

Development of Antifriction Materials Based on Polytetrafluoroethylene Filled with Binary Fillers

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Abstract – The paper presents the results of the study of polymer composite materials (PCM) based on polytetrafluoroethylene (PTFE) filled with carbon fibers (CF) and ultrafine polytetrafluoroethylene (UPTFE). Physic-mechanical and tribological characteristics of PTFE based polymer composite materials containing 1–10 wt.% CF+1 wt.% UPTFE have been studied. Simultaneous introduction of carbon fibers and UPTFE in PTFE causes the deformation-strength characteristics to remain at the level of those of the polymer matrix regardless of the CF content. Increased content of carbon fibers in UPTFE increases the stress during compression and decreases the PCM density. Wear resistance increases up to 310 fold, and the coefficient of friction of polymer composites decreases by 17–19% compared to that of the initial polymer. The results of the study of polymer composites by XRD analysis and scanning electron microscopy are presented. Introduction of fillers in PTFE changes the supramolecular structure, which is followed by an increased degree of crystallinity. The developed materials are promising for use in friction units of machinery and equipment.

Keywords – PTFE; polymer composite materials; carbon fiber; UPTFE; physico-mechanical characteristics; wear; coefficient of friction.

I. INTRODUCTION

Polytetrafluoroethylene (PTFE) is an industrially produced polymer material with a number of unique characteristics due to chemical and molecular structure of the polymer. It is most widely used as an antifriction material due to low and stable coefficient of friction in a wide range of operating temperatures [1]. In addition, PTFE exhibits exceptional chemical inertness, thermal and frost resistance, and therefore it can be used in corrosive environments at high and low temperatures [2]. Unfilled PTFE is typically rarely used in friction units due to high wear and creep indicators under low loads. To increase wear resistance and reduce creep, PTFE is modified using filling technology. Solid fibrous or dispersed fillers are introduced into the polymer matrix, which improve operational characteristics of PTFE. Thus, polymeric composite materials (PCM) based on PTFE with high wear resistance become very

valuable material for machines and apparatuses in the manufacturing and extractive industries due to a number of unique characteristics inherent in the original polymer.

Among fillers, carbon fiber (CF) exhibits the preferred characteristics, which include high strength, wear resistance and minimal (compared to other types of fibers) abrasive effect on the conjugate metal counterbody [3, 4]. For filling PTFE, short carbon fibers are used, which can significantly improve mechanical and tribological characteristics of the original polymer [5, 6]. However, both carbon fibers and PTFE are sufficiently inert materials. As a result, they show low adhesive strength, which reduces mechanical characteristics of PCM made based on them. Therefore, among carbon fillers, modified carbon fibers with low surface energy close to that of PTFE are of interest [7]. It is known that introduction of modified milled carbon fibers makes it possible to maintain the strain-strength characteristics of PCM at the level of those of the original polymer. Such composites possess not only high mechanical characteristics, but also increased wear resistance [8–10].

In recent years, ultrafine PTFE (UPTFE) is of great interest as a solid lubricant for antifriction applications. These additives can significantly improve tribotechnical and antifriction characteristics of various materials [11]. The UPTFE in small quantities can improve the operational characteristics of PCM based on PTFE [3, 12]. In the cited studies, it was found that the effect of low molecular weight PTFE of the FORUM brand is due to their thermodynamic compatibility with PTFE during monolitzation, and the presence of oligomeric fractions provides the convergence of the habit of individual PTFE particles, plasticization of the boundary layers and reduction in the number of the structural macrodefects during pressing and sintering [13].

A wide range of various polymer composite materials is produced in the fluoropolymer market. Moreover these are composites with high degree of filling for the majority of industrially manufactured and used PTFE based materials. Introduction of a large amount of filler decreases the strength characteristics and increase the coefficient of friction and the

elastic modulus of the composites, which limits their field of application [4]. In this regard, a crucial task is to develop materials with low rigidity and high wear resistance.

The aim of the study is to investigate the joint effect of carbon fibers and UPTFE on physico-mechanical and tribological characteristics and structure of PTFE.

II. METHODS AND MATERIALS

Polytetrafluoroethylene of grade PN-90 (Halopolymer, Russia) was used as a polymer matrix. PTFE is an easily clumped white powder with density of 2.16 g/cm³ and the particle size varying in the range of 46–135 μm.

Modified carbon fibers (CF) BELUM (V.A. Bely Institute of Mechanics of Metal-Polymer Systems, National Academy of Sciences of Belarus) modified by the plasma-chemical method in the medium of organofluorine compounds were used as carbon filler. The length of fibers varies in the range of 50–500 μm. The filament diameter varies in the range of 4.5–10.0 μm. To improve the tribological characteristics, low molecular weight fluoroplastic of the FLURALIT brand (Fluralit Synthesis, Russia) was used. Ultrafine PTFE is produced based on industrial PTFE by the method of thermal catalytic decomposition. It is a fine friable white powder with the particle size varying in the range of 1–10 μm.

The samples were manufactured using standard PTFE processing technology: mixing components in a high-speed blade mixer, pressing using a hydraulic press at a specific pressure of 50 MPa and sintering in a programmable furnace "SNOL 180/400" ("SNOL", Lithuania) at 375±5 °C.

Physico-mechanical characteristics of PTFE and PCM were determined using standardized methods. The tensile test method determined the tensile strength σ , the elongation at break ε and the tensile modulus E in accordance with GOST 11262. The samples were used in the form of type II blades, and the speed of movement of the grippers was 100 mm/min. The compression test method determined the compressive stress in accordance with GOST 4651 at 10% deformation. The samples were made in the form of a straight cylinder with a diameter of 10.00±0.01 mm, the test speed was 1 mm/min, and a universal testing machine Autograf AGS-J (Shimadzu, Japan) was used. The density of PTFE and PCM was investigated in accordance with GOST 15139.

The ARL X'TRA X-ray powder diffractometer (Thermo Fisher Scientific, Switzerland) was used to determine the degree of crystallinity of PTFE and PCM with respect to the ratio of the areas of reflections that correspond to amorphous and crystalline regions. An X-ray tube with a copper anode (λ (CuK α)=0.154 nm) was used as a radiation source. Scanning was performed in the range from 3 to 60° with a step size of 0.04° and 3 s accumulation time at each point (error 0.01° depends on different factors). Primary data processing was performed using the WinXRD software, and qualitative analysis was carried out using the Crystallographica Search-Match software. The supermolecular structure and friction surfaces of PTFE and PCM were analyzed using a JSM-7800F LV raster electron microscope (JEOL, Japan). The samples for the study were manufactured by the method of cold cleavage

(liquid nitrogen), and the studies were performed in the secondary electron mode.

III. RESULTS

The results of the physico-mechanical characteristics of the initial PTFE and PCM based on it are given in Table. 1. The study employed carbon fibers of the BELUM brand modified in the medium of organofluorine compounds by plasma-chemical method [7, 8]. To select the optimal content of UPTFE in the composite, its effect on the physico-mechanical characteristics of PTFE was studied. When 1 wt.% UPTFE is introduced into the polymer matrix, the tensile strength is maintained at the level of that of the original polymer. It can be seen that further introduction of UPTFE to 2 wt.% decreases the tensile strength of the polymer (Table 1). The compressive stress at 10% relative deformation remains at the level of the compressive stress of the original PTFE regardless of the content of UPTFE. Relative elongation at PTFE+UPTFE break increased by 19–24% with respect to that of the original polymer, which indicates the plasticizing effect of low-molecular-weight PTFE due to an increased effect of viscous flow of the material under tension [14]. The modulus of tensile elasticity of PTFE upon introduction of 1–2 wt.% UPTFE increased by 9–11% compared with that of the original polymer. This change in the deformation characteristics and modulus of elasticity of PCM is consistent with the results reported in [13]. Thus, the results of preliminary studies showed that the content of 1 wt.% UPTFE is sufficient to modify the PTFE, in which the tensile strength is maintained at the level of that of the original polymer matrix.

TABLE I. PHYSICO-MECHANICAL CHARACTERISTICS OF PTFE AND PCM

Sample	σ_r , MPa	ε , %	σ_c , MPa	E, MPa
Initial PTFE	20±1	320±20	16±1	440
PTFE+1 wt.% UPTFE	19±1	381±18	15±1	481
PTFE+2 wt.% UPTFE	17±1	397±21	15±1	489
PTFE+1 wt.% CF+1 wt.% UPTFE	19±1	329±11	16±1	420
PTFE+2 wt.% CF+1 wt.% UPTFE	20±1	330±22	17±1	428
PTFE+3 wt.% CF+1 wt.% UPTFE	19±1	330±17	18±1	408
PTFE+4 wt.% CF+1 wt.% UPTFE	19±1	315±19	19±1	423
PTFE+5 wt.% CF+1 wt.% UPTFE	19±1	354±16	20±1	452
PTFE+8 wt.% CF+1 wt.% UPTFE	21±1	300±15	21±1	458
PTFE+10 wt.% CF+1 wt.% UPTFE	20±1	289±14	22±1	489

As can be seen in Table 1, indicators of tensile strength and relative elongation at PTFE break upon simultaneous introduction of CF in an amount of from 1 to 10 wt.% and 1 wt.% UPTFE remain at the level of those of the original polymer matrix. Compression stress for PCM monotonically increases as CF content grows. The maximum value of the stress under compression is recorded in PCM containing 10 wt.% CF, where the compressive stress is 30% higher relative to that of the initial PTFE.

One of the important characteristics of sealing materials is the modulus of elasticity, which determines the seal tightness. Unfilled PTFE is typically characterized by low modulus of elasticity, which is optimal for sealing materials. Therefore, when filling PTFE, it is necessary to maintain the elastic modulus index at the level of that of the polymer matrix. In the filling range from 1 to 8 wt.% CF, the PCM modulus of elasticity remains at the level of that of the initial polymer. The modulus of elasticity is observed to increase in PCM that contains 10 wt.% CF+1 wt.% UPTFE.

The effect of the filler content on tribotechnical characteristics of PCM was studied. Table 2 summarizes the results of the study of the rate of mass wear and the coefficient of friction for PTFE and PCM manufactured on its basis.

TABLE II. TRIBOTECHNICAL CHARACTERISTICS OF PTFE AND PCM

Sample	<i>I</i> , mg/h	<i>f</i>
Initial PTFE	160.00	0.22
PTFE + 1 wt.% UPTFE	80.00	0.18
PTFE+1 wt.% CF+1 wt.% UPTFE	3.58	0.17
PTFE+2 wt.% CF+1 wt.% UPTFE	1.27	0.17
PTFE+3 wt.% CF+1 wt.% UPTFE	0.79	0.17
PTFE+4 wt.% CF+1 wt.% UPTFE	0.74	0.18
PTFE+5 wt.% CF+1 wt.% UPTFE	0.59	0.19
PTFE+8 wt.% CF+1 wt.% UPTFE	0.55	0.19
PTFE+10 wt.% CF+1 wt.% UPTFE	0.51	0.19

I – wear rate; *f* – coefficient of friction

The analysis of the data presented in Table 2 shows that introduction of 1 wt.% UPTFE results in a 2-fold decrease in the rate of the PCM mass wear compared to that of the initial PTFE. Complex filling of "CF+UPTFE" leads to 45- to 310-fold increase in the wear resistance of composites compared to the initial polymer with the deformation and strength characteristics maintained at the level of the initial PTFE. The maximum value of wear resistance was observed in PCM with a content of 10 wt.% CF + 1 wt.% UPTFE.

For assembly units with limited or restricted lubrication, a low friction coefficient value is an important characteristic. Table 2 shows that the composites of PTFE+1 wt.% UPTFE, the friction coefficient decreased by 17% compared to the unfilled PTFE. Introduction of a binary filler (CF+UPTFE) into PTFE leads to a decreased value of the PCM friction coefficient by 14–19% compared to that of the initial PTFE and remains at the same level regardless of the degree of CF filling. A decrease in the PCM friction coefficient is due to the fact that in the frictional interaction of the counterbody with the composite, part of UPTFE facilitates the formation of an easily moving stable transfer film with little shear resistance on the friction surfaces. The formation of an unstable film reduces the friction force in the frictional contact, which decreases the wear rate of the friction pair [15].

To explain the changes in the physico-mechanical and tribotechnical characteristics of composite materials, structural studies were carried out by the XRD and SEM methods. Table

3 presents the results of study of the degree of crystallinity and density of PTFE and PCM.

TABLE III. DEGREE OF CRYSTALLINITY AND DENSITY OF PTFE AND PCM

Sample	α , %	ρ , g/cm ³
Initial PTFE	63.7	2.16
PTFE+1 wt.% UPTFE	65.9	2.16
PTFE+1 wt.% CF+1 wt.% UPTFE	66.8	2.15
PTFE+2 wt.% CF+1 wt.% UPTFE	67.8	2.14
PTFE+3 wt.% CF+1 wt.% UPTFE	70.3	2.13
PTFE+4 wt.% CF+1 wt.% UPTFE	69.5	2.12
PTFE+5 wt.% CF+1 wt.% UPTFE	68.9	2.10
PTFE+8 wt.% CF+1 wt.% UPTFE	71.0	2.07
PTFE+10 wt.% CF+1 wt.% UPTFE	70.1	2.04

As can be seen in Table 3, introduction of fillers leads to an increase in the degree of PCM crystallinity compared to that of the initial polymer. Introduction of 1 wt.% UPTFE into PTFE slightly increases the degree of crystallinity, which indicates the effect of this filler on the formation of the polymer matrix (Table 3).

The degree of PTFE crystallinity upon introduction of hydrocarbons of 1 to 10 wt.% increased from 63.7 to 71.0%. This can be due to the increased share of the structurally active surface of the organomodified hydrocarbon filler. The maximum value of the degree of PTFE crystallinity is found in PCM at a content of 8 wt.% CF. Further increase of the fiber content up to 10 wt.% in the composite slightly decreases the degree of the material crystallinity. This can be due to the formation of excessive crystallization centers and decreased mobility of the polymer chains due to steric factors [16]. The obtained results of a change in the degree of PCM crystallinity are consistent with the data in [17, 18]. Thus, carbon fibers within the range of 1–10 wt.%, significantly affect the degree of crystallinity of PTFE based PCM.

The density of composites gradually decreases as the filler content increases, which is likely due to loosening of the supramolecular structure of the polymer during introduction of CF with UPTFE. In addition, the fibers are characterized by a lower density compared to that of the polymer matrix (ρ (CF)=1.45 g/cm³ and ρ (PTFE)=2.16 g/cm³).

For qualitative description of the morphology and quantitative assessment of structural formations in the supramolecular structure of PTFE and PCM, microscopic studies were carried out using the SEM method (Fig. 1). As is known, the degree of PCM crystallinity upon introduction of CF up to 10 wt.% is associated with morphological changes in the supramolecular structure of the polymer matrix [17].

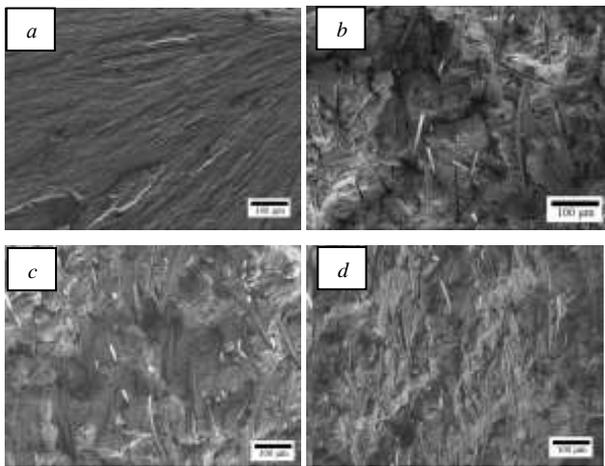


Fig. 1. Micrograph of the supramolecular structure, 150x magnification: a) initial PTFE; b) PTFE+1 wt.% CF+1 wt.% UPTFE; c) PTFE+5 wt.% CF+1 wt.% UPTFE; d) PTFE+8 wt.% CF+1 wt.% UPTFE.

As can be seen in Fig. 1, the supramolecular structure of the initial PTFE consists of lamellar crystalline structures. It can be seen that carbon fibers in all composites are distributed uniformly in the polymer volume and are oriented randomly. The initial lamellar structure of the polymer fragmented during introduction of CF+UPTFE causes formation of spherulitic formations, which can be clearly seen in Fig. 1 b. The size of spherulitic formations in the selected filling range varies from 10 to 100 μm . Similar results were obtained in [19]. In addition, within the concentration range of filling (1–10% CF), the material has a single-type supramolecular structure; the only difference is that the number of fibers on the cleavage surface grows up as their concentration in the material increases.

Fig. 2 shows a micrograph of the supramolecular structure of the PCM composition: PTFE+5 wt.% CF+1 wt.% UPTFE at high magnification (3000 \times).

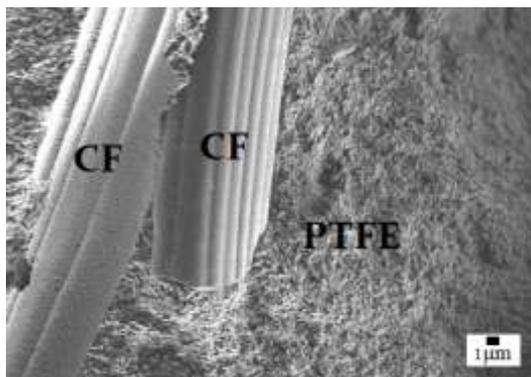


Fig. 2. Micrograph of the supramolecular structure of PTFE+5 wt.%+1 wt.% UPTFE, 3000x magnification.

As can be seen in Fig. 2, the supramolecular structure of PCM, carbon fibers tightly adhere to the polymer matrix. This indicates an increased adhesive interaction between the polymer and the fibrous filler. At the same time, the wear resistance of PCM increased with the deformation-strength characteristics maintained at the level of those of the initial PTFE.

Fig. 3 shows the results of the study of the friction surfaces of PTFE and PCM by the SEM method.

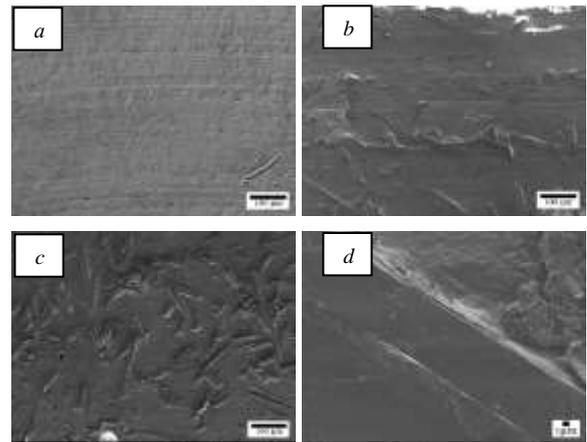


Fig. 3. Micrograph of the friction surfaces, 150 \times magnification: a) initial PTFE; b) PTFE+1 wt.% CF+1 wt.% UPTFE; c) PTFE+5 wt.% CF+1 wt.% UPTFE; d) PTFE+5 wt.% CF+1 wt.% UPTFE (3000 \times magnification).

Fig. 3 a illustrates that the friction surface of the initial PTFE displays grooves along the sliding direction, which is due to the lamellar structure of the polymer. Micrographs in Fig. 3 b and c show that carbon fibers are distributed uniformly over the friction surface and randomly oriented similar to those in the PCM volume (Fig. 1). Carbon fibers on the friction surfaces of PCM act as microprotrusions (Fig. 3 d) to protect the surface layer from destruction [10]. In addition, as the content of CF increases, the number of fibers on the friction surface of PCM grows, which is consistent with the increased wear resistance of the material.

To assess the effect of UPTFE on tribotechnical characteristics of PCM, the values of the friction coefficient of composites with UPTFE and those without it were compared (Fig. 4).

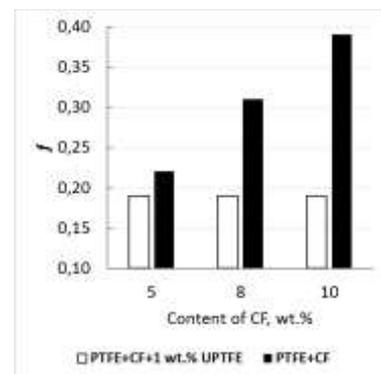


Fig. 4. Comparison of the friction coefficient of PCM with and without UPTFE

As can be seen in Fig. 4, the values of the friction coefficient of materials that contain UPTFE are lower compared to composites PTFE+CF. Additional introduction of UPTFE significantly decreases the friction coefficient of PCM in composites which contain 8–10 wt.% CF.

IV. CONCLUSION

The paper investigates the effect of a binary filler (CF+UPTFE) on the structure and operational characteristics of PTFE. It is shown that the optimal content of UPTFE in the composite is 1 wt. %. The coefficient of friction of materials with a binary filler decreased by 14–19%, and the wear resistance increased 45- to 310-fold with the deformation and strength characteristics maintained at the level of those in the initial PTFE. Structural studies revealed that introduction of fillers changes the morphology and degree of crystallinity of the polymer, thus contributing to the formation of a more structured material characterized by enhanced operational characteristics. Thus, due to acceptable deformation and strength characteristics, relatively low elastic modulus and friction coefficient, the developed PCM can become an alternative to highly filled composites. These materials can be used as sealing and antifriction materials in various friction units without any lubrication.

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