

Technology of polytetrafluoroethylene-based nanocomposite materials: Structural and morphological aspect

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We conducted complex researches of the characteristics of formation of a heterophase structure in the polytetrafluoroethylene (PTFE) based composite materials containing fillers and modifiers of different composition and geometry habit at concentrations of 20-35 wt%. Also, the directions of improvement of manufacturing process of the products with increased parameters of strength and tribological characteristics consisting in the control of the structure composites at various levels are defined. The mode of modifying action of thermogasdynamic synthesis products of polytetrafluoroethylene in a composite is established. We developed the technology of modification of carbon fibers with ultrafine particles of products of the thermogasdynamic synthesis (UPTFE) for PTFE-based composites, which provides wear resistance increase by 1,1-1,2 times and strengths by 1,1-1,35 times when forming products by cold pressing with the subsequent agglomeration.

Keywords: Nanocomposite material, polytetrafluoroethylene, tribological characteristics, stress-strain characteristics

Introduction

The most important components of chemical complex and power-producing enterprises' equipment are sealing devices and units for receiving the compressed and liquefied gases which use the elements providing leakproofness of static and mobile interfaces. The materials for sealing elements have special requirements, especially considering the conditions of operation of such equipment assuming a long production cycle without service, reverse nature of movement, lack of special lubricant environments, influence of hostile environment and increased temperatures. The most common use in the valving for gas and water supply, power system and designs of compressor equipment for chemical industry received the items manufactured from composites on a basis of PTFE, modified by disperse components of various structure and technology of receiving.

Among the PTFE-based composites, applied to production of pressurizing and sealing elements of static and movable interfaces, the wide circulation was gained by materials of a series Flubon and Fluvis which use the dispersed carbon fiber (CF) as a multipurpose filling agent. These materials surpass domestic and foreign analogs in a complex of service characteristics. However, due to the specific characteristics of structure and morphology of macromolecules and disperse particles of PTFE and CF, potential opportunities of PTFE-based composites' components are not realized fully. It leads to a noticeable drop of load and speed range of application of products manufactured from composite materials on the

basis of PTFE, reduces a resource of their effective operation and increases production and processing cost.

Due to stated earlier the urgent task is to develop structures and technology of PTFE-based composites with increased parameters of strength and tribotechnical characteristics by means of directional control of physic-chemical and thermal processes at the interface between the matrix and the carbon filling agent.

Technique of probes

The applications of products from PTFE-based composites are variable, so we chose for probe the components which have been industrially mastered at the enterprises of Republic of Belarus and the Russian Federation and have had the regulated parameters defining the quality. As the matrix we used powdery PTFE of brands 4PN, PN90, 4TM in a condition of industrial supply (GOST 10007-80, specs 2213-021-13693708-2005, specs 2213-022-13693708-2005).

To modify the matrix polymer we used a product of dispergating of carbon fibers of the LO-1-12N brand produced by JSC "SvetlogorskKhimvolokno" (specs 400031289.170-2001). In separate experiments we used the carbon material "Belum" obtained by modifying of industrial fiber in the environment of being polymerized fluorinated products according to the technology developed by the V.A. Belyi Metal Polymer Research Institute of National Academy of Sciences of Belarus. As carbonic modifiers were used carbon black of the P234 brand (GOST 7885-86) and pulverized graphite (specs 48-4802-20-98). To modify the components were used the products of thermogasdynamic synthesis (TGD-synthesis) which are positioned by the developer as ultrafine polytetrafluoroethylene (UPTFE) and marketed under the brand name "Forum" (Institute of Chemistry, FEB RAS).

At production of test samples, blanks and products we used the technology of preparation of components, mixing, pressing and agglomeration, developed for PTFE-based composites Flubon and Fluvis, which is applied now at the enterprises for production PTFE-based composites (JSC Grodno Mechanical Plant, JSC Grodno Khimvolokno). To obtain high-strength products we used original technologies of blanks' agglomeration at the influence of temperature and mechanical tension, both or apart.

Structure of the polymer composite materials (PCM) was investigated by IR spectroscopy (Tensor-27), optical (Micro200T-01) and atomic force (NANOTOP-III) microscopy, X-ray diffraction analysis (DRON-2.0).

The thermal linear expansion factor was defined according to GOST 15173-70. The thermal conductivity of materials was measured with the IT- λ -400 device, based on the method of a dynamic calorimeter with a heat meter and an adiabatic shell.

To determine the phase transition temperatures in PCM depending on the contents, nature of the filling agent and applied production technology we used data of the differential thermal analysis (DTA), differential thermogravimetric (DTG) and thermogravimetric analysis (TGA) (Q-1500).

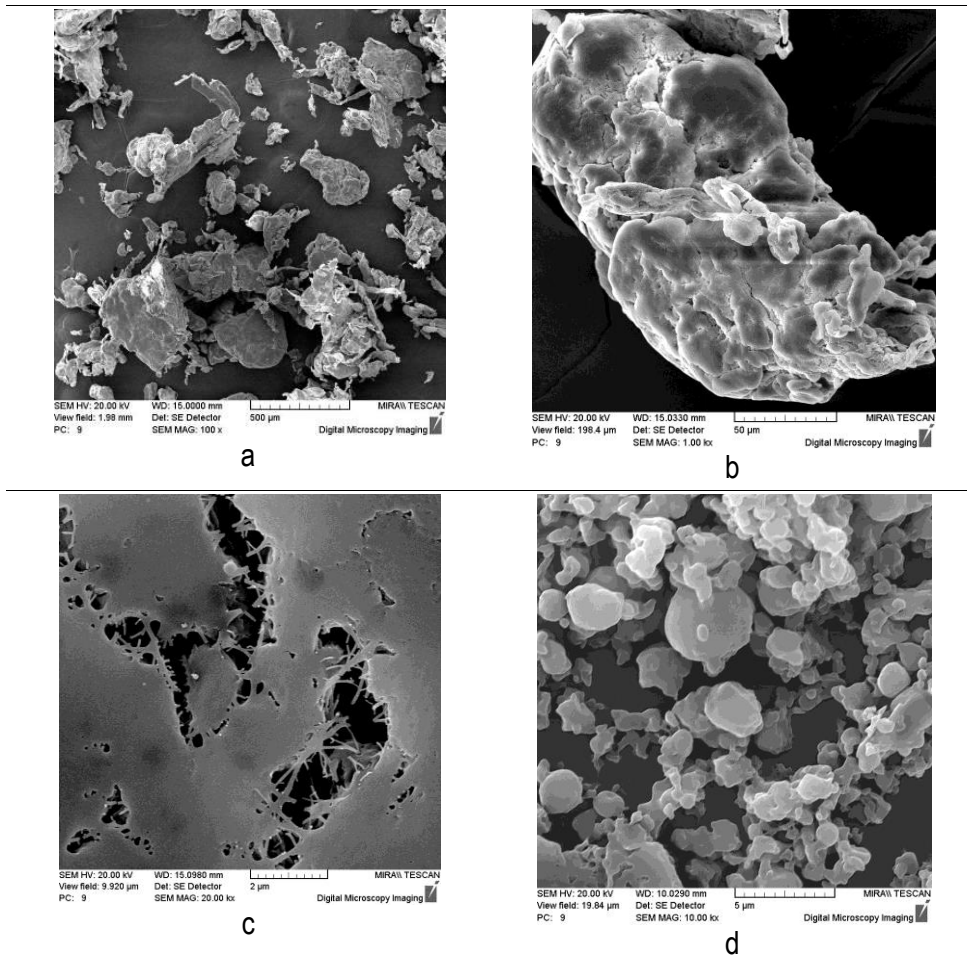
The stress-strain characteristics of PCM were defined according to existing state standard specifications and standard documentation for PTFE-based composites of series Flubon and Fluvis. Strength and elasticity module were defined in accordance with GOST 4651-82 at the ComTen 94C stand.

Tribotechnical characteristics of PCM were estimated by means of friction machines SMC-2 and HTI-72 according to "shaft - partial liner" and "pin-on-disk" schemes in accordance with standard documentation.

Results and discussion

In modern materials science of PTFE-based composites of engineering appointment there are no the common methodological approaches for obtaining commercial batches of materials with stable parameters of strength and wear resistance within one brand. It is experimentally established that there is the parameter spread of service characteristics of composites of one brand because of the lack of reasonable criteria defining quality of initial components, first of all polytetrafluoroethylene (PTFE) and the carbon fibers (CF). Well known that the powdery products of the F4TM, F4PN brands, which are widely applied in PTFE-based composites' technology and positioned by producers as polytetrafluoroethylene, represent particles with uncontrollable parameters of molecular weight and morphology. The analysis testifies to a cluster structure of a semi-finished product of PTFE's particles which are formed by the low-dimensional fragments connected among themselves by filament elements which indicate the special conditions of synthesis and cause dispersion both dimensional and morphological characteristics of a matrix semi-finished product (Figure 1).

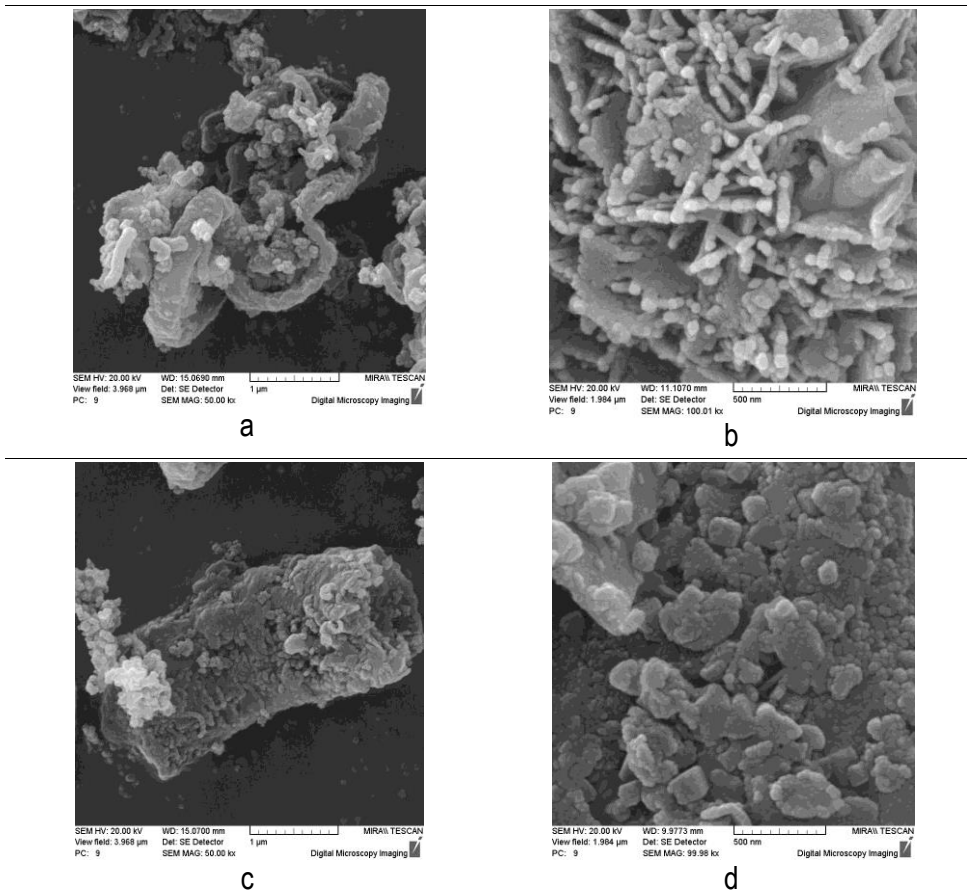
FIGURE 1. A TYPICAL MORPHOLOGY OF THE PARTICLES OF POLYTETRAFLUOROETHYLENE (a, b, c) AND ULTRAFINE POLYTETRAFLUOROETHYLENE (d)



Source: Data of own probes.

It is obvious that the essential contribution to characteristics of the compositions on the basis of PTFE will make a morphological factor of particles. In the case of applying the traditional technology of receiving, based on consecutive stages of mixing of the components, cold pressing of blanks and their agglomeration it is obvious that there is an essential influence of interpartial friction on formation of defects of structure of a composite. Therefore at a choice of PTFE-based composite's components it is necessary to provide correlation of parameters of particles' habitus and morphology of the surface layer. The morphological analysis of disperse particles of the PTFE widespread modifiers (fragments of carbon fibers, carbon nanotubes, mineral products of tripolite and schungite) was made by the means of the REM and AFM methods. The results testify to essential distinction in the structure of the surface layer, which defines the mechanical component of the adhesive interaction on the interface "matrix PTFE - filler" (Figure 2).

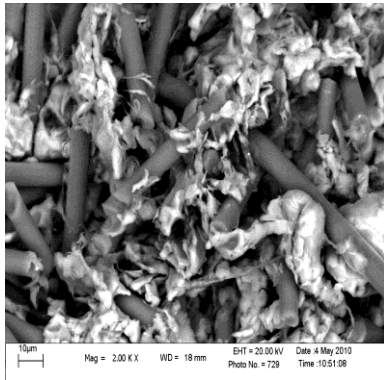
FIGURE 2. THE MORPHOLOGY OF THE SURFACE LAYER OF CARBON NANOTUBES (a), TRIPOLITE (b), CARBON FIBER (c), SCHUNGITE (d)



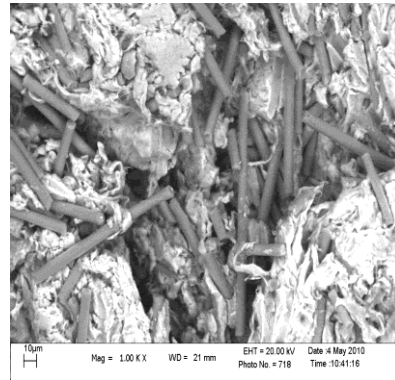
Distinction in the morphology of the surface layer of modifying particles predetermines differences in kinetics of formation of the boundary layer at the stage of cold pressing of blanks because time of pressing is limited to a production

cycle's duration and doesn't exceed 3-6 min. Therefore even at rather high values of pressure at the stage of cold pressing ($P = 60-70$ MPa) the effect of cold flow of PTFE particles isn't shown fully. Meanwhile, this effect defines kinetics of filling of microroughnesses on the surface layer of the filler particles and formation of boundary structure with the minimum quantity of defects. The increase in pressure of cold pressing or duration of holding blanks under pressure has almost no effect on the parameters of strength and tribotechnical characteristics of PTFE-based composites. At the same time these measures will significantly increase power consumption of process and product costs. Besides, an increase in compaction pressure leads to boost of resistance to deformation by clusters of filler particles which have been formed in the course of mixing of components because of distinction in habitus, size, specific weight and the electrophysical parameters causing processes of electrization. The boundary layer, which was created at a stage of cold pressing, doesn't change its structure at the stage of blanks' hot agglomeration in the traditional technological process due to lack of viscous-flow condition of matrix polymer which peculiar to other thermoplastics.

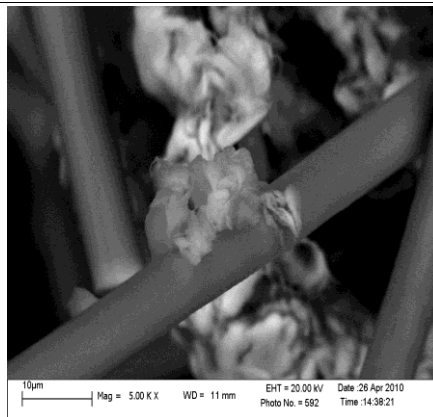
FIGURE 3. THE CLUSTER STRUCTURE OF FRAGMENTS OF CARBON FIBER IN THE COMPOSITE PTFE +10 WT. %: a) SOURCE; b) AFTER COLD-PRESSING AT $P = 70$ MPa; c) THE DISTRIBUTION OF ULTRAFINE PTFE PARTICLES IN A MIXTURE OF CARBON FIBER FRAGMENTS



a



b



c

Therefore, there is the considerable parameter spread of the deformation, strength and tribotechnical characteristics, due to the peculiarities of formation and structure of the boundary layer, as well as the presence of characteristic technological prerequisites for the formation of structural defects. It is significant that the structural defects are found at unconditional observance of requirements of production schedules for products from one structure of a composite material on the basis of PTFE. To number of these defects should be carried the expressed concentration gradient of filler particles on the volume of the matrix polymer, caused by technology of mixing and distinction of their geometrical, electrophysical parameters and weight. These filler particles with sizes, smaller, than industrial PTFE powder (10-500 microns) and close habitus will form clusters in areas of contact pieces of matrix polymer (Figure 3).

Defective sites with almost total absence of the binding (PTFE), formed in the mixing step (Figure 3a), will remain after the stage of cold pressing (Figure 3b). Thus as a result of action of mechanical and electrophysical factors during the mixing process initial particles of PTFE they will also form cluster structures, which increase the concentration gradient in the volume of the composite material and blanks (Figure 3a, 3b). These factors are responsible for technological preconditions for formation of defects in product's heterogeneous structure even under optimal technological modes of preparation of components and manufacturing of products from composite material according to the existing production schedules. The role of distinction in habitus, geometrical and electrophysical characteristics of components is most important when using modifiers in the form of filaments received by dispergation of fibrous (fabric) semi-finished products. The use of traditional methods of preparation, mixing of the components and forming products by cold pressing with the subsequent agglomeration doesn't allow achieving the degree of homogeneity, ensuring the formation of a faultless macrostructure at any ratio of components in composites with fibrous modifiers. The presence of macroscopic defects in products reduces the positive influence of a structural factor on intermolecular and supramolecular levels, which is realized when using the mechanically activated, high-disperse and dressed components of various structures, the nature and technology of receiving.

Considering some features of technology of receiving composites on the basis of PTFE such as prolonged power influence at a temperature of 350-370 °C, the range of modifiers is limited by the components which keep their parameters in the conditions of thermooxidizing influence. The group of such modifiers include carboniferous (carbon fiber, carbon black, ultradisperse diamondlike graphite, graphite, coke) and silicate (schungite, tripolite, zeolites, clays, mica) fillers, which are widely applied in materials science in PTFE-based composites of various functions. In this nomenclature special attention is paid to the action of modifier' particles on the wear process of the interfaced counterbody. Therefore the effective influence of a number of modifiers on the process of reinforcement and increase of wear resistance is leveled by considerable abrasive wear of tribosystem' elements. This factor will amplify at increase in concentration of the modifier while using the traditional technology of formation of composites and products.

Our studies let us to establish the key factors of dropping the level of consumer characteristics of composites on the basis of PTFE within the strategy of power- and resource-saving technologies. These include differences in initial geometrical, dimensional, electrophysical parameters of components,, the instability of molecular, rheological and geometrical characteristics of the PTFE industrial brands, the expressed inertness of a macromolecule of PTFE in the processes of interphase interaction, the lack of viscous-flow condition, the processes of agglomeration of disperse particles at the stage of mixing. On the basis of the carried-out analysis the perspective directions of improvement of structure of composites on the basis of PTFE at intermolecular and interphase levels are

defined. They consist in the use of functional components and special processing methods within traditional production.

To accomplish the task we used various approaches. To stabilize geometrical, dimensional and technological parameters of industrial PTFE powder we applied as the multipurpose modifier the products of thermogasdynamical synthesis of polytetrafluoroethylene (UPTFE). A characteristic feature of particles of UPTFE, which are inclined to the formation of cluster structures (Figure 1d), is the existence in their structure the oligomer components of various molecular weight with different melting points and the increased ability to deformation. When modifying disperse particles of PTFE of the F4TM and F4PN brands by particles of UPTFE, habitus' change occurs as well as an increase in technological parameters, followed by the rise of indicators of strength by 1,1-1,2 times, and elongation (Table 1) and wear resistances by 2,5-3 times (Figure 4).

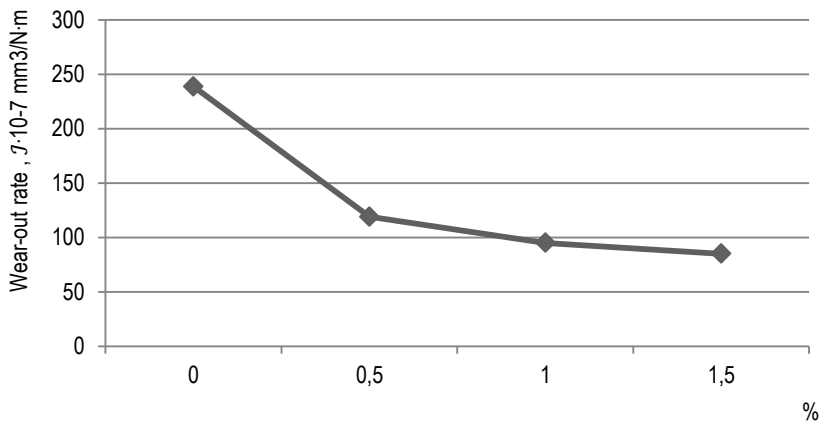
TABLE 1. CHARACTERISTICS OF PTFE MODIFIED BY THE PRODUCTS OF THERMOGASDYNAMIC SYNTHESIS (UPTFE)

Characteristic	Value of the index for the material			
	F4TM	F4TM mod.*	F4PN	F4PN mod.*
Tensile strength, MPa, at least	30	32	25	30
Percentage elongation, %, at least	450	470	350	380
The average particle size, micron	6-20	10-20	46-135	60-140

Source: Data of own probes.

Note: * - the content of UPTFE is 0.5 wt. %.

FIGURE 4. THE RELATIONSHIP BETWEEN THE CONTENT OF UPTFE AND THE WEAR-OUT RATE OF THE PTFE SAMPLES



Source: Data of own probes.

Nearly identical structure of macromolecules of oligomeric and polymeric fractions of UPTFE and PTFE causes their thermodynamic compatibility during the agglomeration process, and existence of oligomeric fractions promotes rapprochement of habitus of PTFE's particles, plasticization of boundary layers and reduction of number of macrodefects of structure in the course of pressing and agglomeration. An important feature of UPTFE's modifying action is formation on the friction surface a separation layer with high resistance to processes of the reformation, which will reduce wear at dry friction.

Ultrafine particles of UPTFE promote an increase in parameters of deformation and strength characteristics of the composites which contain filiform fillers as well as particles of carbon black (Tables 2, 3).

TABLE 2. CHARACTERISTICS OF COMPOSITES ON THE BASIS OF PTFE OF DIFFERENT BRANDS FILLED BY CARBON FIBER WITH THE ADDITION OF UPTFE

The name of parameters	Test data			
	With the addition of modifier		Without modifier	
	The matrix		The matrix	
	PTFE 4TM	PTFE 4PN	PTFE 4TM	PTFE 4PN
Tensile strength, MPa, at least	27	23	24	17
Density, kg/m ³ , at least	2000	1970	1980	1930
Wear-out rate, $J \cdot 10^{-7} \text{ mm}^3/\text{N} \cdot \text{m}$, no more	3,0	3,5	3,3	3,5

Source: Data of own probes.

Note: * - the content of UPTFE is 0.5 wt. %.

TABLE 3. MECHANICAL CHARACTERISTICS OF THE COMPOSITES ON THE BASIS OF PTFE FILLED BY CARBON BLACK WITH THE ADDITION OF UPTFE

Material	Tensile strength, MPa	Density, kg/m ³	Wear-out rate, $J \cdot 10^{-7} \text{ mm}^3/\text{N} \cdot \text{m}$
F4PN	19,29	2147	238,72
F4PN + 2,0% «Forum» + 0,1% carbon black of P234 mark	22,47	2356	211,52
F4PN + 2,0% «Forum» + 0,5% carbon black of P234 mark	24,30	2292	81,51
F4PN + 2,0% «Forum» + 1% carbon black of P234 mark	24,90	2286	54,33
F4PN + 2,0% «Forum» + 3% carbon black of P234 mark	23,08	2292	26,70
F4PN + 2,0% «Forum» + 5% carbon black of P234 mark	22,47	2508	39,81
F4PN + 2,0% «Forum» + 10% carbon black of P234 mark	22,17	2243	30,94
F4PN + 2,0% «Forum» + 0,1% carbon black of P803 mark	23,08	2300	187,65
F4PN + 2,0% «Forum» + 0,5% carbon black of P803 mark	21,56	2292	213,52
F4PN + 2,0% «Forum» + 1% carbon black of P803 mark	24,30	2299	77,14
F4PN + 2,0% «Forum» + 3% carbon black of P803 mark	19,44	2243	66,66
F4PN + 2,0% «Forum» + 5% carbon black of	26,42	2260	66,79

P803 mark			
F4PN + 2,0% «Forum» + 10% carbon black of	26,12	2239	49,52
P803 mark			

Disperse particles of UPTFE at a stage of preparation of a filling agent settle down in the cavities of carbon fiber clusters, thus reducing the presence of defects in the composite material and promoting an equal distribution of particles of carbon black on the surface of modified PTFE. An increase of density testifies to decrease of the presence of defects of heterogeneous structure of composite materials on the basis of PTFE modified by UPTFE. A characteristic consequence of action of UPTFE in composites with fillers of filiform (carbon fiber) and spherical (carbon black) habitus is the change of the tribotechnical characteristics. Wear resistance at friction of PTFE-based composites, which are filled by carbon fiber, is defined mainly by fragments of carbon fiber which form the oriented layer with high resistance to thermal and mechanical loads. In the course of frictional interaction of composites with high-disperse carbon black is formed the separation layer from polymer-oligomeric products of tribochemical reactions of PTFE and carbon black. This layer possesses a high resistance to reformation and an ability to alternating transfer.

The mechanism of multilevel modifying action of UPTFE in composite materials consists both in reduction of defects in the PTFE matrix and in decrease of number of clusters of filler particles (carbon fiber, carbon black) which contain no binding (Figure 3a).

The conducted researches of features of heterogeneous structure of composite materials on a basis of polytetrafluoroethylene and modifiers of various composition, geometry, technologies of receiving and habitus allowed to develop the principles of receiving low-defective products by the means of regulation of processes of interphase interaction at various stages of production.

Conclusion

We investigated mechanisms of formation of defects of heterophase structure of PTFE-based composites, containing raised quantity (25 - 35 wt.%) of carbon fillers. The defects cause fracture and wear of products at operation in tribotechnical and sealing systems. It is found that the main factors creating structural and technological preconditions of appearing of structural paradox of reducing the strength and wear resistance with the increase the degree of filling of PTFE, are the disparity of geometrical, dimensional and electrophysical characteristics of disperse particles of the components, causing formation of clusters of fillers, and low level of the adsorptive interaction in an interphase zone due to structural and rheological features of polymer (Voropaev, Gorbatsevich, Struk, Kravchenko, and Ovchinnikov, 2008; Struk, Gorbatsevich, Voropaev, Avdeichik, and Kravchenko, 2009; Antonov, Avdeychik, Gorbatsevich, Voropaev, and Mikhailova, 2009; Voropaev and Gorbatsevich, 2009; Voropaev, 2009).

The concept of multilevel modification in relation to the creation of the high-filled composites based on PTFE is developed. The mechanism of modifying action of products of thermogasdynamic synthesis of polytetrafluoroethylene (UPTFE) in the composite material is established. It is based on the increase in strength and tribotechnical characteristics of matrix polymer as well as on the increase in adhesive interaction at the interface of the section "PTFE-carbon fiber" and on the rise of separation layer's stability to multi-cycle influences in the area of frictional contact. In accordance with the results of the research we created the technology of modification of PTFE-based composites' components. For instance, modification of carbon fibers by UPTFE will provide an increase in wear resistance by 1,1-1,2 times and rupture resistance increase by 1,1-1,35 times

when forming products by cold pressing with the subsequent agglomeration (Gorbatsevich, Struk, Prushak, and Voropaev, 2011; Mikhailova, Voropaev, Gorbatsevich, and Lauryniuk, 2011).

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