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Polytetrafluoroethylene-Based Polymeric Composite Materials Intended for Triboengineering Applications

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Abstract—The influence of ultradispersed ceramics particles on formation and wear of polytetrafluoroethylene-based polymer composites was elucidated. Factors improving the performance characteristics of the composites were identified.

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INTRODUCTION

Antifriction self-lubricating plastics, when applied in friction units of machines (sliding bearings, separators of rolling contact bearings, tape-transport mechanisms, gear systems, etc.) not only replace metals and alloys but also increase the robustness and durability of technical systems, along with reducing the energy consumed for their manufacture and operation and making their use more environmentally friendly [1].

From the triboengineering viewpoint, the greatest promise is shown by modified polymers containing various fillers. Relevant benefits stem from weakening of intermolecular bonds in the polymer, as well as from formation of an optimal structure of the material, participation of fillers in friction as wear inhibitors, and enhancement of the serviceability of the friction-transfer film [2, 3].

Here, we overview the developments dedicated to new polymer materials intended for triboengineering applications, specifically for manufacturing friction units of technical systems exploited under cold climate conditions. This is topical because of an urgent need in increasing the reliability, safety, and efficiency of exploitation of technical systems, pipelines, and housing and municipal facilities in the Russian North. Sealing materials currently used in Russia's mechanical engineering sector have inadequate frost and wear resistances. From 30 to 50% of failures of technical systems is associated with low efficiency of seals under cold climate conditions [4, 5]; their efficiency in winter periods decreases 1.5 times on the average, the full operating time, 2–3 times, and the actual service life, 2–3.5 times [6].

Among the polymers used for manufacture of friction units, the best physicomechanical and triboengineering characteristics are exhibited by polytetrafluoroethylene, which is applied in the most critical technical systems. A valuable property of polytetrafluoroethylene-based composite materials is serviceability over a wide temperature range, at which low and stable values of the friction coefficient (0.1–0.2) are preserved and smooth sliding is provided [4, 7, 8]. This is of much significance for technical systems exploited under extreme conditions.

The tribological properties of polymers can be controlled by modification of their supramolecular structure [1, 9, 10]. Okhlopkova et al. [11, 12] modified the supramolecular structure of polytetrafluoroethylene with various classes of ultradispersed ceramics: transition metals nitrides, simple, double, and triple oxides, as well as oxynitrides with the average particle size of 4–100 nm. Introduction of ultradispersed ceramics able of forming cluster-like ensembles within the material initiates structure formation and modifies the crystallization mechanism for polytetrafluoroethylene [13, 14]. This yields a reinforced polymeric system characterized by enhan-ced strength and triboengineering characteristics.

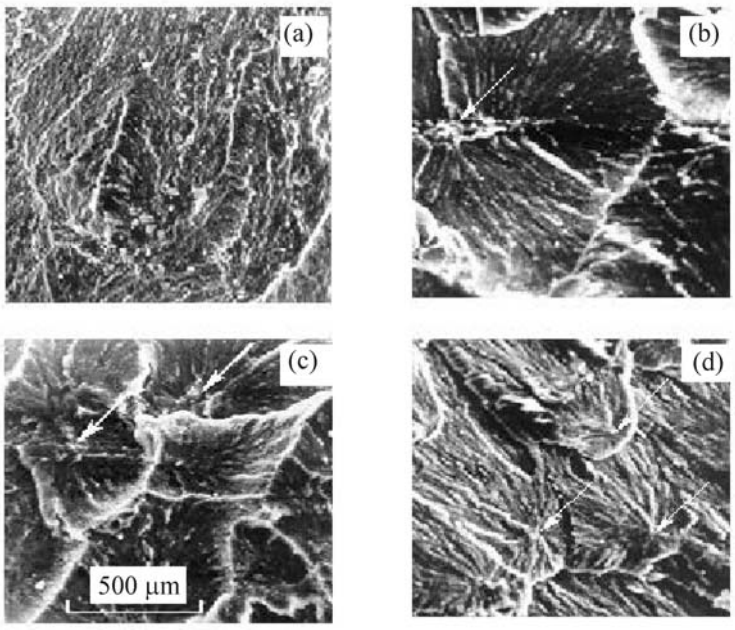

Fig. 1. Electron-microscopic images of brittle splits of samples of polytetrafluoroethylene (PTFE) and composites thereof: (a) PTFE, (b) PTFE+SiO_2, (c) PTFE+Al_2O_3; and (d) PTFE+TiO_2. Ceramics content 2 wt %.

Structure and Thermodynamic Properties of Polytetrafluoroethylene Modified with Ultradispersed Ceramics

The transformation of the supramolecular structure of polytetrafluoroethylene upon introduction of ultradispersed ceramics is underlain by factors associated with the influence of the solid surface of the filler particles on the mobility of macromolecules and formation in the boundary area of adsorbed polymer layers [15–17]. This is responsible for the difference in the structure formation of the polymer in the polymer filler bulk and near the interface, depending on the filler concentration.

An electron-microscopic examination of the structure of polytetrafluoroethylene modified with ultradispersed ceramics (Fig. 1) showed that ceramics particles with a large specific surface area (50–200 $m^2 g^{-1}$) significantly affect crystallization and cause formation of supramolecular structural elements that are not typical for the initial polymer. As subjects of structure examinations we chose low-temperature brittle splits of the polymeric composites prepared at liquid nitrogen temperature. The ultradispersed ceramics particles act as crystallization sites yielding structural formations shaped as symmetric polyhedrons. By contrast to known composites containing traditional fillers like coke and molybdenum disulfide, composite materials filled with ultradispersed ceramics have a more perfect structure characterized by small spherulites and a high packing density of structural elements [13, 17]. For example, the composite containing aluminum oxide with a large specific surface area (200 $m^2 g^{-1}$) and, consequently, with a high surface activity, it comprised of perfect supramolecular elements of identical size with a small diameter (17–20 μm). Formation of spherulites in polytetrafluoroethylene is validated by polarized optical-microscopic data [13].

A differential calorimetric examination of samples of Al_2O_3-modified polytetrafluoroethylene allowed estimating the heat effects of the phase transitions occurring upon introduction of the filler, as well as the polymer–Al_2O_3 interaction energy (Fig. 2).

The occurrence of a ΔH_m maximum for the composite containing 2 wt% ultradispersed Al_2O_3 (curve *1* in Fig. 2) suggests the existence of a critical concentration of highly dispersed fillers, at which the polymer chain and adsorption-active segments on the filler particle surface form the largest number of intermolecular bonds [19].

An increase in the enthalpy of crystallization (curve *2*) suggests acceleration of crystallization of the polymer upon introduction of ultradispersed ceramics. The influence exerted by the filler on the polymers

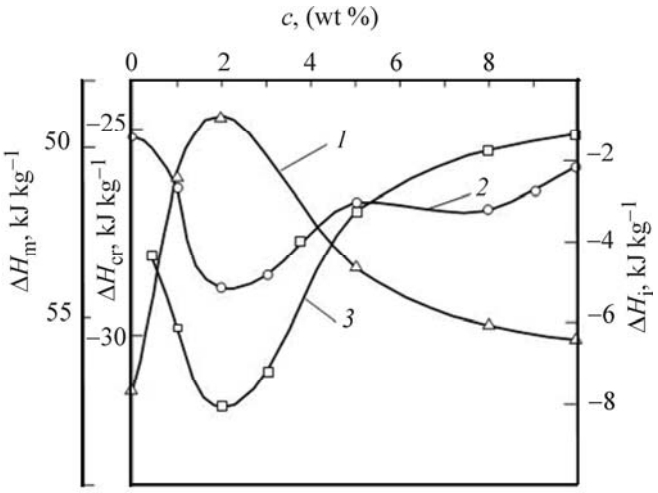

Fig. 2. (*1, 2*) Enthalpy of (*1*) melting ΔH_m and (*2*) crystallization ΔH_{cr} of the aluminum oxide-filled polytetrafluoroethylene samples and (*3*) macromolecules–filler interaction energy ΔH_i vs. the filler content.

crystallization is characterized by two major factors: formation on the polymer-filler interface of adsorbed segments initiating crystallization and growth in viscosity of the composite system with increasing filler content, precluding crystallization. At a low filler content, crystallization is accelerated, since the filler particles act as nucleation sites, and with increasing filler concentration, decelerated because the viscosity growth dominates in the system [15], as confirmed by trends in variation of the enthalpy of crystallization.

As known [20], intensification of crystallization of polymers by highly dispersed filler particles is indicated by enhancement of the exothermic crystallization peaks under cooling of samples. The exothermic crystallization curves of polytetrafluoroethylene at different amounts of the filler suggest that, upon introducetion of up to 2 wt % active particles of ultradispersed ceramics, crystallization of the polymer is accelerated, and uniform spherulites with clearly cut boundaries are formed.

The adhesion to polymeric binder in relation to the energy condition of the filler particle surface was estimated via measuring the enthalpy of Al_2O_3-polytetrafluoroethylene interaction. An absolute maximum of ΔH_i was achieved for 2 wt % filler (curve *3*). A decrease in ΔH_i with increasing filler content is apparently associated with aggregation of the nanopartciles at the filler concentration above 2 wt %, which decreases the activity of the surface layers of the filler, as confirmed by X-ray spectral data for samples of the polymeric composite material [13].

Thus, considering a correlation between the enthalpies of melting, crystallization, and intramolecular interaction, on the one hand, and the structure of a polymeric composite material, on the other, the physicomechanical and triboengineering properties of polytetrafluoroethylene-based composites filled with ultradispersed ceramics can be controlled by varying the filler content during their formation.

Polarization Effects in Modified Polytetrafluoroethylene

The utilized ultradispersed ceramics was synthesized by plasmo- and mechanochemical techniques under highly nonequilibrium conditions responsible for the appearance on the particle surface of uncompensated bonds, reaction centers, defects, etc. [21]. The developed surface of the ceramic substance affects its lattice and electronic subsystem, and the ensuing anomalies in the behavior of electrons, photons, and other elementary excitations cause changes in the physical properties of ultradispersed ceramics relative to those of the corresponding bulky crystals [22].

To elucidate the relationships in polytetrafluoroethylene-ultradispersed ceramics interaction, the surface charge of the ceramic particles and its polarization effect on the polymer were determined. A thermostimulated depolarization examination showed that the ultradispersed ceramics particles bear an intrinsic polarization charge [23]. It was also found that the highly dispersed aluminum oxide particles with large specific surface area bear an increased, relative to aluminum-silicon oxynitride particles, polarization charge [12, 24]. Filling polytetrafluoroethylene with ultradispersed ceramics results in polarization of the polymer and formation of a boundary layer whose thickness depends on the crystallization mechanism of the binder.

Figure 3 shows the spectra of thermostimulated depolarization currents for polytetrafluoroethylene and its composite with ultradispersed ceramics. It is seen that the initial polymer is electrically neutral. Introduction into the polymer of ultradispersed ceramics particles bearing an intrinsic electric charge induces polarization effects in the composite material. The filled polytetrafluoroethylene exhibits stable thermostimulated depolarization current corresponding to relaxation of the charge induced in the filler particle field. The spectrum shows that the polymer composite

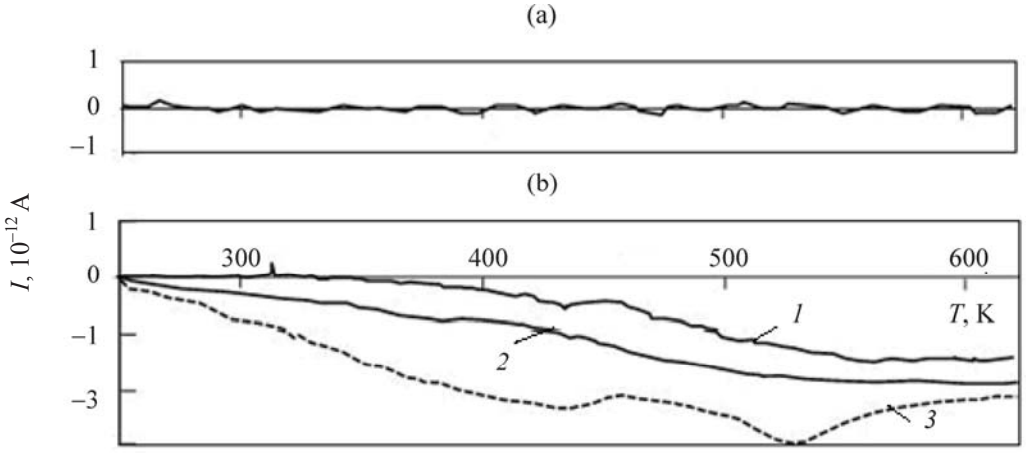

Fig. 3. Spectra of simulated depolarization currents for PTFE and composites thereof: (a) initial PTFE and (b): (*1, 2*) PTFE filled with (*1*) Al-Si oxynitride and (*2*) aluminum oxide and (*3*) PTFE filled with activated Al_2O_3.

containing activated filler exhibits increased current strength, which suggests induction of a fairly high polarization charge by activated filler introduced into the polymer. This is associated with a large specific surface area of particles, as well as with the fact that the crystal lattice of activated filler contains active reaction centers and defects acting as traps with respect to charge carriers.

Based on experimental specific heat values of the polymeric composite material at various degrees of filling and polarization charges of ultradispersed ceramics particles, the boundary layer thickness and proportion of interphase layers in the composite were estimated (Table 1). It is seen that an increase in the ultradispersed ceramics concentration causes the specific heat of the polymer to decrease. The reason is that some macromolecules pass from the bulk to the boundary layers near the solid surface. The proportion of the polymer in the boundary layer tends to increase with increasing content of ceramics in the system, but not in parallel: With increasing content of the ceramics the proportion of the interphase layers tends to a certain limiting value. The maximal thickness of the boundary layer is achieved with 2 wt % filler [24].

Mechanical activation of ultradispersed ceramics causes the boundary layer to substantially (by half) grow in thickness, especially in the case of aluminum oxide. Clearly, active formation of the boundary layer

Table 1. Specific heat, proportion of interphase layers, and boundary layer thickness for PTFE filled with ultradispersed ceramics in relation to the degree of filling[a]

Material	c_f, wt %	τ, s	C_p, kJ kg^{-1} K^{-1}	*b*	δ, Å
PTFE (initial sample)	–	–	0.934	–	–
PTFE + Al–Si oxynitride	1	0	0.894	0.043	200
	2	0	0.842	0.098	234
	2	120	0.805	0.138	323
	5	0	0.785	0.159	140
PTFE + Al_2O_3	1	0	0.845	0.079	266
	2	0	0.804	0.124	309
	2	120	0.779	0.158	434
	5	0	0.768	0.163	215

[a] Designations: (c_f) filler content; (τ) activation time; (C_p) specific heat; (*b*) fraction of interphase layers; and (δ) boundary layer thickness

in the case of this filler is associated with a high polarization charge on its particles.

The above-described results underlay a concept of the physicochemical processes involved in formation of polymeric composite materials filled with ultradispersed ceramics. The structure and performance characteristics of the composites were correlated with the polarization charge borne by the filler particles [24, 25].

It was shown that the modification effect of ultradispersed ceramics on the polymer crystallization mechanism is associated with the polarization charge borne by the particles, in whose field the binder undergoes polarization and structure formation. The polarization mechanism concept supplements the traditional views on the physicochemical nature of polymer filling and provides explanation to high performance characteristics of ultradispersed ceramic fillers [12, 25].

Tribochemical and Triboengineering Examinations of Polymeric Composite Materials

As known [26], of much importance for the wear behavior of polymeric materials are tribochemical processes. The tribochemical reactions involved in friction of polytetrafluoroethylene–ultradispersed filler composites were examined by mass spectrometry in relation to the concentration and chemical nature of the filler.

The nature of tribochemical reactions can be judged from the temperature dependence of the total ionic current associated with wear products [13] (Fig. 4). The first broad maximum is due to low-molecular-weight (m/z to 431) fragments of the polymer chain.

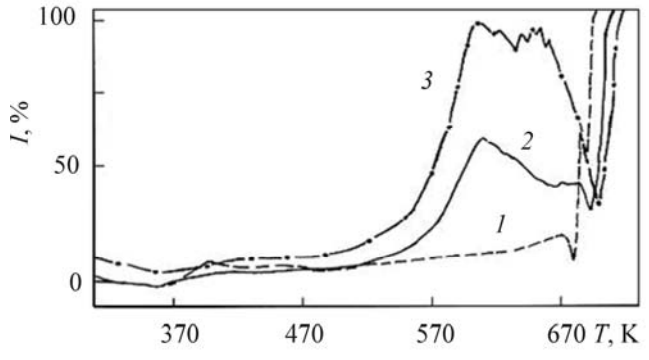

Fig. 4. Temperature dependence of the total ionic current associated with wear products of PTFE and composites thereof: (*1*) PTFE, (*2*) PTFE + Si_3N_4–Al_2O_3–AlN (2 wt %); and (*3*) PTFE + Si_3N_4–Al_2O_3–AlN (10 wt %).

Active evolution of these products in the low-temperature region (to 670 K) suggests intensive tribodestruction of the filled polytetrafluoroethylene. The most vigorous gas evolution was observed in reactions of the composites containing 10 wt % ceramics. This formulation of the polymeric composite material was characterized by a multiplet peak in the temperature dependence of the total ionic current, which suggests tribodestruction of cross-linked fragments of the macromolecule [27].

The results of the above-described studies suggest the following relationships in wear behavior of polymeric composite materials [27, 28].

(1) Tribochemical transformations in the initial polytetrafluoroethylene involve the C–C bonds, and this is accompanied by elimination of large fragments of the macromolecules.

(2) The tribochemical reactions are intensified by introduction of up to 2 wt % ultradispersed ceramics into polytetrafluoroethylene. The destruction is paralleled by structure formation, whose rate depends on the chemical nature of the filler catalyzing the macromolecular cross linking. With increasing filler content to 10 wt % the tribochemical processes are intensified and involve C–F bonds, as suggested by mass-spectrometric data for the tribodestruction products of polymeric composites [13, 28]. An increase in the concentration of the reactive radical and ionic species resulted from tribochemical destruction of the polymer binder is accompanied by intensification of the structure formation involving ultradispersed ceramics and by formation near the friction surface of polymeric composite material layers distinguished by high structural organization.

The chemical nature of the ceramics determines not only the intensity of tribochemical reactions but also the morphology of the surface layers of the composites. It was shown that friction involves localization of the reactive ceramics particles on the friction surfaces in amount increasing with the filler concentration, as suggested by examinations of the chemical composition and topography of frictional surfaces.

Introduction of mechanically activated ultradispersed ceramics particles results in formation on the friction surface of polytetrafluoroethylene with a network structure. This layer acts as protective shield confining the contact strain and performing the antiwear functions in the material.

Table 2. Strain, strength and tribiengineering characteristics of modified PTFE[a]

Composition	σ, MPa	ε, %	$I\times10^{-6}$ kg h^{-1}	f
PTFE	20–22	300–320	70–75	0.04
PTFE+$CoAl_2O_4$ (2–5 wt %)	19–25	330–400	0.2–2.6	0.15–0.18
PTFE + Si_3N_4-Al_2O_3-AlN (2–5 wt %)	18–25	275–330	0.8–8.0	0.17–0.19
PTFE + Si_3N_4-Y_2O_3-YN (2–5 wt %)	19–24	260–310	0.4–3.6	0.16–0.18
PTFE + Si_3N_4-B_2O_3-BN (2–5 wt %)	16–18	200–250	0.4–2.6	0.16–0.18
PTFE + 2MgO-$2Al_2O_3$-$5SiO_2$ (1–2 wt %).	22–23	310–320	6.0–6.4	0.18–0.19
PTFE + Cr_2O_3 (2 wt %)	22–24	320–330	1.8–2.8	0.22
PTFE + ZrO_2 (2 wt %)	22–24	300–320	2.8–3.2	0.20
PTFE + Al_2O_3 (0.5–2 wt %)	24–26	350–450	0.2–0.4	0.10
PTFE + $MgAl_2O_4$ (2–5 wt %)	21–22	330–340	0.2–0.4	0.15

[a] Designations: (σ) tensile strength; (ε) breaking elongation; (*I*) wear rate; and (*f*) friction coefficient.

The developed antifriction materials based on polytetrafluoroethylene and activated synthetic ultradispersed ceramics and natural fillers (zeolites, diamond waste) [13] surpass the initial polymer in wear resistance (100–370 times) and strength characteristics (by 20–30%) (Table 2).

CONCLUSIONS

A comprehensive study of the formation mechanism for filled systems based on polytetrafluoroethylene and ultradispersed ceramics identified the following physicochemical principles of development of triboengineering materials:

– the occurrence of an intrinsic polarization charge on ultradispersed ceramics particles, in whose field crystallization of a polymer proceeds;

– control of the structure of the materials via modification of the supramolecular structure of the binder and formation of three-dimensional cluster structures from nanometer-sized filler particles;

– special surface properties and high surface energy, responsible for adsorption activity of the ultradispersed ceramics particles with respect to the polymer and, thereby, for intensive structure formation in the binder, yielding structural elements characterized by high adhesion at the polymer-filler interface;

– control of the tribochemical reactions on the frictional contact and formation of the cluster structure from coordinated filler particles on the friction surface.

The developed materials are successfully applied in friction units of various systems exploited by "Zoloto Yakutii" Open Joint-Stock Company, Almazy Rossii – Sakha, Joint-Stock Company, and Yakutugol' Open Joint-Stock Company, as well as by oil and gas extraction enterprises of Sakhaneftegaz Open Joint-Stock Company, etc. In particular, this concerns technical systems available from foreign firms, like M-200 and ND-1200 career autodumpers, Marion elevator dredges, and Komatsu bulldozers.

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