# Composites Based on Polymers Doped with Disperse Particles of Inorganic Compounds

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## Abstract

The results of investigations into new wear-resistant polymer composites based on polytetrafluoroethylene filled with disperse synthetic and natural compounds are presented. The efficiency of using similar fillers in the crystalline polymers is shown, which cardinally modify the polymer properties. The materials developed have passed field tests as the components of friction units of equipment that are functioning in conditions of the North and process equipment of mining industry. Their application allowed the resource of friction units to be raised manyfold and also the problem of import substitution for regular seals and bearings to be solved.

## INTRODUCTION

Progress in modern-day engineering industry is associated in many respects with application of polymers and polymer composites (PC) to produce sealings, plain bearings, diamond abrasive tools, *etc*. However, the materials now in use and articles produced both in Russia and abroad occasionally do not meet operational requirements, which suggests a specific set of properties of these materials. Priority branches of modern polymer science are polymer materials science, physicochemical mechanics, and molecular simulation of polymers [1, 2]. In the field of tribotechnical materials science, application of antifriction self-lubricating plastics in the friction units of machines (plain bearings, separators of rolling bearings, tape drive systems, gear systems, *etc*.) allows the reliability and durability of technical equipment to be raised with reduced energy consumption in manufacture and improved environmental situation when machines are at work.

Methods for modifying the polymer matrix by introducing various fillers, *i. e.*, creation of PC, optimization of their composition and technology of producing the preforms and articles from them, are envisioned as the most promising ones. PC are mostly made by traditional techniques, namely, by filling polymer binders with various modifiers. This technique is the main one among those applied to improve the properties of polymer materials [3]. The beneficial impact of filling the polymers on improvement of the tribotechnical characteristics of materials is attributable to three factors [4, 5]:

1) Weakening of intermolecular bonds in the polymer;

2) Formation of optimum material structure;

3) Involvement of fillers in the friction process as inhibitors of attrition.

Among the scientific directions of the Institute of Nonmetallic Materials, SB RAS, and sub-faculty of high-molecular compounds of the Yakutia State University is the development of the new tribotechnical materials for the friction units of machines,

which are in service in cold climatic conditions, within the limits of the big problem to increase the reliability and operating efficiency of technical equipment in the North. Modern machines and mechanisms total tens, hundreds, and thousands of sealing devices in their structure; and the reliability of functioning of the whole mechanism depends to a large degree on the working capacity, reliability, and durability of these devices. Rubber sealing materials applied in present-day domestic engineering industry do not possess the sufficient frost and wear resistance. For the machinery in the North where the main part of work is made in the open air, the low working capacity of sealings is the cause of 30 to 50 % failures [7, 8]. As implied by analysis of the efficiency of work in the North area, the productivity of technical equipment during winter period tapers off by an average of 1.5 times, the mean time to failure decreases by a factor of 2–3, and actual lifetime compared with the nominal lifetime decreases by a factor of 2–3.5 [9]. In this relation, development of promising sealing materials with the maximally enhanced complex of physicomechanical and tribotechnical properties, and creation of sealing devices of new design that ensure the required lifetime and working capacity of technical and process equipment under extreme climatic conditions represent currently central directions of polymer materials science.

Among the polymers now being applied to manufacture the details of friction units of the most crucial technical systems, polytetrafluoroethylene (PTFE) possesses the requisite complex of physicomechanical and tribotechnical properties. The nanometer-sized solid particles of high-melting inorganic compounds were used as the modifying agents in the present work: the particles of simple and complex oxides, nitrides, oxynitrides, and natural materials, which provide the structural change of a polymer matrix. The main physical properties of ultrafine particles significantly differ from the properties of materials under normal conditions [10], which is caused by dimensional effects.

Methods of obtaining disperse particles by fine grinding in highly energy-intensive mills, and also by means of mechanochemical reactions running in them have been developed in the Institute of Solid State Chemistry and Mechanochemistry (ISSChM), SB RAS [11]. In the latter case, particles of interaction products are being formed at contact sites of reagents, first in the form of two-dimensional nuclei, and then grow bigger. If a reaction during mechanical activation does not proceed to completion, the particle size can be controlled by variation of temperature and time of the subsequent thermal treatment of reaction mixtures. Oxides with particles 1–5 μm in size are available through fine grinding; particles sized 0.02–0.2 μm can be produced with the use of mechanochemical reactions. Continuous devices which can provide production of powders on a large scale [12] have been worked out in ISSChM.

In the present work, disperse simple oxides ($Al_2O_3$, $ZrO_2$, $Cr_2O_3$) are obtained by fine grinding in a planetary mill, and complex oxides ($MgAl_2O_4$, $CoAl_2O_4$, $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) are obtained by mechanochemical synthesis. The physicochemical and tribotechnical characteristics of composites around PTFE with the specified additives, and also with additives of other compounds (oxynitrides of aluminum and silicon, ultradisperse diamond, zeolite, *etc.*) were investigated. Calorimetric and electrophysical studies of compositions were carried out with the aim of clarifying the nature of physicochemical interaction during composite formation and polymer crystallization.

## EXPERIMENTAL

Fine grinding and mechanochemical synthesis were conducted in an AGO-2 planetary mill [13]. Its two rolls rotated around the common and planetary axes due to frictional cohesion with the internal surface of the cylindrical case. The rolls and balls were made of steel. The diameter of the balls was 8 mm, ball mass 200 g, 5–10 g samples. The volume of the rolls was 0.15 $dm^3$, rotation rate 12.5 $s^{-1}$, power consumption 40 W per gram of a mixture. The particle size before and after mechanical activation was defined by means of laser granulometer, and specific surface was defined by gas desorption.

A filler was introduced into powdered PTFE following the standard technology that involves preliminary dispersion of nanomodifiers in an AGO-2 planetary mill for 2–5 min. The samples for physicomechanical, tribological, and structural studies were obtained in accordance with GOST 11262–80.

The physicomechanical properties of PC, namely, ultimate tensile strength $\sigma_t$ and breaking elongation $\varepsilon_b$ were determined with a UTS-2 tension testing machine at the moving rate of mobile grips of 100 mm/min. The tribotechnical parameters were determined with an SMC-2 friction machine according to the "shaft – hub" scheme at the load of 67 N, sliding rate of 0.39 m/s, and friction path of 7–10 km.

The structural research of the composites was conducted by the raster electron microscopy method with an XL-20 (Phillips) scanning microprobe.

Methods of electric polarization and thermostimulated depolarization (TSD) were applied to research a charge state of inorganic components and PC and also its impact on the formation processes of the filled systems.

The spectra of TSD currents of samples were obtained by method of electret thermal analysis; surface density of polarization charges was measured by the induction static method in accordance with GOST 25209–82.

Research of thermodynamic parameters of composites was conducted in a Shimadzu differential scanning calorimeter (instrumental error of no more than ±1 %). The tablets 3 mm in diameter and 2 mm in height, which were obtained from the disperse compositions by cold pressing at $p = 50$ MPa, served as samples. Sintering of tablets was performed with the standard technology of PTFE processing in the calorimetric cell of the device; cooling rate of sintered samples was 2 °C/min. Temperature and enthalpies of fusion, crystallization, and filler interaction with polymer were determined from thermograms.

## RESULTS AND DISCUSSION

The AGO-2 planetary mill provides grinding of oxide particles from 20 μm to 1–5 μm for 5 min of the device operation. Grinding process proceeds more effectively in the presence of water (10 % relative to shot weight), and then the particle size may be of about 0.5 μm. The powders of oxides of aluminum, zirconium, and chrome with specific surface of 40.6, 5.6, and 13.5 $m^2/g$ respectively were produced through dry grinding. They were added in PTFE in proportion from 2 to 5 %.

TABLE 1

Physicomechanical and tribotechnical characteristics of PTFE modified with simple and complex oxides and oxynitrides

| Composition, mass % | Ultimate tensile strength, MPa | Breaking elongation, % | Mass wear rate, $10^{-6}$ kg/h | Friction coefficient |
|---|---|---|---|---|
| PTFE | 20–22 | 300–320 | 70–75 | 0.04 |
| PTFE + coke | 16–18 | 290–300 | 12–16 | 0.15–0.30 |
| PTFE + $MoS_2$ | 18–20 | 160–180 | 40–45 | 0.20–0.30 |
| PTFE + $Al_2O_3$ (2 %) | 20–25 | 300–320 | 0.4–1.2 | 0.18–0.20 |
| PTFE + $Cr_2O_3$ (2 %) | 18–22 | 310–330 | 5.0–5.6 | 0.20–0.22 |
| PTFE + $ZrO_2$ (2 %) | 17–20 | 300–320 | 4.6–4.8 | 0.17–0.19 |
| PTFE + $CoAl_2O_4$ (2–3.5 %) | 19–24 | 330–400 | 1.2–4.3 | 0.15–0.18 |
| PTFE + $MgAl_2O_4$ (2–5 %) | 18–22 | 300–310 | 0.6–3.4 | 0.17–0.19 |
| PTFE + $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ (2–5 %) | 22–23 | 310–320 | 3.0–5.4 | 0.18–0.19 |
| PTFE + $Si_3N_4$–$Al_2O_3$–AlN (2–5 %) | 18–25 | 275–330 | 0.8–8.0 | 0.17–0.19 |
| PTFE + $Si_3N_4$–$Y_2O_3$–YN (2–5 %) | 19–24 | 260–310 | 0.4–3.6 | 0.16–0.18 |
| PTFE + $Si_3N_4$–$B_2O_3$–BN (2–5 %) | 16–18 | 200–250 | 0.4–2.6 | 0.16–0.18 |
| PTFE + UDA (0.1–1.5 %) | 20–25 | 260-320 | 3.2–3.6 | 0.20–0.22 |

The basic physicomechanical and tribotechnical characteristics of the material based on PTFE filled with disperse oxides are listed in Table 1.

The procedure of soft mechanochemical synthesis was used to yield disperse complex oxides [14]. Aluminum, magnesium, and cobalt hydroxides were taken as initial components to yield spinels; and talc, kaolinite, and gibbsite were taken to yield cordierite. Mixtures were activated in the planetary mill for 5 min and annealed for 2 h at 800 °C in the case of spinels, and at 1260 °C in the case of cordierite. Spinels of 79 $m^2/g$ specific surface and particle sizes of 20–40 nm were obtained. Introduction of these additives in the composite also significantly raises wear resistance relative to PTFE without additives (see Table 1).

Depending on the chemical nature of oxides, the character of discrete structures on the friction surface that were formed from the agglomerated ultrafine particles varies. With the use of cordierite as a filler, the local micrometer-sized particle clusters are formed, together with the ones widely-spaced on the friction surface, which form irregularities 1–1.2 μm in height. Introduction of the same amount of spinels in PTFE results in the formation of a surface layer with a higher proportion of filler particles. The area occupied by spinel clusters exceeds three times the area of localization sites of cordierite particles. A decreased wear of the spinel-bearing composite in comparison with cordierite composite is testimony to greater resistance of the surface layer of the sample to contact deformations once it is practically completely covered by micrometer-sized clusters from spinel particles. Meanwhile, the reduction of the friction coefficient by 1.2 times is obviously associated with the optimum roughness of the friction surface, which is caused by agglomerates of disperse particles of spinels.

According to the present view [16], physicochemical interaction of components during PC formation is controlled by the history of several concurrent processes, the major ones of which are: 1) wetting of the filler surface with the melt; 2) adsorption of binder molecules on the filler surface; 3) formation of the adhesion contact as a result of action of molecular and electric forces. Some of the features of physicochemical interaction have been recognized during the research of composites around PTFE doped with silicon-aluminum, silicon-yttrium, silicon-boron oxynitrides (see Table 1).

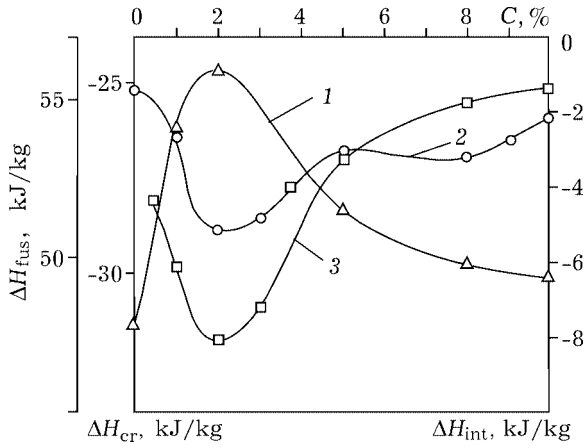


Fig. 1. Change in enthalpies of fusion $\Delta H_{fus}$ (*1*), crystallization $\Delta H_{cr}$ (*2*), and interaction $\Delta H_{int}$ (*3*) of PTFE PC "aluminum-silicon oxynitride" *vs.* filler content.

Research by differential scanning calorimetry has suggested that the enthalpy of fusion $\Delta H_{fus}$ of compositions (system 'low-temperature polymer – high-temperature filler') corresponds to the heat effect of wetting the filler surface by polymer melt. Figure 1 presents the outcomes of research into the heat effects of phase transitions in the process of composite formation and enthalpy of PTFE interaction with $Si_3N_4$–$Al_2O_3$–AlN additive depending on the content of the latter.

The enthalpy of interaction $\Delta H_{int}$ of the surface of ultradispersed filler (UDF) with the polymer matrix was calculated from the law of constant heat summation by the procedure of [17] and from the experimentally obtained enthalpies of fusion of the composites.

The maximum values $\Delta H_{fus}$ and $\Delta H_{int}$ of PC for UDF mass concentration of 2 % indicate that it is at this filler content that active interaction occurs at interfaces due to realization of the greatest possible number of contacts of chain segments with the active adsorption sites of the filler surface. An increase of more than 2 % in the filler mass fraction inside the composite leads to a decrease in enthalpy of fusion that is indicative of the immobilization of polymer macromolecules in the melt.

The value of $\Delta H_{int}$ is negative over the whole range of UDF content and reaches the greatest absolute value of 8.2 kJ/kg for the filler content of 2 %. This implies that it is at this composition that the maximum chemical interaction between the polymer and filler is evidenced.

A tangible difference in the enthalpies of crystallization of the initial and filled polymers is related to the kinetics of melt crystallization. Crystallization of initial polymer occurs as a result of formation of the primary three-dimensional (homogeneous) crystal nucleus. A thermodynamic barrier for the crystal nuclei of this kind to form is higher when compared to the barrier that is essential to the formation of two-dimensional (heterogeneous) nucleus formed on the surface of the structurally-active component. Owing to this phenomenon, the crystallization rate of the polymer is higher in the presence of the disperse filler. Having originated on the secondary nuclei on the surface of the heterogeneous centre, the crystalline phase of the polymer during further crystallization propagates along the radii in the bulk of melt in the form of rodlike aggregates of constant width, corresponding to the macromolecule folding period [18] registered in our study of the supramolecular structure of PTFE with reinforcing fillers. In this case, the elements of supermolecular structure of PC represent rather symmetric formations with a clearly defined crystallization centre whose part is played by the active particles of the filler and which are the origins of crystallization in the form of radial-oriented crystallites.

Based on the data obtained it may be inferred that structurization in PTFE in the presence of highly active UDF starts in the melt.

Model calculations and thermodynamic analysis of UDF structure have suggested that a periodic lattice does not correspond to a minimum of energy because of the following imperfections of atomic structure: variation in interplane distances, an increase in the root-mean-square values of the atomic shifts, the presence of vacancies, microdistortions, non-uniform deformation, and amorphization [19]. This is responsible for the high reactivity of UDF that leads to their active interaction with the components of the medium, in which the particles are generated.

The electronic state and the crystal lattice define many properties of UDF. It was demonstrated [20] that the values of microstresses inside the UDF are significantly higher than the yield limit, which is testimony to the high resource of elastic deformation of the lattice. An increase in UDF plasticity is related to the reduction of stress concentration near the particle boundaries; therefore, when compared to bulk crystal, the sliding within the limits of a small particle can be significantly easier.

Research into polarizing effects of nanomodifiers of the various chemical nature (aluminum oxide and aluminum-silicon oxynitride) showed the existence of a specific charge state on nanoparticles caused by the features of their crystalline structure or technology of their obtaining, and it can play a considerable role during composite formation. Shown in Fig. 2 are the spectra of currents of thermostimulated depolarization for the UDF samples.

Stable peaks are visible in the temperature range $T$ = 450–570 K and bear witness to the high-temperature traps for charge carriers. Relaxation of charge carriers at lower temperatures takes place because of the presence of traps in the crystalline structure of aluminum oxide, these traps being capable of easier capture of charge carriers.

Electron-microscopic studies have demonstrated that morphology of the polymer filled with disperse particles differs considerably from the morphology of the initial polymer (Fig. 3). The basic structural elements of the initial PTFE are so-called belts made up of packs of lamellae. Incorporation of oxide particles with developed specific surface leads

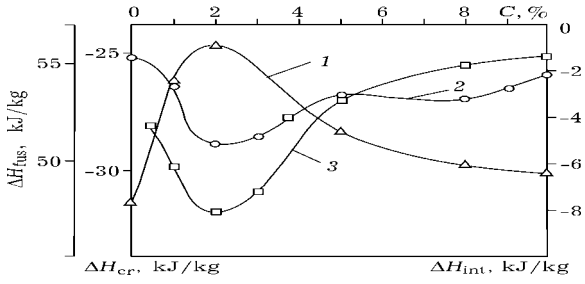


Fig. 2. Spectra of thermostimulated currents of UDF: *1* – aluminum-silicon oxynitride, *2* – aluminum oxide.

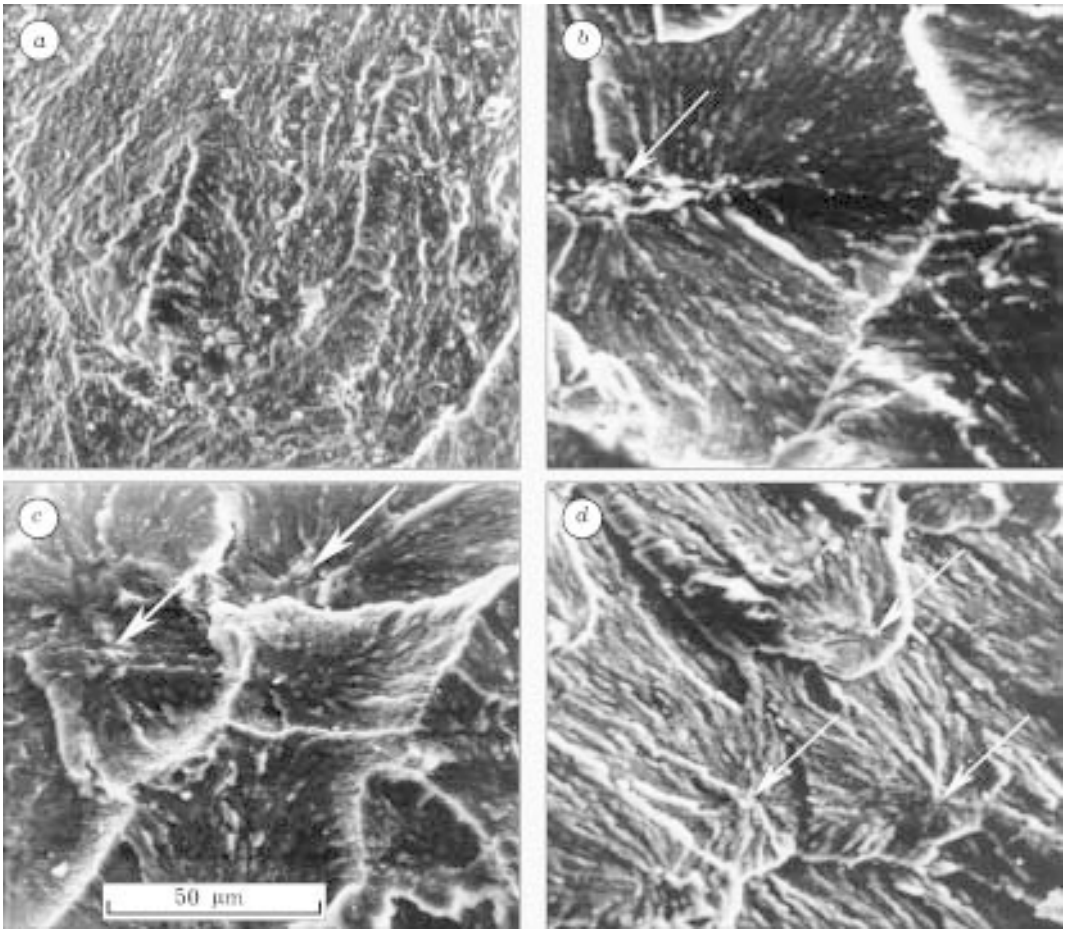


Fig. 3. Supramolecular structure of PC (2 mass % fraction of UDF): *a* – PTFE; *b* – PTFE + $Al_2O_3$; *c* – PTFE + aluminum-silicon oxynitride ($Si_3N_4$–$Al_2O_3$–AlN); *d* – PTFE + cobalt spinel ($CoAl_2O_4$).

to significant changes in crystallization, giving rise to various supermolecular structural elements in PTFE. It is evident that the oxide particles serve as crystallization centres from which symmetric formations grow in the form of polyhedra. Once the mass fraction of particles is above 5 %, a displacement of filler particles into the inter-element non-crystalline space and their coordination with each other is observed. Research of PTFE morphology as a function of the chemical nature of oxide demonstrated that the structure of composite upon aluminum oxide addition is made up from more regular supermolecular features of identical size that were identified as spherulites. Ultradisperse fillers alter the mechanism of polymer crystallization owing to the polarization charge existing on the particles, in the field of which a polarization and structurization of the binder occurs [20–23]. The crystallization kinetics, and transformation of supermolecular structure are caused by formation of interfacial layers on the boundary "polymer – UDF" [24]. As distinguished from the known materials containing traditional fillers like coke and molybdenum disulfide, the structure of UDF-doped PC is described as more regular, fine spherulitic, with high packing density of structural elements (see Fig. 3). Tribotechnical and stress-strain indices of this structure are characterized by higher values.

As is obvious, a continuous "network" from nanoparticles identified as cluster structure is formed. Clusters, as a rule, do not have translation symmetry of elements and genetically determine noncrystalline symmetry of the amorphous state. In all cases, the appearance of a non-uniform structure in the form of clusters brings about a substantial increase of wear resistance of composites with

preservation of strength, elasticity, and reagent resistance inherent in the polymers under investigation.

Comparison of composites possessing the properties of initial PTFE and industrially produced composites based on PTFE shows that, being practically identical in strength and elasticity, the developed PC have wear resistance that is hundreds of times higher. This affords a possibility to create reliable and durable frost-proof seals of a high degree of leak tightness that hold much promise for a widespread use under northern conditions. Changes in properties for all investigated PC correlate with the structural transformations inside a binder, which take place under the impact of UDF. Mass-spectrometer research demonstrated that UDF particles initiate thermal-oxidative degradation of polymer macromolecules during their processing even at the temperatures of 250–300 °C. When the temperature is decreased, the low-molecular fragments of the macromolecules possessing higher mobility readily crystallize into more regular supramolecular features [25]. The character of structural elements depends on the chemical nature, phase composition, polarization charge on the particles, and concentration of UDF.

The character of tribochemical reactions proceeding during PC wear could be inferred from the temperature dependences of the total ionic current of wear products (Fig. 4).

The first broad maximum corresponds to the emission of the low molecular mass ($m/z \leq 431$) fragments of the polymer chain.

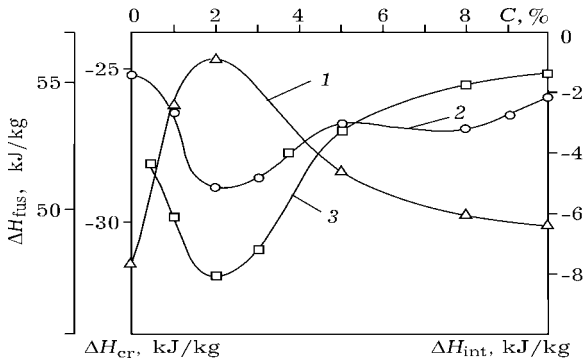


Fig. 4. Total ionic current of wear products *vs.* temperature: *1* – PTFE; *2* – PTFE + $Si_3N_4$–$Al_2O_3$–AlN (2 %); *3* – PTFE + $Si_3N_4$–$Al_2O_3$–AlN (10 %).

Active emission of these products in the low-temperature region (lower than 670 K) is indicative of intense tribodestruction of filled PTFE. The intensity of gas release for PC that involve 10 % UDF is high owing to more intense tribochemical reactions. Multiplicity of peak in the relationship between the total ionic current and temperature, which bears witness to the tribodestruction of the cross-linked fragments of the macromolecule, is registered for this composition of PC.

It has been shown that thermal resistance of the filled composites can be increased by 10 °C upon the introduction of 2 % of UDF, and by 15 °C – 10 %. This bears witness to the formation of the structures in UDF-filled PTFE cross-linked during tribochemical reactions.

Based on the obtained results, the following regularities of PC wear are established [26, 27]:

1. Tribochemical transformations in the initial PTFE involve C–C bonds, large fragments of macromolecules being formed in the process.

2. Introduction of up to 2 % UDF in PTFE promotes an increase in the intensity of tribochemical reactions. Besides destruction, structurization proceeds, the speed of which depends on the chemical nature of the filler that plays the catalytic role in the processes of the macromolecules cross-linking. As mass fraction of UDF increases to 10 %, tribochemical processes become more intense, and C–F bonds start to be affected by them. An increase in concentration of active radical and ionic fragments of the binder tribodecomposition is accompanied by intensification of structurization processes with UDF involved under the donor-acceptor mechanism. This is accompanied by the formation of PC layers in the neighbourhood of the friction surface, these layers being distinguished for their high structural organization. Increased wear resistance of UDF-bearing PC is associated with the formation of cluster structures from the particles of UDF on the friction surface; these particles localize shearing and protect the surface layer of the material from destruction. Distribution of clusters on the friction surface and the height of microirregularities formed by them depend on the chemical nature of the filler.

TABLE 2

Physicomechanical and tribotechnical characteristics of PC around PTFE and natural zeolites subjected to mechanical activation

| Mass fraction, % | Activation time, s | Ultimate tensile strength, MPa | Breaking elongation, % | Mass wear rate, $10^{-6}$ kg/h |
|---|---|---|---|---|
| 0 | 0 | 20 | 300 | 74–75 |
| 2.0 | 0 | 19 | 260 | 10.4–10.8 |
| 5.0 | 0 | 17 | 210 | 6.3–6.9 |
| 0.5 | 120 | 22 | 340 | 12.2–12.6 |
| 2.0 | 120 | 22 | 390 | 3.2–3.6 |
| 2.0 | 300 | 20 | 360 | 4.0–4.4 |
| 5.0 | 120 | 21 | 310 | 2.6–2.9 |
| 5.0 | 300 | 16 | 220 | 3.0–3.2 |

In view of the increased requirements placed on the machine equipment that is working under low temperature conditions, searching for the new modifiers of polymeric materials, including the ones based on the mineral raw material, and development of the new processes of production and long-term conservation of the compounds in the ultradisperse state present the topical problems. An active research in this field is conducted on the various ways of activation of PC components using mechanical activation, which is performed beforehand or in the process of combining the polymer with the filler. Mechanical activation in the high-energy planetary mills results not only in grinding of particles, but, owing to strong plastic strains, also gives rise to various kinds of structural defects. When put together, these processes change the free energy of the substance, thus reducing the energy potential of physicochemical processes. The results obtained bear witness to the viability of this direction. Adoption of technology of PC components mechanoactivation made it possible to develop materials that are functional under conditions of higher than usual load and sliding speeds. The wear resistance of PC under load of 1.6 kN increased by a factor of 2–3, and the strength indices increased by 40–50 % in comparison with the composites containing the same concentration of non-activated filler. The results of transformation of ordinary compounds, including the ones of natural origin (zeolites, diamond production waste), into the ultradispersed state with high reactivity are of peculiar interest.

Service characteristics of PC that contain mechanoactivated zeolites as fillers are presented in Table 2. It is evident that the optimum time of mechanical treatment of the filler brings about a significant increase in the stress-strain and tribotechnical indices.

## CONCLUSIONS

Hence, the viability of UDF adoption in tribotechnical materials science as polymer modifiers is based on the following facts.

1. Ultradisperse fillers (mechanochemically produced oxides) are electron donors, and this affects both the processes of PC formation, and tribochemical reactions during friction and wear of the composite.

2. Special surface characteristics and high surface energy provide the adsorptive activity of UDF particles in respect to polymer, and as a consequence, lead to the intensive structurization in the polymer to form the structural elements with the high adhesion level on the phase boundary “polymer – filler”.

3. An elevated plasticity of UDF particles ensures easy sliding and low friction coefficient of PC.

4. Capability of UDF to self-coordination and to formation of cluster systems with the definite structure (“architecture”) inside the materials gives rise to higher rigidity of PC

and provides an active involvement in formation of secondary structures on the friction surfaces.

The developed materials are employed to advantage in the friction units of various machines that are in service at the plants of Gold of Yakutia JSC, Diamonds of Russia – Sakha, Yakutugol JSC, oil and gas producing companies Sakhaneftegaz *etc*., including the ones of foreign production: open-pit dump trunks M-200 and ND-1200, dredges Marion, and bulldozers "Komatsu".

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