependence of tensile strength and relative elongation depending on the structural state of PTFE: industrial, activated and filled

4. CONCLUSIONS

It is shown that mechanical activation of PTFE leads to the formation of granules with micron dimensions and filamentous bands of nanoscale thickness, not inherent in its industrial samples. In the composition of activated PTFE, there is an increased concentration of CF_2 end groups, which correspond to the low molecular weight fraction and provide small sizes of its macromolecules. Filling the polymer reduces their number, which contributes to the formation of a nanoscale structure with fewer defects.

The difference in the morphology of industrial and activated PTFE leads to changes in their physical and mechanical properties. Compared with industrial PTFE, the strength level of activated PTFE is increased by 2.6 times and relative elongation by 4.3 times. Mechanical activation of powdered PTFE as a result of elastic and plastic deformations promotes the formation of new reaction centers in the nanostructure of the polymer with an increased value of the surface energy of the formed macromolecules. Filling the fluoropolymer has a positive effect on its performance properties.

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Механічно активований політетрафторетилен: морфологія та супрамолекулярна структура

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В роботі комплексно досліджено нанорозмірну структуру політетрафторетилену до та після механічної активації сукупністю сучасних фізичних методів досліджень. Методом електронної мікроскопії доведено утворення полідисперсної суміші механоактивованого фторполімеру з різною молекулярною масою, габітусом одиничних частинок і довільною масою, розміром та морфологією кластерних наноструктур. В роботі для інтерпретації результатів ІЧ-спектроскопії були використані два показники: відношення інтенсивностей максимумів смуги та ширина смуги при половині поглинання. Досліджено, що у складі активованого полімеру присутня підвищена концентрація кінцевих груп CF₂, які відповідають низькомолекулярній фракції та забезпечують малі розміри його макромолекул. Доведено, що наповнення політетрафторетилену призводить до зменшення їх кількості, що сприяє формуванню наноструктурованого полімеру з меншою дефектністю. Встановлено, що комплексне застосування енергетичного впливу та дисперсного наповнювача позитивно впливає на фізико-механічні властивості фторполімеру. Застосування механічної активації сприяє зростанню рівня міцності в 2,6 рази та відносного подовження в 4,3 рази у порівнянні з неактивованим полімером; наповнення активованого полімеру хлоридом натрію підвищує межу міцності в 2 рази та відносного подовження в 3,8 рази.

Ключові слова: Політетрафторетилен, Фторполімер, Структурна модифікація, Механічна активація, Енергетична ефективність, Наповнювач.