

Development of Materials and Coatings Based on Polytetrafluoroethylene

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Abstract

Results concerning the development of the new polymeric composite materials and coatings based on PTFE are presented. Experimental results obtained testify that application of such composites allows one to enhance operating performance and reliability of machines and mechanisms.

INTRODUCTION

Enhancing the wear resistance of parts of machines and mechanisms is one of the priority directions in science and national economy, because it involves a gain in the useful life of equipment now in operation and eventually results in saving material and financial resources. "The strategy of development of the Russian Federation up to 2010" defines an issue of wear of the basic production assets as one of the main negative factors that will hinder economic development of the country. In recent years the problem escalates in connection with the intensive deterioration of domestic and import machines fleet and with increased expenses for purchase of spare parts that is especially typical for machine-building and transport industries, agriculture, and mining industry. At the same time, there is an especially sharp question regarding the extension of overhaul periods, *i.e.*, regarding a gain in the durability and reliability of parts through adoption of the resource-recovery materials and technologies.

Presently, the conventional polymer base of antifriction composite materials is fluoropolymers, in particular fluoroplast-4 or polytetrafluoroethylene (PTFE). As the operation

life of the equipment and vehicles is controlled in most cases by wear of friction units (bearings, reducers, shafts, *etc.*), creating and development of composite materials and protective coatings on the friction surfaces in the self-regulatory mode with the enhanced set of performance characteristics will make it possible to compensate partially or completely for the wear, to reduce friction, and to increase wear resistance of units.

It is common knowledge that PTFE [1, 2] possesses a number of the unique properties, which set off it from the body of the rest polymers. At the same time, PTFE has the number of properties, which hinder its use as antifriction material ("pseudo-plasticity", low wear resistance and hardness). The traditional way to solve the problem, specifically, incorporation of various mineral and carbon fillers into PTFE matrix, allows one to decrease the wear by a factor of 200–1000, to increase thermal conductivity several times, and to increase hardness 5–10 times. However, an introduction of a great enough deal of the disperse fillers (up to 20–40 vol. %) results in a sharp decrease in strength indices of the material. Thus, F4K20 composite material (PTFE + 20 vol. % of coke) shows twofold decrease in

TABLE 1

Properties of composite materials based on PTFE

Index	PTFE (GOST 10067-86)	F4K20 (TU-6-05-1412)	F4K15M5	KVN-3 (OST 26- 13-5878)
Density, kg/m ³	2200	2050	2170	2500
Breaking strength σ_{br} , 10 ⁶ Pa	14-35	12-15	13-16	20-22
Breaking elongation ϵ_{br} , %	250-500	60-120	80-150	160-180
Elastic modulus, 10 ⁶ Pa	450-850	1200	1100	620-900
Thermal conductivity, W/(m K)	0.24	0.34	0.32	0.27
Linear expansion coefficient α , 10 ⁻⁵ K	25	10-12	10-12	5.5-6.5
Friction coefficient f_{fr}	0.20	0.27	0.23	0.25
Wear intensity J , 10 ⁻⁷ kg/s	167	0.17	0.13	0.11

breaking strength and threefold decrease in specific elongation as compared to pure PTFE (Table 1). At present, both polymeric powdered (disperse) fillers, and polymer reinforcing materials based on synthetic fibres are in widespread use to yield composite materials. Their use (in comparison with mineral fillers) provides the distinct advantages of these materials: a higher than usual impact resistance, a smaller density, an elevated water resistance, *etc.*

The present work is devoted to creation and development of composite materials and protective coatings based on PTFE.

EXPERIMENTAL

PTFE of PN specification, GOST 10067-86 (fluoroplast-4) was used. Samples for investigation were prepared by PTFE mixing with filler, then pressing at (50-55) 10⁶ Pa, and sintering at (643 ± 5) K. Exposition time comprised 1.08 10² s per 1 10⁻³ m of sample thickness.

Tribotechnical tests of composite materials were conducted with the shaft-sleeve rubbing pair in the friction machines SMT-1 and SMC-2 under the dry friction conditions with the load of 200 N and the sliding speed of 1 m/s. Testing time comprised 8 h (the friction path was 2/88 10³). A counterpart (steel shafts) was polished to roughness $R_a \cong 0.63$ before each test. Breaking strength σ_{br} (GOST 1262-68) and breaking elongation ϵ_{br} (GOST 1262-42) was determined with tension testing machine R-05 at the speed of grips movement of 16/7 10² m/s.

RESULTS AND DISCUSSION

The potential ways we have chosen to increase the durability and reliability of friction units and seals based on PTFE include the following ones:

- Creation of the new bulk composite anti-friction materials with various ultrafine fillers;
- Creation of polymer-polymer wear-resistant coatings;
- Creation of the process to obtain bimetallic materials with the steel substrate and antifriction layer made from bronze-brass mesh with fluoroplastic composition;
- Increasing the wear and corrosion resistance of inverse friction pair by thermochemical treatment.

It is well known [3] that the use of ultrafine fillers for PTFE even in the case of their relatively low content allows the wear resistance to be raised sharply without essential change of strength indexes. However, the main manufacturer of like production, Kirovo-Chepetsk integrated chemical plant, produces just 5-6 simple compositions involving PTFE, which poorly meet the requirements of industry, in particular, the requirements placed on the friction units that are in service under special conditions (space, vacuum, low temperature, *etc.*) where the materials with elevated mechanical and tribotechnical properties are needed.

The processes to obtain the finely dispersed powders, among them the powders of volcanic glass (by means of levigation), bronze and lead powders (by means of concurrent reduc-

TABLE 2

Physicomechanical and tribotechnical features of compositions

Material	η_{red} , dl/g	σ_{br} , 10^6 Pa	ϵ_{br} , %	f_{fr}	Δm , 10^{-6} kg
PTFE		23.2–24.3	278–290	0.1	2380–2420
PTFE + PAIS		11.9–13.9	137–155	0.08	530–40
PTFE + PABI	0.60	13.0–16.2	175–195	0.09	50–60
PTFE + PI	0.54	12.6–14.2	140–160	0.085	45–60
PTFE + PBI	0.57	16.6–18.5	175–195	0.09	65–70
	0.88	18.1–19.6	200–210	0.09	60–70
	0.94	18.9–20.3	205–215	0.09	70–80
PTFE + (PBI */PAIR) (50/50)		12.8–13.7	150–165	0.085	40–45
PTFE + (PBI */PAIR) (90/10)		21.0–22.4	210–220	0.09	65–70

* $\eta_{\text{red}} = 0.94$ dl/g.

tion of the grinded oxides of metals with colloidal graphite and coke), are developed for these purposes [4–6]. Based on them, KVN-3 composite material is developed [7], the use of which is made in cryogenic engineering (see Table 1). From evidence of Table 1, one can see that stress-strain properties of KVN-3 are superior to the parameters of industrially produced materials, which permits using KVN-3 for cup seals functional in inert atmosphere and vacuum, and in the high-load hydraulic pressure drive systems.

The new composites based on PTFE, heat-resistant polyheteroarylenes, and polymer-polymer mixtures based on polyheteroarylenes with the structure of semi-interpenetrating polymer networks (semi-IPN) are obtained and explored in the present work. Choosing polyheteroarylenes for chemical modification of PTFE friction surface is caused by their high thermal resistance, mechanical, and antifriction properties [8, 9]. The key feature of the developed way to modify the friction surface of PTFE consists in that the use of heat-resistant polyheteroarylenes and their mixtures is made not in the form of powders, as usually, but in the form of solution in organic solvent, namely, in N,N-dimethylformamide (DMF). Sintering point of polymer-polymer composite materials comprised 653/15 K [10]. It is worth noting that such a way of PTFE surface modification allows the wanted (1–2 mm) thickness of polyheteroarylene protective layer to be attained with the small ($\leq 2\%$ of PTFE mass) consump-

tion of expensive heat-resistant polymers. At the same time, the properties of both polymers are preserved, which also simplifies the technology of polyheteroarylenes processing to finished products and expands the scope of their application as thermal and heat-resistant materials. The analysis of the obtained results (Table 2) suggests that application of various polymeric components ambiguously changes its stress-strain properties. It is evident that mechanical properties (σ_{br} , ϵ_{br}) of composites slightly decrease as compared with those of pure PTFE. And as one would expect, the least decrease of σ_{br} and ϵ_{br} was registered for polybenzimidazole resin (PBI) that features the greater molecular weight (or reduced viscosity η_{red}). For polyamide-imide resin (PAIR) that is characterized by rigid three-dimensional structure formed on heat treatment, this change is more distinct (indices σ_{br} and ϵ_{br} are given below). As may be seen from Table 2, the weight loss Δm in the wear process for the investigated materials decreases by a factor of 30–80. The maximum increase of wear resistance is evidenced when PAIR layer is applied, although the values of σ_{br} and ϵ_{br} in this case are the least ones, which is likely to be caused also by formation of rigid three-dimensional structure. The friction coefficient for all obtained compositions varies slightly; its value is stable throughout the test.

In addition, physicomechanical and tribotechnical properties of the radically new composites with the structure of superficial layer

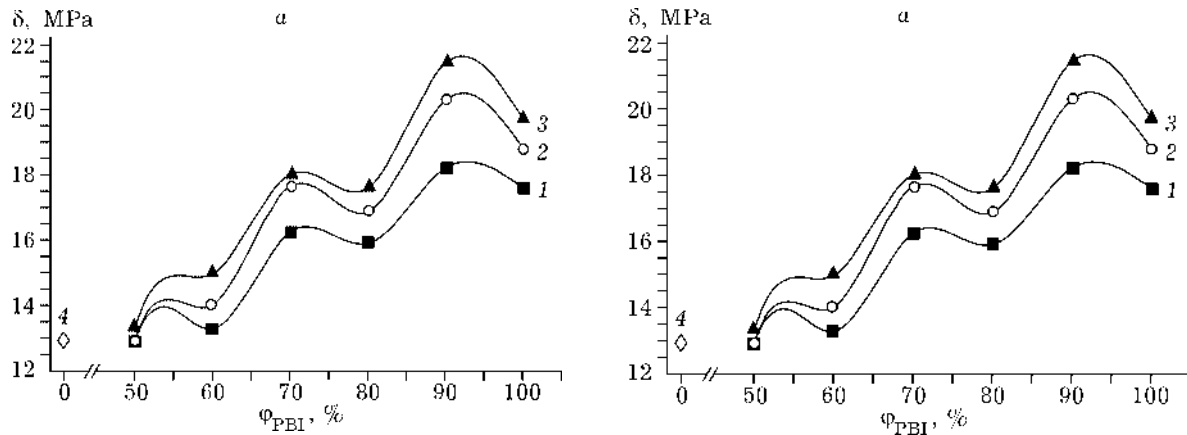


Fig. 1. Breaking strength η_{red} (a) and breaking elongation ϵ_{br} (b) of composite materials versus the composition of dopant layer and molecular weight of PBI. η_{PBI} , dl/g: 0.94 (1), 0.88 (2), 0.54 (3), PAIR (4).

of semi-IPN type [11] have been obtained and investigated. Figure 1, *a*, *b* presents the outcomes of stress-strain investigation of the materials. Change in composition of dopant layer ambiguously alters the stress-strain properties of composite materials. As is obvious, σ_{br} and ϵ_{br} vary non-linearly throughout the whole composition range. A distinctive feature is that σ_{br} and ϵ_{br} for a mixture of composition 90/10 (PBI/PAIR) with semi-IPN typed structure are slightly higher than for pure PBI. The principal cause for the stress-strain properties changing like that is the different thermodynamic stability of the polymer-polymer mixtures obtained [12]. Thus, on the basis of the physico-mechanical research performed, the following conclusions can be made. First, the use of the appropriately composed mixtures of PBI/PAIR as a modifying component for PTFE is preferred rather than the use of separate polymeric components (PAIR or PBI). Second, the use of less thermodynamically unstable PBI/PAIR mixture of composition 90/10 as a modifying component for PTFE enables one to obtain composite materials with the better physico-mechanical indices than in the case when more thermodynamically unstable mixture is used. An introduction of greater (>50 %) amount of PAIR in polymer-polymer mixture causes deterioration of stress-strain performance. The wear of the investigated polymer composites by weight decreases (as compared to the pure PTFE), on the average, by a factor of 30–80. As the composition of the modifying layer changes (with

an increase of PAIR proportion inside the mixture), virtually linear increase of wear resistance takes place.

The process to produce metal-fluoroplastic materials by bar mould method [13] has been developed. The similar materials are industrially produced by the Glacier Company (England) and Klimov Machine Building Plant. The process of their production is a time consuming one, it requires sophisticated industrial equipment, and does not allow one to manufacture tailor-made products. We succeeded in considerable simplification of the technological process and in obtaining the products with the predictable performance. For such materials, adhesion, which is the necessary condition for an antifriction coating to work, is controlled by the composition make up, by substrate preparation features, and by the technology to produce the coating. Preparation of a substrate consists in creating the porous layer from bronze-brass mesh on the low-carbon and stainless steel. The mesh is sintered onto the steel sheet that was previously bronzed in two and more layers at a temperature of 1153–1163 K. The porous layer is filled with the composition from PTFE. The powder of lead dioxide treated with sulphuric acid is used as a filler for PTFE. For mesh sintering onto the stainless steel, the technology of bronze-brass plating of its surface by means of the diffusion method is developed. The studies performed have demonstrated that tribotechnical properties of such material depend on the number (the size) of the bronze

TABLE 3

Effect of the material of counterparts and of the coating on the tribotechnical properties of composites

Material	Friction pair	f_{fr}	$J \cdot 10^9$	T^* , K
PTFE/PbO ₂ (50/50)	Steel 45	0.22	3.0	363
	The same with chromium coating	0.27	10.3	366
	The same with borated coating	0.23	1.3	359
	Brass	0.28	13.0	369
	The same with polymeric coating	0.12	0.16	343
	Aluminium V95	Intensive wear of the counterpart		
	The same with anodic coating	0.14	0.22	347
	The same with polymeric coating	0.12	0.16	345
F4K20	Steel 45	0.27	5.6	365

*The temperature in the sleeve of the composite material was determined at a distance of $1.5 \cdot 10^{-3}$ m from the contact zone.

brass mesh, on the quantity and the nature of filler, and also on the adhesion of fluoroplastic material to the mesh. In its tribotechnical indexes, this material surpasses metal-fluoroplastic ribbon of Klimov Plant: the friction coefficient at a load of $1 \cdot 10^6$ Pa and at the sliding speed on hardened steel of 1 m/s comprises 0.11–0.12, and the wear is 2–2.5 times less. High indices of mechanical characteristics are likely to be related to the freedom from step-type behaviour of porous layer, to the good cohesion with the metal matrix. Adhesion between the layers of priming and base coatings is ensured by interpenetration and the subsequent fusion of PTFE.

It is common knowledge that the frictional properties of metal-polymer friction pairs substantially depend both on the antifriction composite material, and on the material and treatment of the metal surface of an inverse friction pair [14]. In this connection, a superficial treatment of counterparts by various polymeric coatings [15, 16] and by means of chemical thermal procedure [17, 18] was conducted. Results of the investigations are presented in Table 3. It is evident that the choice of material of the counterpart is of prime importance for the reliable work of friction unit, but applying the wear-resistant coatings to these parts by means of present-day techniques makes it possible to increase significantly the service-life, to reduce the friction coefficient by a factor of more than two and the wear intensity almost

100 times (brass), to lower the temperature in the friction zone. An effect of solid coatings on the wear resistance of this pair is ambiguous. Thus, the galvanic chromium plating causes an increase in the wear of material by almost an order of magnitude in comparison to a borated counterpart.

The developed polymeric composite antifriction materials and coatings can find application for sealing compressor devices and conjugated friction surfaces; they can be used also in cryogenic engineering, in operations under high vacuum, in the friction units (both with and without lubricant). Investigations of the manufactured experimental batches of sleeves for plain bearings from metal fluoroplastic materials for automobile starters and autotremblers have demonstrated that such bearings (in domestic cars) 2–2.5 times surpass the standard bronze graphite ones in their service-life and reliability.

CONCLUSIONS

The developed procedure to produce metal fluoroplastic material is distinguished for the simplicity of technology. Application of the bronze brass mesh has allowed an evenly distributed porous layer to be obtained on the steel substrate with the connected channels, with the polymeric composition filling of more than 50 vol. %. Sintering of fluoroplastic composition

under pressure provides high density and the higher than usual adhesion of a polymer composition to the metal base.

Modification of the friction surface of PTFE by means of incorporated polymeric components not only makes simpler the technology of polyheteroarylenes processing, but also expands the scope of their application as heat-resistant anti-friction materials. The properties of modifying polymeric components in the process are preserved, and physico-mechanical properties of PTFE change in the desired direction.

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REFERENCES

- 1 L. A. Wall (Ed.), *Fluoropolymers*, Wiley, New York, 1972.
- 2 I. I. Cherskiy, *Polimernye materialy v sovremennoy uplotnitelnoy tekhnike*, Izd-vo YaF SO RAN, Yakutsk, 1975.
- 3 O. A. Adrianova, A. V. Vinogradov, Yu. V. Demidova *et al.*, *Mekhan. Kompozitn. Materialov*, 3 (1986) 399.
- 4 Pat. 683245 USSR, 1979.
- 5 Pat. 1208672 RF, 1993.
- 6 V. E. Rogov, D. M. Mognonov, N. V. Kornopoltsev *et al.*, *Trenie i Iznos*, 22, 1 (2001) 104.
- 7 Pat. 769887 USSR, 1980.
- 8 A. S. George, *J. Polym. Sci.*, 34a, 7 (1996) 1123.
- 9 S. V. Vinogradova, V. A. Vasnev, *Polikondensatsionnye protsessy i polimery*, Nauka, Moscow, 2000.
- 10 Pat. 2170667 RF, 2001.
- 11 E. V. Lenskaya, V. E. Rogov, D. M. Mognonov, *Trenie i Iznos*, 23, 2 (2002) 188.
- 12 E. V. Lenskaya, V. I. Zheivot, D. M. Mognonov, *Struktura i dinamika molekulyarnykh sistem (A Collection of Papers)*, vol. 10, Izd-vo Kazan. Un-ta, Yalchik, 2003, part I, pp. 155-158.
- 13 Pat. 2212307 RF, 2003.
- 14 N. P. Istomin, A. P. Semenov, *Antifriktsionnye svoystva kompozitsionnykh materialov na osnove ftorpolimerov*, Nauka, Moscow, 1981.
- 15 Pat. 940495 RF, 1993.
- 16 Pat. 1051912 USSR, 1984.
- 17 Pat. 1349326 RF, 1993.
- 18 Pat. 1487484 USSR, 1989.