

STRUCTURE AND PROPERTIES OF POLYMER-SILIKATE NANOCOMPOSITES BASED ON POLYTETRAFLUOROETHYLENE

Sardana A. Sleptsova, Aitalina A. Okhlopko

North-Eastern Federal University, 58th Belinsky str., Yakutsk 677000, Republic of Sakha, Russia

Abstract

The results of physicomechanical, tribological, and structural investigation of polytetrafluoroethylene-based polymers and natural layered silicates are reported. It is shown that the tribological behaviour of the composites can be significantly improved by introducing a small amount of activated silicates. The results of structural examination of the composite friction surfaces by scanning-probe microscopy and IR spectroscopy are discussed.

Key words: polytetrafluoroethylene, layered silicates, wear resistance, friction coefficient, structure, IR-spectrum.

1. INTRODUCTION

Using layered silicates as fillers holds promise in structural modification of polymers. The interest in silicates as effective modifiers of the polymer matrix is attributed to their capability of forming spatially continuous structures in the composite owing to the specific structural arrangement of minerals [1, 2]. The modifying ability of layered silicates can be fully used through intercalating polymer macromolecules in the interlayer spaces (galleries) of the filler particles [3, 4]. Further exfoliation of the fillers into singular layers ~ 1nm thick possibly results in nanocomposites having properties exceeding those of the starting polymer. Improvement of the compatibility of the composite component and provision of intercalation are the main problems in nanocomposite development. Mechanical activation of silicates under optimal treatment conditions is the simplest, and fairly productive, solution.

The goal of the work is to study the effect of layered silicates on the structure and tribological behavior of polytetrafluoroethylene by using mechanical activation of the filler.

2. MATERIALS AND METHODS

Industrial polytetrafluoroethylene (PTFE, GOST (State Standard) 10007-80) and vermiculite and serpeninite fillers mined in the Republic of Sakha and classified as layered silicates [5] were the objects of study. Serpentinite ($\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$) is a rock produced mainly by serpentine minerals. It is a mineral that arises from metamorphosis of magma rocks, primarily belonging to the peridot and picrite groups. Vermiculite ($\text{K}_2(\text{Mg, Fe}^{+2})_6(\text{Al}_2\text{Si}_6\text{O}_{20})(\text{OH})_4$) is a mineral of the hydromica group. It is a hydrated form of biotite and contains a relatively large amount of bound water (11-21%).

The composites were produced by mixing of the components in a paddle mixer with preliminary mechanoactivation of the fillers. The filler was activation during 1 – 5 min in the planetary mill, using 2 regimes: 1 - carrier rotation frequency 400 rpm, centrifugal acceleration developed by milling bodies 400 m/s^2 , and 2 - 730 rpm and 1000 m/s^2 , accordingly.

The physicomechanical properties of the composites (tensile strengts and relative elongation upon rupture) were found on a UTS-2 rupture machine (GOST 11262-80). The tribological characteristics

(friction coefficient and mass wear rate) were found on an SMTs-2 friction machine by the shaft-bush scheme according to GOST 11629-5. The composites structure was examined by IR spectroscopy using an FTS 7000IR-Fourier-step-scan-spectrometer (Varian, USA).

3. RESULTS AND DISCUSSION

Analysis of the results of physicomechanical and tribological tests of the composites has shown the advantage of mechanical activation on the 1 regime. With fillers introduced at up to 2 wt %, the strength characteristics of the composites remain at the starting level. Further increase in the filler content results in a gradual decrease of the physicomechanical properties of the composites. Significant improvement of the tribological characteristics of the composites should be mentioned: the mass wear rate decreases 1000 times for the composite containing 5 wt % of serpentine and 1500 times for the composite containing 10 wt % of vermiculite. Almost in all composites decrease in the friction coefficient is observed. This fact can be related to the structure modification of the surface layer of the polymer composite in friction and wear. In work [6], dealing with the investigation of tribochemical processes running in PTFE-based composite wear, the formation of high-oriented structure of the material surface layers with crystallinity exceeding the original values is reported. It results in reducing the contact area, as well as the mechanical and molecular components of the friction force, which leads to decreasing friction coefficient.

The structurally active filler encourages the ordering and orientation of macromolecules in friction trough involvement in polymer tribodestruction and further structuring.

Table 1. Characteristics of PTFE – serpentinite composites

Composite	Activation regime	Rupture strength, MPa	Elongation at rupture, %	Modulus of elasticity at rupture, MPa	Mass wear rate, mg/h	Friction coefficient
PTFE	-	20	320	479	78,00	0,20
PTFE + 1 wt% of serpentinite	w/a	14	132	464	2,60	0,14
	1	19	373	691	1,10	0,19
	2	22	373	637	1,20	0,17
PTFE + 2 wt% of serpentinite	w/a	15	124	531	1,80	0,18
	1	18	320	696	0,18	0,17
	2	20	320	630	0,50	0,15
PTFE + 5 wt% of serpentinite	w/a	14	102	526	1,18	0,20
	1	16	220	692	0,30	0,19
	2	17	219	669	0,07	0,14
PTFE + 10 wt% of serpentinite	w/a	12	106	575	1,50	0,20
	2	13	214	694	0,50	0,20

Note: w/a — without activation. Activation time was 2 min in all cases.

In order to evaluate the effect of fillers on the friction and wear of the composites, their structure was examined using IR spectroscopy. Figures 1 and 2 show the absorption IR spectra of the activated fillers and studied composites depending on the filling degree before and after friction. Comparison of the composite spectra before and after friction shows the filler introduction to give rise to end C-H groups (one can see the peaks characteristic of valence variations within a 2700-2900 cm^{-1} range and the peaks characteristic of deformation variations of C-H bonds within a 1400-1500 cm^{-1} range). The intensity of the corresponding absorption bands increases with increasing filler concentration. With fillers introduced, fragmentation of PTFE macromolecules probably starts. Wear of the composite results in a considerable increase in the intensity of the peaks; consequently, the number of fragments of PTFE macromolecules increases in friction. In addition, friction initiates oxidation. Over a range of 3200-3400 cm^{-1} the number of fragments containing oxidized groups of polymer macromolecules increases. The filler concentration increases the intensity of the bands corresponding to the variations of these groups.

Table 2. Characteristics of PTFE – vermiculite composites

Composite	Activation regime	Rupture strength, MPa	Elongation at rupture, %	Modulus of elasticity at rupture, MPa	Mass wear rate, mg/h	Friction coefficient
PTFE	-	20	320	479	78,00	0,20
PTFE + 1 wt% of vermiculite	w/a	21	297	483	7,20	0,16
	1	19	313	559	5,20	0,18
	2	22	291	523	6,20	0,18
PTFE + 2 wt% of vermiculite	w/a	17	328	538	5,30	0,18
	1	17	280	582	4,50	0,18
	2	20	366	702	3,70	0,18
PTFE + 5 wt% of vermiculite	w/a	11	130	650	1,80	0,18
	1	14	238	667	0,80	0,16
	2	17	289	602	0,40	0,18
PTFE + 10 wt% of vermiculite	w/a	11	75	523	1,30	0,20
	2	11	143	545	0,04	0,20

Note: Activation regime see in the Note to Table 1

Thus, it is shown that introduction of fillers into PTFE increases the intensity of its tribodestruction and oxidative processes in friction. On the other hand, over a range of 1600-1700 cm^{-1} , peaks of different intensity according to the filling degree are revealed that are not characteristic of the original PTFE. In a spectrum database it has been found that the peaks falling in the range can be either fragments of double bonds or fragments of molecules of carbonic acid salts [7-9]. In work [10] the influence of metals on the thermo- and tribooxidation of polymers is reported. It is shown that metal at the initial stages of polymer processing initiates oxidative processes, resulting in carboxyl groups. Subsequently, the metal

interacts with carboxyl groups, forming salts that act as inhibitors of oxidative processes. Thermooxidative decay of macromolecules leads to a cross-linked, more ordered, densely packed structure characterized by an increased wear resistance.

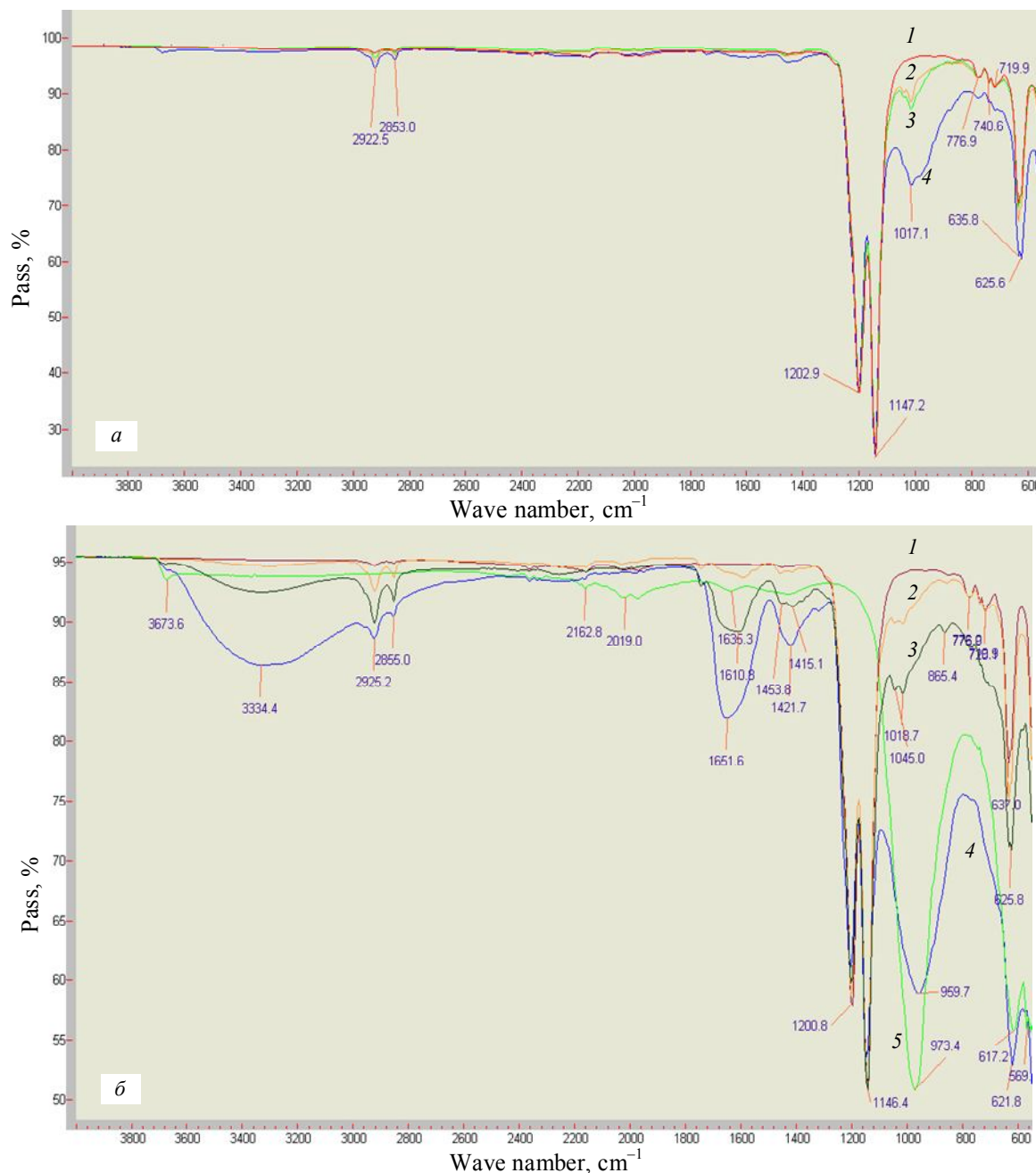


Fig. 1 IR spectra of serpentine and serpentine-modified PTFE versus its content taken before (a) and after (b) friction: 1 – original PTFE; 2 - PTFE + 2 wt% of serpentine; 3 - PTFE + 5 wt% of serpentine; 4 - PTFE + 10 wt% of serpentine; 5 – serpentine.

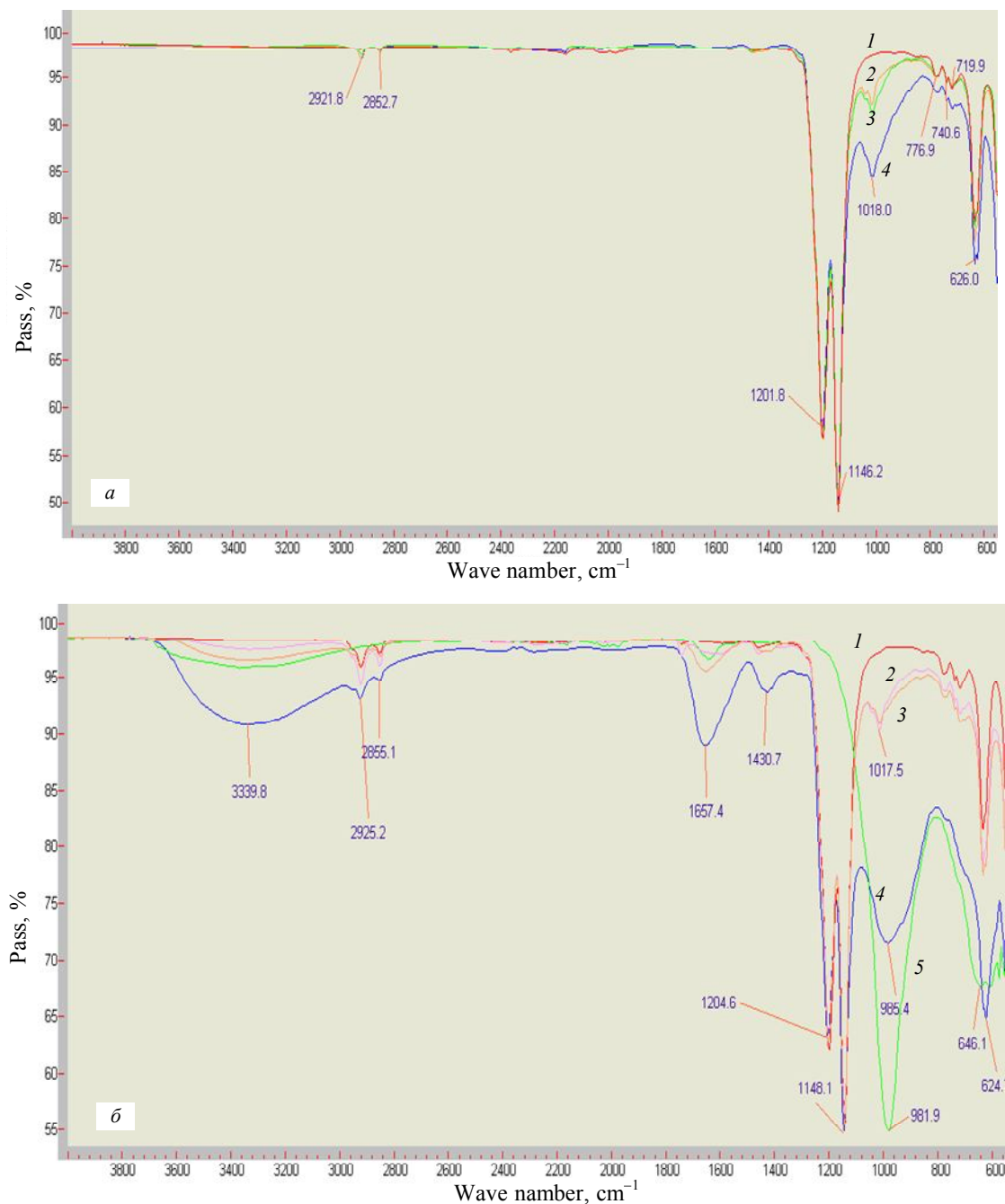


Fig. 2 IR spectra of vermiculite and vermiculite-modified PTFE versus its content taken before (a) and after (b) friction: 1 – original PTFE; 2 - PTFE + 2 wt% of vermiculite; 3 - PTFE + 5 wt% of vermiculite; 4 - PTFE + 10 wt% of vermiculite; 5 – vermiculite.

ACKNOWLEDGEMENTS:

The work was implemented under financial support of the Russian Foundation for Basic Research, project 09-03-98504_vostok_a.

REFERENCES

1. Tretyakov, Yu.D., Oleynikov, N.N., Shlyakhtin, O.A. Cryochemical Technology of Advanced Materials London: Chapman & Hall 1997
2. Kuznebov, B.V. Lanin, T.S., Rakhmanov, N.A., et al. Adsorption Properties of Layered Silica, Zh. Fiz Khim 2007; 81; 5: pp781-787
3. Gerasin, V.A., Zuhova, T.A., Bakhov, F.N., et al. Structure of Polymer/Na⁺ - Montmorillonite Nanocomposites. Obtained via Mixing in Melt. Rossiiskie nanotekhnologii 2007; 2 ;1-2: pp. 90-105
4. Chvalun, S.N., Novokshonova, L.A., Korobko, A.P., and Brevnov, P.N. Polymer-Silica Nanocomposites: Physicochemical Aspects of Synthesis by Polymerization in situ. Zh. Ros. Khim. Obshch-va im. D.I. Mendeleeva 2008 ; LII ; 5 : pp. 52-57
5. Krasil'nikov, P.V. Praktikum po geologii (Practical Work on Geology) .Petrozavodsk: PetiGU 2000
6. Okhlopko, A.A., Adrianova, O.A., Popov, S.N. Modifikatsiya polimerov ultradispersnymi soedineniyami (Polymers Modification by Superdispersed Compounds) Yakutsk: Yakut. filial Izd-va SO Rossiisk. Akad Nauk 2003
7. Pretsch, E., Bullman, F. and Affolter, L. Opredelenie stroeniya organicheskikh soedinenii (Structure Determination of Organic Compounds). Moscow: Mir 2006 : Heidelberg: Springer. 2000
8. Sverdlov, L.M., Kovner, M.A., and Krainov, E.P. Kolebatel'nye spektry mnogoatomnykh molekul (Vibration Spectrums of Polyatomic Molecules) Moscow: Nauka 197
9. Beloborodov, V.L., Zurabyan, S.E., Luzin, A.P., and Tyukavkina, N.A. Organicheskay khimiya (OrganicChemisiry) Moscow: Drofa 2003
10. Belyi, V.A., Egorenkov. N.I., and Pieskachevskii Yu.M. Termo- i tribookislitel'nye protsessy v polimerakh (Thermo-and Tribo-Oxidation Processes in Polymers) Moscow: Khimiya 1987