Polyolefin Composites for Tribotechnical Application in Friction Units of Automobiles

A. A. OKHLOPKOVA[1], P. N. PETROVA[1], S. A. SLEPTSOVA[2] and O. V. GOGOLEVA[1]

[1]Institute of Non-Metallic Materials, Siberian Branch of the Russian Academy of Sciences, Ul. Avtodorozhnaya 20, Yakutsk 677007 (Russia)

E-mail: aitalina@inbox.ru

[2]Ammosov Yakutsk State University, Ul. Belinskogo 58, Yakutsk 677000 (Russia)

Abstract

The results of investigation aimed at the development of new wear-resistant polymeric composite materials for friction units on the basis of polytetrafluoroethylene and super-high molecular polyethylene modified by nanometer-sized inorganic compounds are reported. It is shown that their use in crystallizing polymers has a positive effect on the changes in material characteristics and helps one to intensify structural processes in polymers during crystallization.

INTRODUCTION

The modern level of the use of polymeric materials (PM) in motor car construction accounts for about 100–120 kg per one car. These materials are mainly used to manufacture the parts included into friction units [1]. Advances in modern mechanical engineering is to a large extent connected with the use of antifrictional PM possessing the effect of self-lubrication. In the area of tribological mechanical engineering, the use of these materials in friction units of automobiles allows one to improve the reliability and lifetime of machinery, decrease energy consumption for manufacture and improve the ecological situation with automobile performance.

The many-year experience in developing and using the polymeric composite materials (PCM) for antifrictional purposes on the basis of commercial polytetrafluoroethylene (PTFE) and super-high molecular polyethylene (SHMPE) revealed the main factor determining the nearest outlooks of modifying the materials of this class, that is, the structural and morphological factor. Non-conventional fillers were chosen as the modifying agents for polymers: solid nanometer-sized particles of high-melting inorganic compounds, including nanoceramics (NC), providing the maximal transformation of the polymeric matrix at different levels of structural arrangement [2].

As a result of the complex investigation of the mechanisms of formation of filled systems on the basis of PTFE and NC, the following physicochemical principles of the development of tribotechnical materials were formulated and substantiated from the scientific point of view:

– the presence of natural pooarization charge on NC parpticles;

– control of the material structure by governing the supramolecular structure of the binder and by forming the three-dimensional cluster structures from nanometer-sized filler particles;

– control of tribochemical reactions at the friction contact and the processes of cluster structure formation from the coordinated NC particles on friction surfaces.

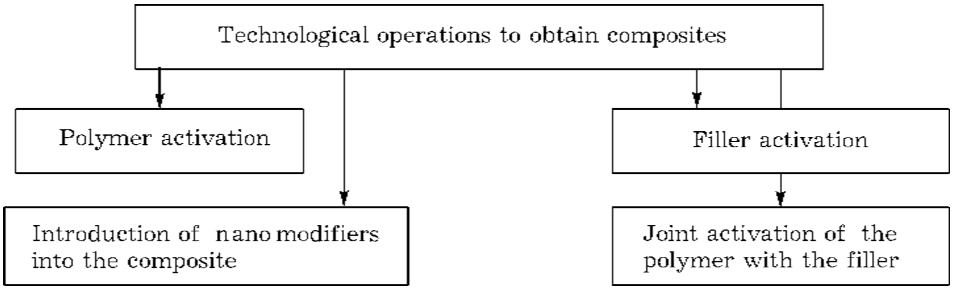

Fig. 1. Technological operations to obtain composites.

EXPERIMENTAL

Polymers PTFE (State Standard GOST 10007–80) and SHMPE (Hostalen Gur-212) and composite materials based on them and containing NC as filler (aluminium oxide and nitride, aluminium and silicon oxynitride, cobalt, magnesium, copper spinels obtained using plasmochemical and mechanochemical procedures) were used as the subject of investigation. The mean size of filler particles was 70–100 nm, specific surface 30–170 m^2/g.

Mechanical activation of the fillers was carried out in a planetary mill AGO-2 for 1–5 min with the planet carrier rotation frequency of 730 rpm, cylinder rotation frequency of 1780 rpm in order to destroy the agglomerates and increase their surface activity.

Physical-mechanical properties (stretching strength, relative breakup elongation) were determined with the tensile-testing machine UTS-2 with the clutch traverse speed of 5 and 100 mm/min (GOST 11262–80).

Tribological characteristics (friction coefficient, mass wear rate, temperature in the contact zone) were determined with SMTs-2 friction machines (friction scheme: roller-bush, loading force: 67–6700 N, slide velocity: 0.39 m/s, sliding distance: 7–10 km).

The structural investigation of PCM was carried out by means of scanning electron microscopy with XL-20 (Philips) microanalyzer.

RESULTS AND DISCUSSION

As a rule, NC is synthesized using high-tech procedures: plasma and mechanochemistry, cryo- and detonation synthesis. Due to the changes in economy and ecological situation that occurred during the recent decades, the development of new technologies of obtaining and long-term storage of compounds in the ultrafine state becomes urgent. In this active, intense research is being performed into the methods of activation of PCM components using the technology of mechanical activation carried out preliminarily or while mixing the polymer with a filler (Fig. 1).

A diagram illustrating changes in PCM characteristics connected with the use of the technology of mechanical activation of fillers is shown in Fig. 2. One can see that preliminary mechanical activation of NC in a planetary mill causes an increase in the wear resistance of materials loaded by 67 N by a factor of 2 and under the load of 1600 N by a factor of 3. Elasticity increases by a factor of 1.5 in comparison with the characteristics of PCM obtained by usual mixing in an agitator mixer. The compositions of the developed materials and their properties are shown in Table 1.

A comparison between the PCM characteristics and the properties of the initial

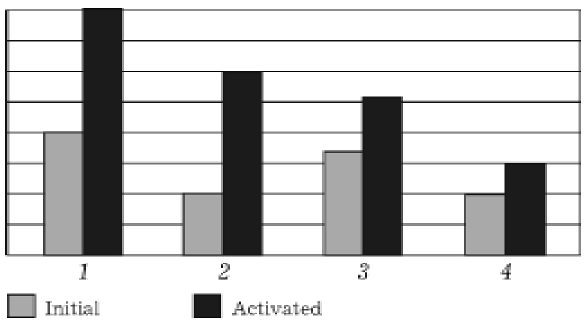

Fig. 2. Effect of the mechanical activation of cobalt spinel on the properties of PCM based on PTFE: *1*, *2* – wear resistance for $N = 67$ (*1*) and 1000–1600 N (*2*), respectively; *3* – relative breakup elongation, *4* – tensile strength. Activation time: 2 min.

TABLE 1

Physicomechanical properties and tribotechnical characteristics of PCM

Composition	σ_s, MPa	ε_e, %	I, 10^{-6} kg/h	f
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 + $CoAl_2O_4$	19–25	330–400	0.2–2.6	0.15–0.18
PTFE + $MgAl_2O_4$	18–22	300–310	0.6–3.5	0.16–0.18
PTFE + Si_3N_4–Al_2O_3–AlN	18–25	275–330	0.8–8.0	0.17–0.19
PTFE + Al_2O_3	22–23	320–340	0.4–1.2	0.18–0.20

Note. Here and in Tables 2, 3: σ_s is tensile strength; ε_e is relative breakup elongation; I is rate of mass wear; f is friction coefficient.

PTFE and commercial composites based on it (PTFE + coke, PTFE + MoS_2) shows that with almost the same strength and elasticity the developed PCM possess a hundreds times higher wear resistance. Due to this fact, it is possible to make reliable and long-lived frost-resistant seals with the high degree of impermeability, which would be promising for wide use, including the application in friction units of automobiles.

Unlike the known materials containing conventional fillers like coke and molybdenum disulphide, the structure of PCM with NC is characterized as a more perfect one, fine-spherulite with the high density of packing of structural elements. With an increase in the mass fraction of the filler from 0.1 to 10 %, the dimensions of structural elements decrease by a factor of 1.5–2; for the content of NC 5 mass % and above, filler particles are displaced into the interelement non-crystalline areas and get coordinated with each other. As a result, a continuous network of nanoparticles is formed in the boundary regions of the PCM; the network is identified as a cluster structure (Fig. 3).

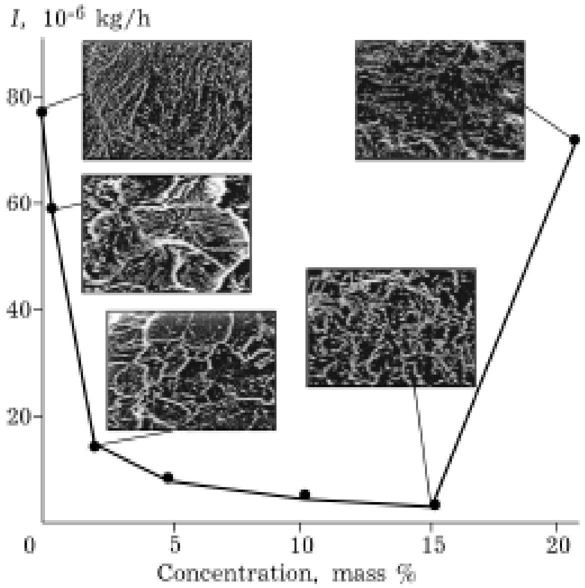

Fig. 3. Effect of cobalt spinel content on the supramolecular structure and wear rate of PTFE.

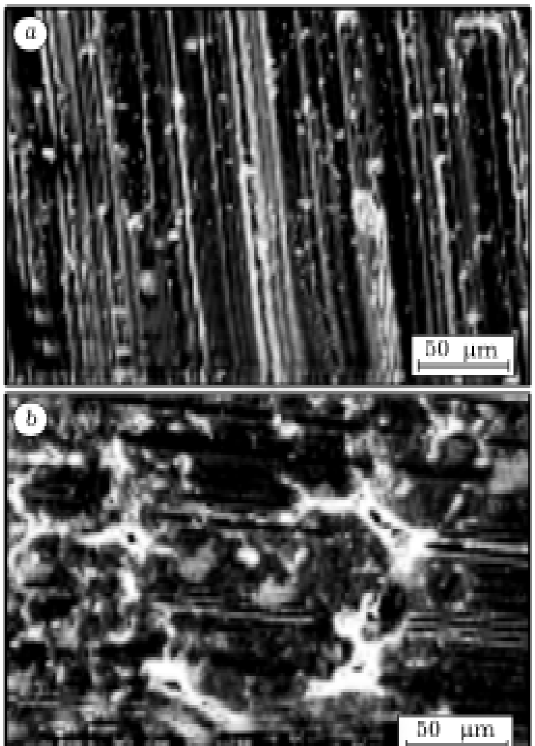

Fig. 4. Structure of friction surfaces for PCM based on PTFE with NC: non-activated (*a*) and activated for 2 min (*b*). Concentration of NC: 2 mass %.

It was established that the formation of a non-uniform structure in the form of clusters leads to a substantial increase in the wear resistance of the composites, though other their physicomechanical characteristics are close to those of the non-filled PTFE (see Table 1).

Friction and wear of PCM are realized under the conditions of increased gradient ratios of temperature, strain, concentration of filler components, crystallinity degree, other parameters of supramolecular structure and involve a complicated set of physicochemical processes [3]. Because of this, the investigation of the effect of fillers on these processes will allow one to predict the behaviour of construction PM under different performance conditions, including extremal ones.

The regularities of PCM wear with the account of structuring processes going with the participation of NC are investigated in the

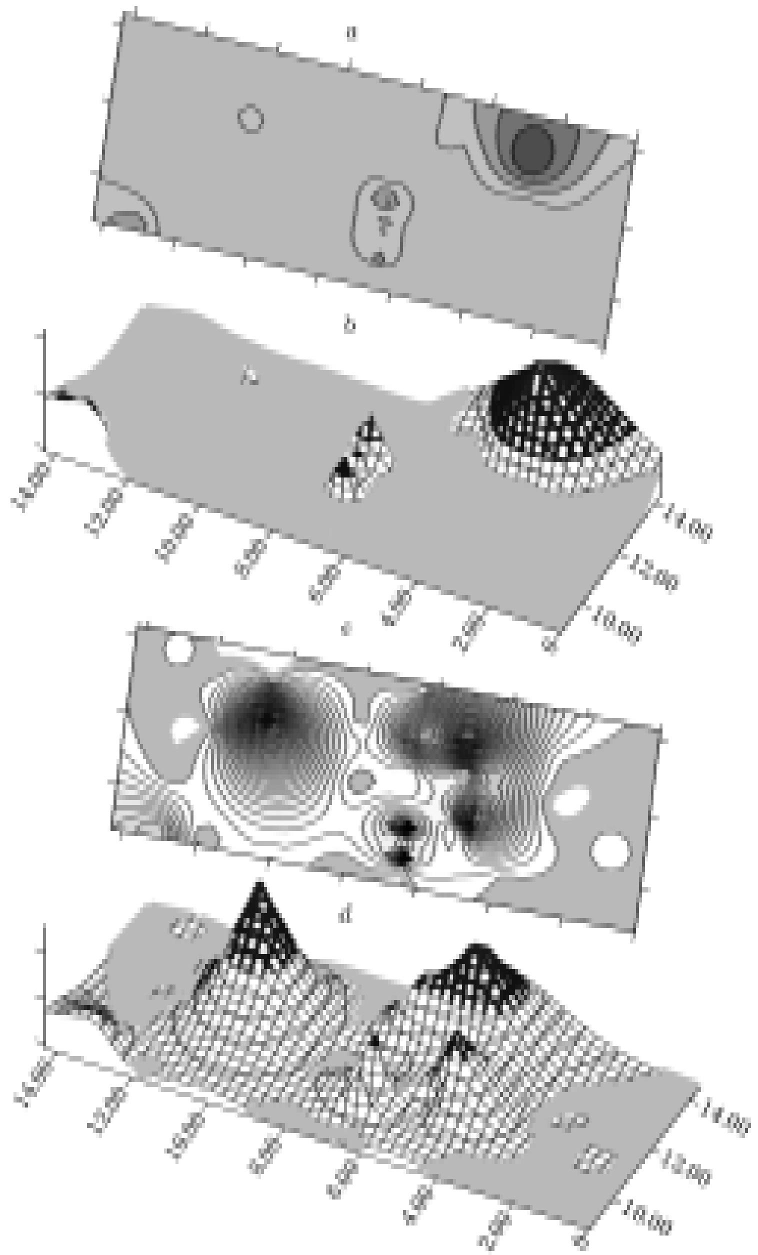

Fig. 5. Friction surfaces of PCM PTFE + 5 mass % Al_2O_3 activated for 2 min: *a*, *c* – two-dimensional; *b*, *d* – three-dimensional; charts of the distribution of iron (*a*, *b*) and aluminium (*c*, *d*); scanning field: 14×14 μm.

present work. One can see in the electron microphotographs of the structure of friction surfaces of PCM (Fig. 4) that the structure of friction surfaces of PCM containing non-activated NC is built of composite layers oriented along the sliding direction. The introduction of activated NC provides the conservation of spherulite structure observed in the bulk material also on friction surfaces.

The surface layer of the materials is characterized by the high concentration of NC particles which coordinate each other and form micrometer-sized clusters of NC with a definite height of microroughness elements in the regions around spherulites. Microroughness elements play a part of the protective screen preventing the surface layer of materials from destruction (Fig. 5).

One can see that iron gets concentrated in the sites with increased localization of filler particles. This is an evidence of the fact that iron of a counter-part is transported with the filler particles. Local micrometer-sized clusters of NC particles are formed on friction surface.

Among PM developed on the basis of polyolefins, SHMPE is distinguished due to its valuable technical characteristics, which allows one to use this material in manufacturing the parts for special purposes in different branches of industry. Modification of SHMPE with NC allowed one to obtain materials with improved deformation strength characteristics (higher by 20–40 %) and wear resistance (by a factor of 1.5–2.5) in comparison with the initial polymer (Table 2).

The effect of mechanical activation of fillers in a planetary mill AGO-2 on the properties of SHMPE was investigated with spinels of cobalt and copper (Table 3). It was established that modification of SHMPE with activated nano-spinel results in an increase in deformation strength and friction characteristics.

In allt he cases, an optimal set of properties is achieved after activation of the fillers for

TABLE 2

Physicomechanical and tribotechnical characteristics of modified SHMPE

Composition	σ_s, MPa	ε_e, %	I, 10^{-6} kg/h	f
SHMPE	34.0	320	0.14	0.15
SHMPE + $Si_3N_4-Al_2O_3-AlN$ (2 mass %)	30.5	325	0.06	0.19
SHMPE + $Si_3N_4-Al_2O_3-AlN$ (5 mass %)	30.5	300	0.05	0.20
SHMPE + AlN (2 mass %)	34.5	320	0.01	–
SHMPE + MoS_2 (2 mass %)	28.0	290	0.62	0.25
SHMPE + MoS_2 (5 mass %)	26.5	270	0.81	0.30

TABLE 3

Tribotechnical characteristics of PCM based on SHMPE and nanospinels of cobalt and copper

Material	τ, min	σ_s, MPa	ε_e, %	I, 10^{-6} kg/h, under load, N		f	T, °C
				67	6700		
SHMPE	–	34	340	0.72	37.40	0.15	50–60
SHMPE + $CoAl_2O_4$	–	35	330	0.54	35.50	0.18	45–55
The same	1	36	400	0.46	32.14	0.16	40–50
«	2	42	460	0.30	19.40	0.15	40–50
«	3	40	420	0.26	16.40	0.12	40–50
SHMPE + $CuAl_2O_4$	–	36	350	0.48	37.30	0.19	55–65
The same	1	40	420	0.36	36.60	0.17	45–55
«	2	43	450	0.24	32.40	0.15	45–55
«	3	37	390	0.12	22.80	0.13	45–55

Note. τ is the time of filler activation, T is temperature in the friction zone.

2 min. Strength increases by 20–25 %, elasticity by 30–35 %, wear resistance by a factor of 3.5–6 for the load of 67 N and by a factor of 2 for the load of 6700 N.

Activation of the filler causes a decrease in wear rate and in friction coefficient; tribotechnical indices decrease with an increase in activation time. It is possible that the activated filler nanoparticles are localized during PCM wear on friction surface forming a layer that prevents the material from destruction, which is accompanied by a sharp decrease in the material wear rate. In addition, activated ultrafine fillers can increase adhesion of the film of transfer to the counter-part, which would be accompanied by a decrease in friction coefficient.

The introduction of activated spinels into SHMPE leads to some decrease in temperature in the friction zone and conservation of this temperature for a long time, which ensures also lower and more stable friction coefficient.

Investigation of the effect of the chemical nature of spinels on tribotechnical characteristics revealed the advantage of copper spinel as a filler for SHMPE. For instance, PCM containing SHMPE are characterized by higher wear resistance. The fillers investigated have identical particle size and specific surface but differ in chemical nature, namely, in the nature of oxides. It is known [4] that copper oxide initiates oxidative processes at the initial stages of PE processing; these processes further lead to the formation of carboxylic groups. Then copper enters the interaction with carboxylic groups forming salts that act as inhibitors of oxidative processes. During subsequent thermal treatment of PE, cross-linking of separate fragments of thermooxidative decomposition of macromolecules occurs, along with the formation of a more ordered tightly packed cross-linked structure with increased wear resistance. In the case under consideration, copper oxides incorporated into the fillers are likely to participate in tribochemical processes according to a similar mechanism, which promotes an increase in wear resistance of PCM.

Investigation showed that the fibrillar structure of the initial SHMPE is crushed into

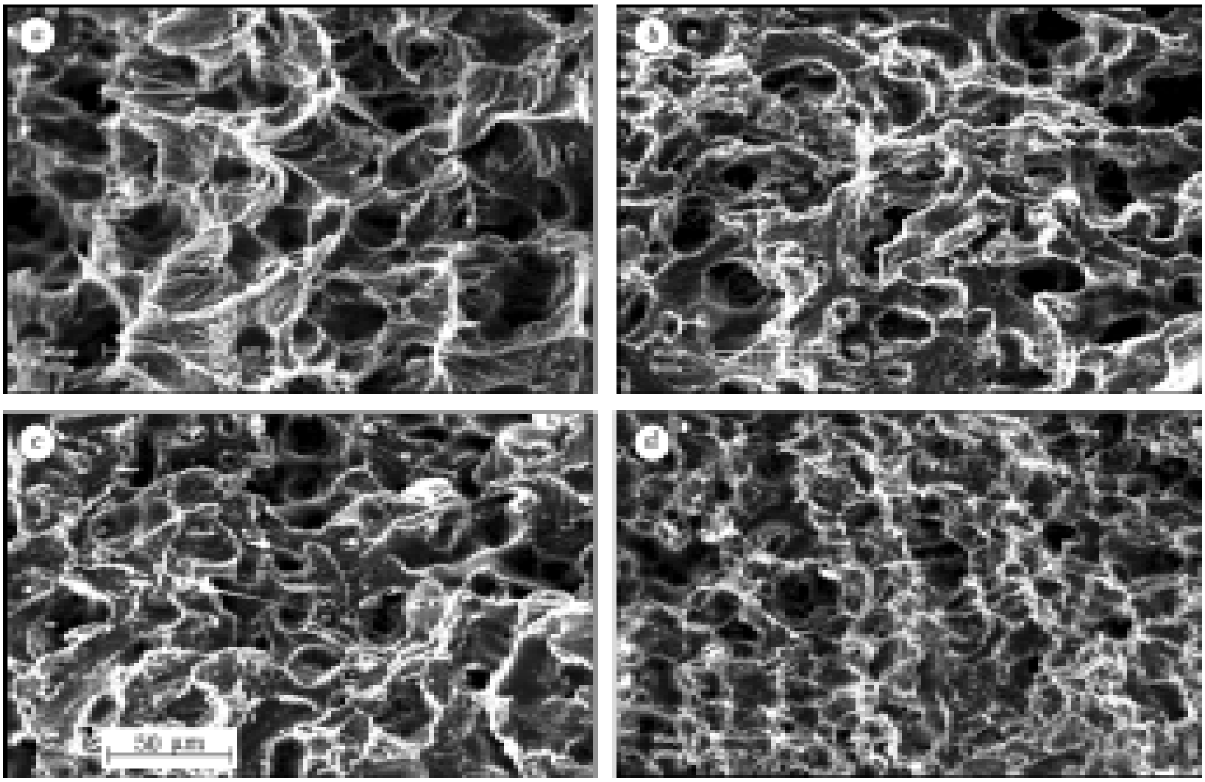

Fig. 6. Supramolecular structure of SHMPE: the initial sample (*a*), the sample filled with non-activated copper spinle (*b*), activated for 2 min cobalt (*c*) and copper (*d*) spinels.

the crystal structural elements identified as imperfect spherulites (Fig. 6). The size of spherulites and their geometric shape depend both on chemical composition and on filler activation time. The most ordered structure characterized by fine spherulites of identical size and shape was observed for the composite containing copper spinel activated for 2 min. It is this composite that provides higher wear resistance and strength.

CONCLUSION

The developed tribotechnical materials are characterized by stable and low friction coefficient and wearing intensity, increased deformation-strength parameters providing coupling rigidity and high bearing capacity. So, replacement of standard seals in automobiles by the developed polymer composites will lead to an increase in time resource of friction units in automobiles due to the improvement of performance characteristics of seals (an increase in wear resistance, strength and elasticity), a decrease in the cost of seals due to import substitution, and a decrease in expenses for the performance and repair of equipment.

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