

Polymer Composites Based on Polytetrafluoroethylene Modified with Motor Oil

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Abstract—The production of wear-resistant polymer composites from polytetrafluoroethylene modified with motor oil is considered. Porous polymer blanks are steeped with motor oil and then heated.

Keywords: polytetrafluoroethylene, friction, strength, wear resistance, motor oil, IR spectroscopy

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We know that the properties of polymer composites may be considerably improved by modification of the filler [1–3]. Many filled composites have good anti-frictional properties and high wear resistance, but they must also have satisfactory physicochemical properties and be convenient to machine and use. At present, the use of filled polymer composites such as those based on polytetrafluoroethylene improve the reliability and durability of mechanisms and permit their stable operation in aggressive media, in deep vacuum, and at cryogenic temperatures. Filled composites based on polytetrafluoroethylene are used for piston rings, sealing rings, and supporting rings in high- and moderate-pressure compressors operating without lubricant [4–6].

In the present work, we develop wear-resistant polymer composites based on polytetrafluoroethylene modified with motor oil. Porous polymer blanks are steeped with motor oil and then heated to solidify the liquid phase.

In the present work, we study polytetrafluoroethylene (State Standard GOST 10007–80) and its composites modified with motor oil and activated natural zeolites. The modifiers employed are M-8V, Ravenol 5W30, and Motul 5W30 motor oils based on poly-alpha-olefins, as well as a mixture of spent oils.

The production technology for polymer composites based on polytetrafluoroethylene modified with motor oil includes the shaping of a porous polymer blank, steeping in motor oil for 24 h, and baking. In the production of polymer composites based on polytetrafluoroethylene with natural fillers, the polymer is mechanically mixed with activated natural zeolites before shaping. The natural zeolites are activated in an AGO-2 planetary mill with a shaft speed of

730 rpm and a drum speed of 1780 rpm for 2 min. The samples for testing are prepared by standard methods.

The mechanical characteristics of the polymer composites are determined by standard methods (State Standard GOST 11262–80) on a UTS-20K universal test machine.

Frictional tests are conducted on an SMT-1 machine in a shaft–bush configuration (frictional pressure of 1–2 MPa, slipping speed 0.39 m/s, frictional path 7 km). The sample takes the form of a sleeve (internal diameter 26 mm, external diameter 34 mm, height 20 mm); the counterbody is a steel 45 disk (hardness 45–50 HRC).

The wear rate of the polymer composites is estimated from the loss of sample mass per unit time

$$I = \Delta m / t, \quad (1)$$

where $\Delta m = m_1 - m_2$; m_1 and m_2 are the mass of the sample before and after friction, mg; t is the test time, h.

To obtain information regarding the state of the oil before and after heating to 370°C, we analyze spectra obtained using a Varian FT-IR 7000 infrared spectrometer, with an attachment for disrupted total internal reflection. The supermolecular structure of the polymer composites is investigated by means of a JEOL JSM-7800F scanning electron microscope. Low-temperature brittle chips of the composites obtained at liquid-nitrogen temperatures are studied.

To introduce the liquid oil in the polymer, blanks with microporous structure are produced. To obtain porous blanks, the pressure during the formation of the blank from powder is lower by a factor of 2–4 than in the standard technology. The porous polymer blanks obtained are immersed completely in motor oil for 24 h and then heated. The composite obtained by this technology is relatively strong and maintains its

Table 1

Composite	p_{pr} , MPa	σ_{co} at 25% strain, MPa	E , MPa
Initial PTFE (standard technology)	50	23	328
Porous PTFE	25	22	267
Porous PTFE + 5 wt % zeolite	25	25	295
PTFE + 5 wt % zeolite, modification by motor oil	25	26	390

Table 2

Composite	p_{pr} , MPa	ε_f , %	σ_{ten} , MPa	E , MPa
PTFE	50.0	320	21.3	597
	25.0	443	18.7	651
	12.5	471	17.4	688
PTFE + oil	25.0	448	19.4	640
	12.5	340	16.4	590
PTFE + 5 wt % zeolite	25.0	316	16.9	786
	12.5	311	16.7	694
PTFE + 5 wt % zeolite + oil	25.0	241	12.4	848
	12.5	268	12.2	739

Table 3

Composite	p_{pr} , MPa	C_{oil} , %	I , mg/h
PTFE	50.0	—	106.5
	25.0	—	253.3
	12.5	—	283.9
PTFE + M-8V oil	25.0	0.28	76.2
	12.5	2.80	1.2
PTFE + 5 wt % zeolite modified with M-8V oil	25.0	2.84	0.1
	12.5	3.35	1.5

shape in the subsequent operations. Table 1 presents the strength σ_{co} and elastic modulus E is the compression of samples modified with M-8V oil.

We see in Table 1 that the compressive elastic modulus of polytetrafluoroethylene (PTFE) produced at reduced pressure p_{pr} is less than that of standard polytetrafluoroethylene, while the strength is practically unchanged. The introduction of 5% zeolite in the polytetrafluoroethylene somewhat increases the compressive strength σ_{co} in comparison with standard polytetrafluoroethylene, but the elastic modulus E , although somewhat increased, is still less than for the

initial polymer. If the composite containing zeolite is modified with motor oil, both its strength and elastic modulus in compression are greater than for the initial polytetrafluoroethylene. This may be attributed to the formation of a rigid chain structure when the composite is heated. That considerably increases the resistance of the surface layers of the polymer composite to plastic deformation in friction and hence reduces the wear rate.

Table 2 presents the mechanical properties of the polymer composites as a function of the pressure p_{pr} used in their production. In comparison with the initial polytetrafluoroethylene obtained by the standard method, the porous polytetrafluoroethylene and zeolite-free composites that are produced by liquid-phase filling are characterized by greater relative elongation ε_f at failure, with some decrease in tensile strength σ_{ten} . This is associated with the loose packing of the macromolecules in the porous materials. That structure facilitates change in their configuration on extension and hence favors the appearance of induced elasticity of the samples when stress is applied. Hence, the relative elongation ε_f at failure will be greater than for the initial polymer [7].

Composites containing zeolite, with or without steeping in oil, are characterized by smaller ε_f and σ_{ten} , but their elastic modulus E is somewhat greater. In that case, the decrease in σ_{ten} and ε_f is due to premature sample failure on account of the many defects at the phase boundary between the polymer matrix and the filler particles; those defects act as stress concentrators. On the other hand, the filler particles increase the stress at the polymer–filler boundary and so accelerate the solidification of the polymer [8]. The increase in the elastic modulus is also a benefit, since it improves the resistance of the material to plastic deformation under load.

Table 3 presents the frictional characteristics of polymer composites modified with M-8V oil. With decrease in p_{pr} , the composite becomes less dense and more porous, which reduces the wear resistance. If composites produced with lower p_{pr} are steeped with motor oil and heated, their wear resistance is increased, because the initial structure of the polytetrafluoroethylene is modified, probably because the oxidation of the oil on heat treatment is accompanied by solidification of the oil components, with the formation of rigid-chain structure within the volume and at the frictional surfaces of the composite. That results in increase in hardness, strength, and wear resistance of the composite.

Table 4 presents the results of frictional tests as a function of p_{pr} , the steeping temperature T , and the motor oil employed. With increase in T , the natural steeping of the porous samples is intensified. The volume of oil assimilated is 2–7 times that at normal temperature. The wear resistance of such samples

Table 4

Composite	p_{pr} , MPa	T , °C	Wear rate I , mg/h, with modification by oil			
			M-8V (SAE 20)	Motul 5W30	Ravenol 5W40	mixture of spent oils
PTFE	12.5	25	1.23	1.17	2.00	—
		150	0.42	0.36	0.60	—
	25.0	25	76.23	14.90	97.0	0.36
		150	0.90	1.23	0.90	0.32
PTFE + zeolite + oil	12.5	25	1.50	0.20	—	—
		150	0.16	0.13	—	—
	25.0	25	0.14	0.63	1.20	0.13
		150	0.10	0.53	0.80	0.10

increases. Thus, with increase in T to 150°C, the wear rate falls, regardless of the oil employed.

The wear resistance of the composites is greatest after modification of the polytetrafluoroethylene by M-8V mineral oil and a mixture of spent oils. Their use offers economic and environmental benefits. Mineral oils are 2–3 times cheaper than synthetic motor oils, while spent oils are practically cost-free. As a rule, spent motor oils are not recycled but simply poured away, polluting the environment. There is little recycling of motor oil on account of the costs involved and the stringent requirements on commercial oils. We know that spent motor oil is more difficult to regenerate than industrial oil, since the operating conditions—such as the high temperatures, the catalytic action of the metals in contact with the oil, and admixtures of fuel, dirt, and water—greatly change the properties [9].

Research shows that the frictional coefficient f of slightly modified composites (Fig. 1) is little different

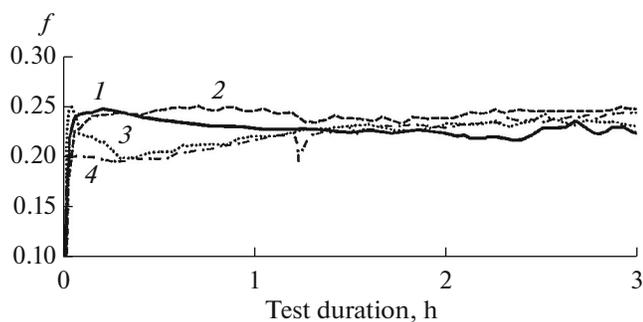


Fig. 1. Frictional coefficients of samples: (1) polytetrafluoroethylene; (2) polytetrafluoroethylene modified with M-8V oil; (3) polytetrafluoroethylene modified by a mixture of spent oils; (4) polytetrafluoroethylene + 5% zeolite modified by a mixture of spent oils.

from that of the initial polymer and meets to the requirements imposed on antifrictional polymers [10].

Structural changes in the surface layers due to friction may significantly affect the frictional characteristics of the polymer. In the IR spectra of the initial motor oils and the oils after holding at the PTFE processing temperature (Fig. 2), we see bands at 1707, 1600, 1630, 1230, and 1150 cm^{-1} for M-8V oil and the mixture of spent oils. In the spent oils, these bands indicate oxidized functional groups (aldehydes, ketones, acids, etc.) and aromatic structures [11–13].

To obtain information regarding the change in oil composition in the polymer composites on baking, the motor oils are held at the processing temperature (380°C). Increased content of oxidized groups and aromatic structures is indicated by the change in intensity of the peaks at 1714, 1603, and 1230 cm^{-1} . This is associated with the fact that oxidation of the oil may be catalyzed by old oxidation products and also, in the case of spent oils, by zeolite. In this case, the accumulation of oxidized products and polycyclic aro-

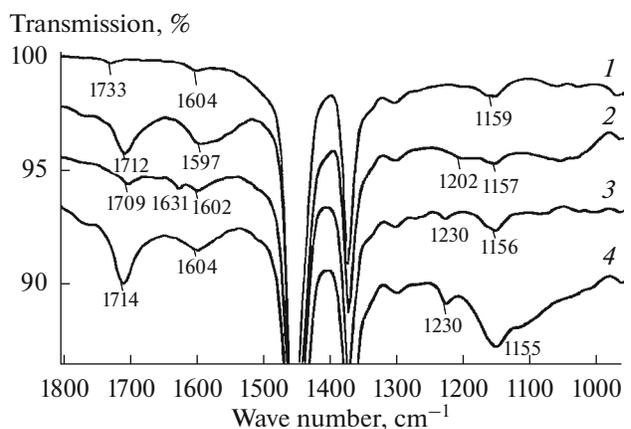


Fig. 2. IR spectra of M-8V motor oil before (1) and after (2) heating to 380°C and a mixture of spent oils before (3) and after (4) heating to 380°C.

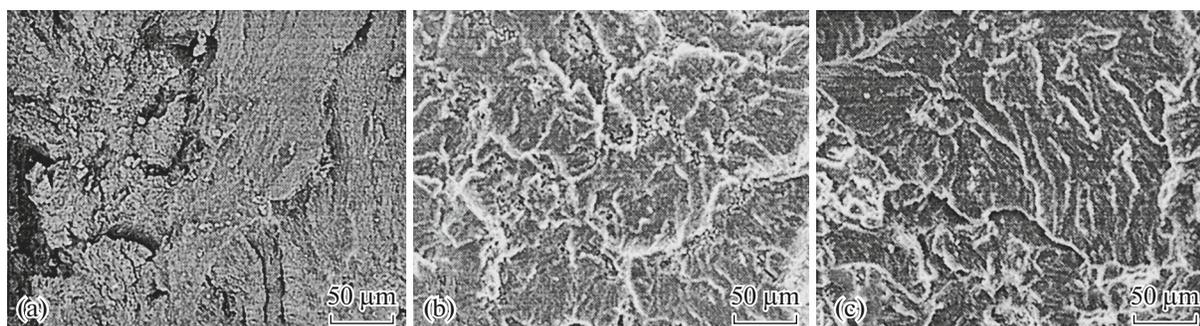


Fig. 3. Supermolecular structure of polymer composites: (a) initial polytetrafluoroethylene; (b) polytetrafluoroethylene modified by oil; (c) polytetrafluoroethylene modified by zeolite and oil.

matic structures is greater on steeping at high temperatures than in unused motor oils, as confirmed by the IR spectra. We know that the spent oils consists of a carbon–oil suspension, in which carbon compounds (carbides, carboids, and soot) constitute up to 90% of all the impurities.

In the heat treatment of oil-filled polymer composites, solid tars (asphaltenes, carbenes, and carboids) are formed as a result of oxidation of the oil [9]. These products impair lubricant quality but probably boost the wear resistance of the polymer composites. Carbides and carboids are polycondensed compounds with high carbon content; they are formed in the thermal decomposition of oils and fuel. Carboids are highly associated materials that form the main component of coke, soot, fusain, anthracite, kerites, and anthraxolites. They are often used as surfactant fillers in polymers. Thanks to the high density of their molecular structure, they have high carbon content. They are highly insoluble and nonvolatile. In appearance, they are black and highly opaque. Carbenes and carboids are crosslinked polymers with a distinctive crystalline structure and presumably confer hardness and wear resistance on the polymers.

Carbenes are unstable and recombine to form dimers. Their analogs form higher cyclic oligomers and polymers. Of all aromatic hydrocarbons, they are the most likely to form carboids (petroleum coke). At the temperatures of 375–380°C used in processing polymer composites based on polytetrafluoroethylene, carboids are formed about ten times more commonly than heavy tars. Carboids do not dissolve in any solvents and generally contain up to 99% carbon [14, 15].

The supermolecular structure of the polymer composite significantly affects the wear rate. The components of the oil introduced in the polymer act as centers of solidification. Accordingly, the initial strip structure of the polytetrafluoroethylene is converted to spherulitic structure, characterized by greater strength and wear resistance (Fig. 3).

Thus, the use of mineral oil and spent oils in modifying polytetrafluoroethylene is a promising means of

producing wear-resistant composites. The use of solid fillers with good sorptional properties—zeolites, in the present case—improves the wear resistance of the oil-modified polymer composites. Modification with oil leads to the formation of spherulitic structure and hence to increase in the wear resistance.

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