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WORKING OUT POLYMERIC NANOCOMPOSITES THE TRIBOTECHNICAL APPOINTMENTS FOR THE OIL AND GAS EQUIPMENT [1]

A.A. Okhlopkova, P.N. Petrova, O.V. Gogoleva

Institute of Oil and Gas Problems
of the Siberian Branch of the Russian Academy of Science
Russia, Yakutsk, Avtodorozhnaya, 20,
e-mail: oli-gogoleva@yandex.ru

In the given work perspectives of combined modification of polytetrafluorethylene (PTFE) by fluoroplastic F-4MB in a combination with nanospinel magnesium for the purpose of reception of new cold-resistant polymeric composite materials the tribotechnical appointments with improved deformation-strength characteristics for the oil and gas equipment is shown.

Keywords: *polytetrafluorethylene, a copolymer, nanofillers, structure, wear resistance, friction factor, a friction surface.*

INTRODUCTION

Materials existing now and products from them for knots of a friction of the oil and gas equipment (sliding bearings, gear gearings, etc. for the chisel technics and the process equipment, consolidation for oil pipelines) both Russian, and foreign manufacture in some cases do not meet operational requirements which assume presence in materials of absolutely specific complex of properties. Requirements to such materials become tougher at their operation in extreme conditions, for example in regions of the Far North. They should possess not only the raised mechanical characteristics (durability, wear resistance, the elasticity module), but also not to worsen operational properties in the conditions of low temperatures that is a necessary condition for maintenance of working capacity of technics in North environmental conditions. As shows the analysis of an overall performance of oil and gas technics and the equipment in North regions, productivity during the winter period is reduced in 1,5 times, actual service life in comparison with the normal is reduced in 2-3,5 times [1].

Fluoroplastics possess a complex of unique properties which correspond to a modern rhythm of a life and the high requirements shown by the enterprises chemical, oil, metallurgical and many other industries for maintenance of high reliability and sta-

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bility of work of the process equipment. Among fluoroplastics, details of knots of the friction applied to manufacturing, the most preferable complex physico-mechanical and tribotechnical properties possesses polytetrafluorethylene, it is used in knots of a friction of the most responsible technical systems. Lack PTFE is relative low wear resistance and the raised creep (deformation) at long influence of compressing loading that limits a resource of work and possibility of its wider application. One of approaches to increase of wear resistance PTFE is modifying of structure of polymer various particles.

The purpose of the given work is working out PCM the tribotechnical appointments on the basis of PTFE with raised tribotechnical and physico-mechanical characteristics of knots of a friction for the technics of the oil and gas equipment.

TECHNIQUE OF RESEARCHES

Objects of research: polytetrafluorethylene (PTFE) - an industrial product (GOST 10007-80), fillers: spinel the magnesium, received mechanochemistry synthesis, the average size of particles of 70 nanometers, a specific surface 170 m^2/g; fluoroplastic marks F-4MB with fusion temperature cristalls 270-290 ºC and density 2,14-2,17 g/sm^3 (TU 301-05-73-90).

The filler was injected into PTFE by the technology of dry mixing in high-speed mill. The samples for physico-mechanical and structural investigations were produced by the technology of cold compacting followed by agglomeration.

Physico-mechanical properties PCM defined on standard samples (GOST 11262-80). Tests spent by explosive car “UTS-2“ (Germany) at speed of moving of mobile captures of 100 mm/minutes. Tribotehnichal characteristics (friction factor, mass speed of wear process) defined by the car of friction СМЦ-2 (the scheme of a friction "shaft-plug", loading – 0,45-1 МПа, speed of sliding - 0,39 km/s). A counterbody – a steel shaft from a steel 45 with hardness 45-50 HRC and a roughness 0,06-0,07 microns.

Physical and chemical interaction at combination PTFE with F-4MB and HC characterized on the basis of thermodynamic parameters: enthalpy of melting and crystallization, temperature of melting and crystallization on a differential scanning calorimeter «Shimadzu» (an error no more ± 0,1 %). Samples tablets in diameter of 5 mm, as height 1mm, received by cold pressing served at p = 50 МПа.

Super-molecular structure PCM was investigated a method of raster electronic microscopy with the roentgen spectral analysis on the micro analyzer «XL-20 Philips», raster electronic microscope JSM-6480LV by firms JEOL (Japan), atomno-power microscope NTEGRA (Russia), Ik-spectrometer FTS 7000 Varian.

RESULTS OF RESEARCH AND THEIR DISCUSSION

Table 1 presents basic physical, mechanical and tribotechnical characteristics of composites based on PTFE and NP.

Table 1

Physico-mechanical and tribotechnical characteristics of modificated PTFE

Composition	σ_r, MPa	ε_r, %	*I*, mg/h
PTFE	20-22	300-320	78-80
PTFE+1 wt %. F-4MB	21-22	350-360	94-96
PTFE +2 wt %. F-4MB	23-24	530-540	87-87
PTFE +3 wt %. F-4MB	23-24	620-630	80-82
PTFE +5 wt %. F-4MB	22-23	600-610	70-75
PTFE +2 wt %.NN	17-19	300-310	3,7-4,2
PTFE +5 wt %.NN	15-17	250-270	0,4-0,8
PTFE +2 wt %. F-4MB +1 wt %.NP	22-23	420-430	3,6-4,0
PTFE +2 wt %. F-4MB +2 wt %. NP	22-23	390-400	0,6-0,7
PTFE +3 wt %. F-4MB +1 wt %. NP	24-25	440-450	4,0-4,3
PTFE +3 wt %. F-4MB +2 wt %. NP	21-22	420-430	1,1-1,3
PTFE +5 wt %. F-4MB +1 wt %. NP	21-22	420-430	2,3-2,6
PTFE +5 wt %. F-4MB +2 wt %. NP	21-22	360-370	0,3-0,6

σ_r – yield strength in rupture; ε_r – relative elongation with rupture; I – wear rate.

From the data resulted in table 1 it is visible that introduction of polymer F-4MB in PTFE leads to strength increase at a stretching on 10-15 %, relative lengthening at rupture in 1,5-2 times, the increase in speed of mass wear process PCM to 270 times that is connected, apparently, with plastificity action F-4MB on PCM [2] is thus observed. Intensity of wear process PCM with spinel magnesium varies at increase of loading from 0,45 to 1 MPa a little that is connected with increase in firm, wearproof inclusions at friction surfaces at growth of degree of deformation.

It provides possibility of creation not only wearproof bearings of sliding, but also reliable and durable cold-resistant consolidations with high degree of tightness, perspective for wide application, including in knots of a friction of cars and mechanisms of the oil and gas industry.

For the purpose of studying of influence of a copolymer (F-4MB) on strengthening of adhesive interaction in system PTFE-NP thermodynamic parameters of filled composites by means of scanning differential calorimetric method (SDC) were investigated.

The table 2 presents results of thermodynamic researches of PCM.

Table 2

Dependence of thermodynamic characteristics ПКМ on concentration Ф-4МБ and NP

Composite	$C_{F\text{-}4MB}$, wt. %	C_{NP}, wt. %	T_{mel}, K	ΔH_{mel}, J/g	T_{cr}, K	ΔH_{cr}, J/g
PTFE	-	-	604	17,03	588	22,65
PTFE +F-4MB	2	-	598	23,53	593	28,05
PTFE +F-4MB	3	-	597	25,03	593	31,12
PTFE +F-4MB	5	-	598	23,81	593	33,63
PTFE +F-4MB	10	-	598	23,50	593	27,25
ПТФЭ+NN	-	2	599	19,58	595	23,70
PTFE +F-4MB + NN	3	1	598	28,37	595	26,02
PTFE +F-4MB + NN	3	2	597	28,78	595	28,78
PTFE +F-4MB +NN	5	1	598	25,60	595	28,48
PTFE +F-4MB + NN	5	2	598	21,40	595	24,68

$C_{F\text{-}4MB}$ - concentration F-4MB; C_{NP} - concentration nanopartucles; T_{mel}, T_{cr} - temperature of melting and crystallization; ΔH_{mel}, ΔH_{cr} – enthalpy of melting and crystallization.

It is obvious that introduction of F-4MB only in PTFE as well as in PCM structure (PTFE+NP) is accompanied by some decrease in melting temperature and slight increase of crystallization temperature in comparison with unfilled polymer. Change of melting and crystallization temperatures of PCM consisting PTFE + F-4MB points to formations of single-phase system with characteristics distinct from initial components [3].

It is established that introduction F-4MB in system PTFE-NP leads to value increase enthalpy of melting, therefore, this system have lower mobility of macromolecules at heating owing to formation of a considerable quantity of intermolecular bonds between a polymeric chain and a surface of nanoparticles.

Increase of values of temperature and crystallization enthalpy points to increase of speed of crystallization PTFE at presence nanoparticles. Presence of the second polymer that close on a chemical compound to PTFE, accelerates processes of crystallization of polymer, obviously owing to diffusion in an interphase layer.

To establish an particles of the various nature influence on processes of the structurization in PTFE and, accordingly, on character of change of properties, the method of electronic microscopy structural researches were conducted. Introduction of the polymeric fillers has led to formation of the structural elements having indistinct borders, in the form of large extended spherolites (fig. 1b), is observed their certain orientation that explains increase in values of relative elongation at rupture. Additional introduction in a polymeric mix structurally-active nanoparticles spinel of magnesium with the developed specific surface provides essential change of crystallizations, leading to formation various super-molecular structural elements in PTFE, having accurately expressed borders (fig. 1c,d).

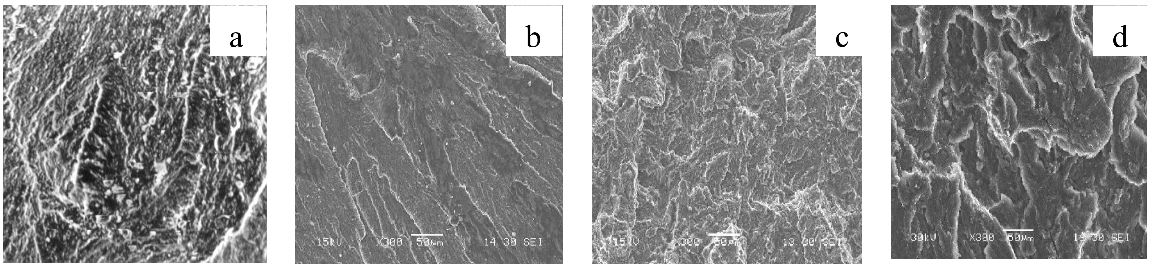


Figure 1. Super-molecular structure PCM:

a) PTFE; b) PTFE +3%F-4MB; c) PTFE +3%F-4MB + 2 % NP;
d) PTFE +3%F-4MB+2 % NP (activation for 2 minutes). Zoom x300.

In micro-photos it is obvious that NP are crystallization centers from which spherolites formations are growing. Formation of biphasic heterogeneous system with the developed interface and a transitive layer (fig. 1) in which mobility of elements super-molecular structures raises is observed. Thanks to that relaxation processes rate is increase, that promotes reduction of local pressure in a composite, leading to increase physical-mechanical characteristics PCM.

For the purpose of studying of the mechanism of a friction and wear process PCM caused by participation nanoparticles, structural researches of surfaces of a friction are conducted. On fig. 2 are presented micro-photos of surfaces of a friction of composites on the basis of mixes flouroplastics, modified by NP.

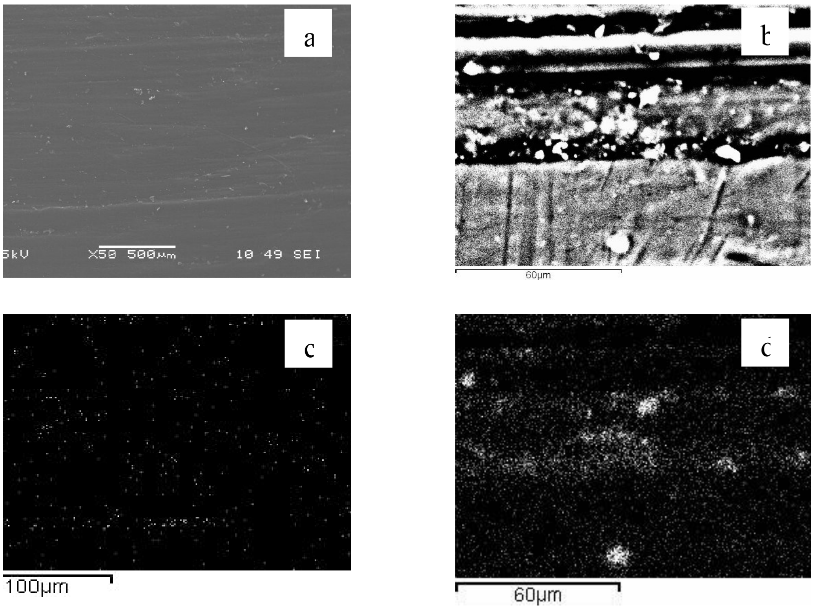
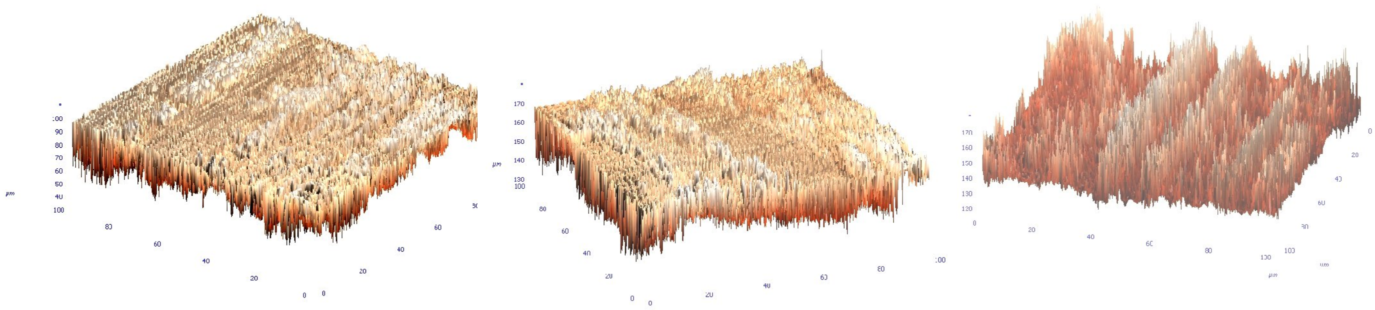


Figure 2. Micro-photos of surfaces PCM: a) to a friction; b) after a friction.
A raster picture of magnesium spinel distribution on surface PCM (in X-rays on magnesium): c) before sliding; d) after sliding.

The topography of a surface of friction PCM is characterized as homogeneous with the small furrowed relief formed of agglomerated nanoparticles. The grooves formed at focused movement of structural elements of blanket PCM, are characterized by insignificant depth. Formation of similar structure of a composite in the course of a friction testifies to stable work of the tribo-attend [4]. Increase in wear resistance PCM, containing NP (in 270 times) can be explained by that particles concentrating on surfaces of a friction in the form of islets form clusters structures with the polymer fragments, playing a role of the filter localizing in the volume of deformation of shift and protecting blanket PCM from destruction.

For the acknowledgement of change of the mechanism of crystallization PTFE caused by participation of NP in structurization binding, researches of images of phase contrast of surfaces of a friction of samples by a method of atomic-power microscopy which are resulted on fig. 3 are conducted. It is visible that micro-geometrical development of surface PCM increases at filling of a mix of polymers nanoparticles. On the image of phase contrast of a mix of the polymers, containing 2 wt. % NP, the contrast ordered structures which are absent in initial polymer are registered. Change of a phase of fluctuations corresponds to increase of contact adhesion on local sites of surface PCM. Level of the maximum change of value of a phase of fluctuations characterizes maximum changes in structure, increase in density of packing of structural elements that leads to change of properties of a material.



a) b) c)

Figure 3. Phase contrast of a surface of a friction:

a) PTFE; b) PTFE+F-4MB; c) PTFE+F-4MB+NP.
A scanning field 100x100 a micron

CONCLUSION

The developed materials are characterized by stable and low values of factor of a friction and intensity of the wear process raised physico-mechanical characteristics the indicators providing rigidity of interfaces and high bearing ability. In comparison with serial polymeric composites the developed composite materials possess the raised wear resistance, durability and bearing ability.

Replacement of regular consolidations and sliding bearings by the developed materials will allow to raise a resource of knots of a friction of the oil and gas equipment and technics at the expense of improvement of technical characteristics (increase of wear resistance, durability, frost resistance), and decrease in expenses for operation and repair.

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