Knowledge E
Engaging minds

Conference Paper

Wear-Resistant Polymer Composites Based on Polytetrafluoroethylene and Layered Silicates

S.A. Sleptsova, Yu.V. Kapitonova, N.N. Lazareva, and M.M. Makarov

North-Eastern Federal University, 677019 Yakutsk, Russia

Abstract

To improve interaction on the phase boundary of polymer composites, we used functional additives, mechanoactivation method, and ultrasound. In the case of the use of serpentine as a modifier of polytetrafluoroethylene (PTFE), the introduction of magnesium nanospinel (NS) as functional additive resulted in the increase of wear resistance of composite in 2500 times. Effect of ultrasonic irradiation on the composites comprising phlogopite was considered. IR data have shown that NS influences the intensification of the tribological processes. In sonicated composites the intensity of the IR spectra of oxidized fragments depends on the content of NS and correlates with the wear resistance.

Keywords: polytetrafluoroethylene, composite, layered silicate, magnesium nanospinel, ultrasonic irradiation, tribological processes, infra-red spectrum, X-ray diffraction analysis, wear resistance, friction coefficient

Corresponding Author: S.A. Sleptsova; email: ssard@yandex.ru

Received: 9 September 2016
Accepted: 19 September 2016
Published: 12 October 2016

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the ASRTU Conference Committee.

1. Introduction

Specificity of the climatic conditions of the Arctic regions limits the choice of base polymer to create a polymer composite material for manufacturing the parts of friction units operated in the regions of industrial machinery. Among all the existing plastics, the polytetrafluoroethylene (PTFE) is notable for super-high frost-resistance, unique chemical inertness, and the lowest and stable friction coefficient. PTFE disadvantages such as low wear resistance and creep are eliminated by introducing a variety of fillers. In our opinion, the layered silicates are promising modifiers of PTFE. Significant improvement in properties of the starting polymers is achieved in the case of intercalation of polymer into the interlayer space macromolecules silicates with subsequent exfoliation into individual nanolayers dispersed inside the polymer [1, 2]. But because of the low adhesion of the PTFE its contact with mineral fillers is becoming an urgent problem. Primarily, this is due to the hydrophilicity of silicates – the main problem of incompatibility with the organic polymer matrix. Most natural layered silicates belong to a structural family of type 2:1. In the layered silicates with similar structure the octahedral grid is enclosed between two grids of silicon-oxygen tetrahedra. In such tetrahedra some part of the tetravalent silicon is replaced on the trivalent aluminum. As a result, a negative charge is formed on the layer, which is compensated by hydrated cations of alkali or alkaline earth metal located between the layers [3]. So in each of the cations inside the gallery a partial positive charge is created making layered silicates

How to cite this article: S.A. Sleptsova, Yu.V. Kapitonova, N.N. Lazareva, and M.M. Makarov, (2016), “Wear-Resistant Polymer Composites Based on Polytetrafluoroethylene and Layered Silicates,” in *IV Sino-Russian ASRTU Symposium on Advanced Materials and Materials and Processing Technology*, KnE Materials Science, pages 149–154. DOI 10.18502/kms.v1i1.577

hydrophilic. This feature silicate with structure 2:1 allows them to be most effective modifiers for polar polymers such as polyamide [4, 5]. Until now layered polymer nanocomposites with nonpolar or weakly polar polymers do not have such high metrics as materials based on polar polymers [6]. There is practically no information on the effect of these fillers on the properties of composites based on PTFE. Besides, there are layered silicates with the aforesaid structure, such as serpentine and kaolinite, which are characterized by a structure of the crystal lattice of 1:1 when at the one silicon-oxygen tetrahedral layer there is one octahedral layer. In this case, the charge of the tetrahedra is compensated fully by charge of octahedra [3]. Consequently, these silicates not possess a pronounced hydrophilicity.

The aim is to study the effect of layered silicates with different structures on the properties of PTFE.

2. Methods

The objects of the study were polymer composite materials based on grade PN PTFE (GOST 10007-80). The polymer was filled with natural layered silicates, such as serpentine (the Kovdor deposit, Murmansk Region, Russia) with structure 1:1 and phlogopite (the Emeldzhak deposit, Republic of Sakha (Yakutia), Russia) having type of structure 2:1.

The preparation of PTFE included its drying for 4 h at a temperature of 180 °C. Dried PTFE was milled and bolted through sieve no. 1K. Silicates were dried in a furnace for 4 h at a temperature of 120 °C in order to remove surface-bound moisture [7]. To improve compatibility silicates with the PTFE we used functional additive, mechanical activation, and in the case of phlogopite – sonication. The magnesium nanospinel (NS) was chosen as a functional additive, which is a double oxide with a general chemical formula $MgAl_2O_4$. A feature of the NS is high dispersion (about 70-80 nm particle size) and a developed surface area (170 m^2/g). The dried silicates and NS were activated in a planetary-type mill "ASC-2" for 2 minutes [8]. Samples without sonication were prepared by dry mixing polymer with filler and subsequent sintering. The sonication was conducted by mixing the components in an ethanol in the ultrasonic disperser IL100-6/3 (volumetric ultrasound power 3000 W) for 15 min. Next, samples were formed by cold pressing and then sintered in a temperature range of 300-375 °C. The physicomechanical properties of the composites were tested in accordance with GOST 11262-80 using an Autograph AGS-J testing machine (Shimadzu, Japan). The wear rate and coefficient of friction were determined in accordance with GOST 11629-75 using the shaft-bushing test arrangement implemented in SmTs-2 friction machine (Russia) under a load of 0.45 MPa at a velocity of sliding of 0.39 m/s. For structural studies we used methods of scanning electron microscopy (SEM), IR spectroscopy, and X-ray photoelectron spectroscopy (XPS). The friction surfaces of the composites were examined using a JSM-7800F SEM (Jeol Ltd., Japan). Structureless conductive films were produced on the surfaces using the plasma deposition of platinum, which provided the highest secondary electron yield. IR spectra were recorded using a FTIR 7000 spectrometer (Varian Inc., USA). XPS spectra were recorded using a K-Alpha

Samples	**Elongation at break**, %	**Tensile strength**, MPa	**Speed of mass wear, 10^{-6} kg/h**	**Coefficient of friction, f**
PTFE	300–320	20–22	70–75	0.04 -0.2
PTFE + S	245–316	15–17	0.05–0.2	0.02–0.03
PTFE+S+NSh	317–356	19–22	0.03–2.2	0.03–0.04
PTFE+F	274–386	15–22	0.7–4.9	0.06–0.1
PTFE+F+NSh	250-350	13-18	0.1-0.2	0.1-0.16

Table 1: Characteristics of the Composites based on PTFE.

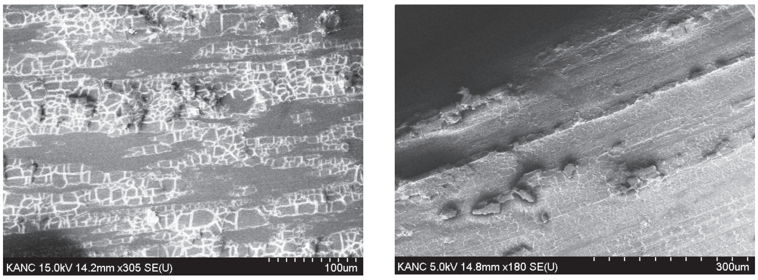

Figure 1: Structure of the surface layers of the composites after friction: a) PTFE + 2 wt.% serpentine; b) PTFE + 2 wt.% serpentine + 0,5 wt.% NS.

spectrometer (Thermo Scientific, USA) in AlK_α radiation at a power of 100W and voltage of 12 kV. The zone of analysis was 30-400 μm in diameter.

3. Results

Analysis of the results of physicomechanical and tribological tests of the composites (Table 1) has shown the advantage of using functional additive. We observe a significant improvement in the properties of composite parameters.

Tribological characteristics of the PTFE composites significantly improved: the mass wear rate decreases 2,500 times in case of sample (PTFE+S+NS). Besides, these composites kept low meaning of friction coefficient. One reason for the significant reduction in wear rate of mass may be a change in the structure of the surface layer material by tribochemical reactions occurring during abrasion. In this case, the process of abrasion is accompanied by the formation on the friction surface of portions of the filler particles transferred from the border zones of different supramolecular structures. On the micrographs of surface friction of the composites the areas of the silicate particles are clearly visible. These areas act obviously as a lubricant, thanks to the layered structure, and it is the cause of emergence conditions for boundary lubrication. This fact can explain such low values of friction coefficients of the composites containing layered silicates (Fig. 1).

Studies of the composites structure have shown that the use of functional additive allowed achieving uniform distribution of the filler in the polymer. The element analysis of the friction surface has shown that after friction the surface is enriched with

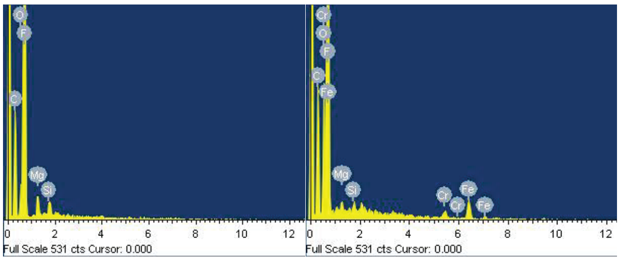

Figure 2: Element analysis of composites containing 2 wt.% serpentinite + 0,5 wt.% NS before (a) and after (b) friction.

elements of friction counter body (Fig. 2). The presence of these elements may indicate the participation of metal counter surface in friction and wear processes.

To assess the effect of excipients on friction and wear processes, composites were analyzed by surface IR spectroscopy. The IR spectra of the composites, which have been recorded after friction in the range of 3600-2600 cm^{-1}, contain a wide absorption band. In accordance with the data from Ref. [9], the appearance of such band in this range is due to the formation of associated of the hydrogen bond; moreover, typically peroxides are also found in this range. The presence of these bands in the spectra indicates the formation of an intermediate product of the carbon chain oxidation. The appearance of these oxygen-containing groups serves as an evidence of the participation of peroxide radicals in the destruction reactions. The further oxidation of these products inevitably leads to the formation of carboxylates with the participation of cations of the metals contained in the fillers or the counter body material. This is confirmed by the presence of two characteristic peaks in the range of 1680-1400 cm^{-1} in the IR spectra of all composites (Fig. 3). It is possible that the formation of carboxyiates favors the inhibition of the oxidation processes since carboxylic acids are the end product of oxidation. The probability of the simultaneous processes of structure formation and destruction of polymer macromolecules is high, because the radical particles will react with each other to form a new bond or in this case a cross link, thus creating secondary wear-resistant layer on the surface of friction.

To prove the formation of an intercalated or exfoliated structure of polymer layered nanocomposites, X-ray diffraction method is typically used. The results of studies of the composites structure by XRD are presented in Fig. 4. As a rule, disappearance of the so-called basal reflex of silicates that is responsible for the layers' periodicity is a confirmation of formation of the exfoliated nanostructures. As seen from the X-ray (Fig. 4), only composites containing magnesium nanospinel and serpentine are characterized by disappearance of this reflex. Thus, administration of magnesium nanospinel helped to complete exfoliation of serpentine particles on monolayers as a result of intercalation of the polymer macromolecules in the interlayer space of silicate (formation of exfoliated nanostructure). Therefore, this composite is distinguished by the high physical-mechanical and tribological properties. Probably, formation of exfoliated nanostructures associated with structural type of serpentine.

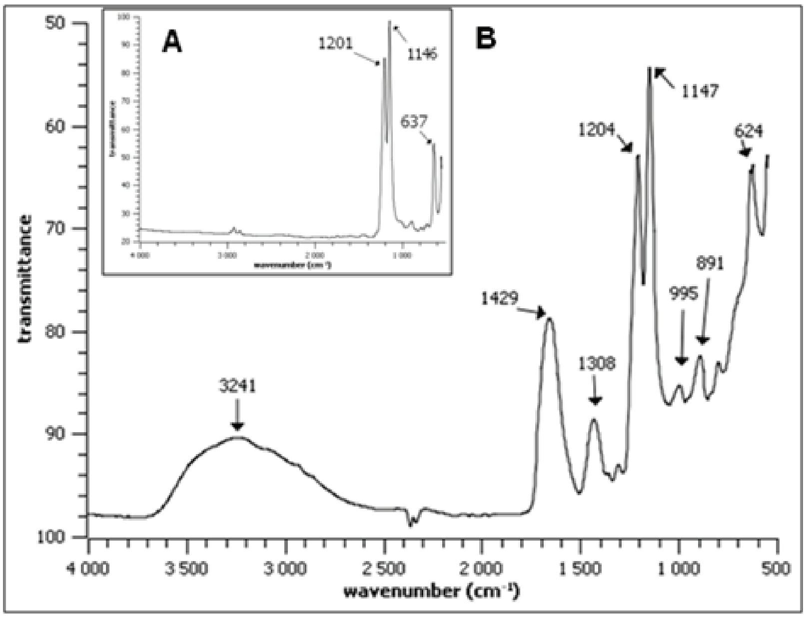

Figure 3: IR spectra of specimens of PCMs recorded (a) before and (b) after friction.

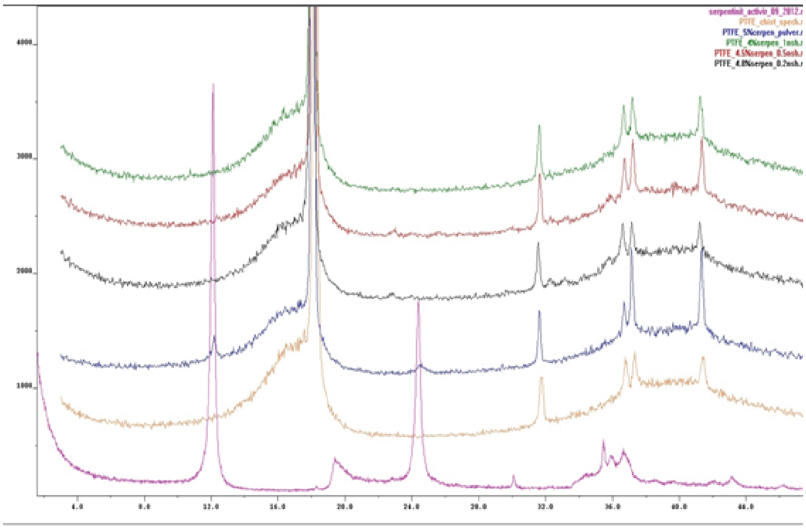

Figure 4: Radiographs: 1) serpentine treated in a planetary mill; 2) neat PTFE; 3) PTFE + 5 wt. % serpentine; 4) PTFE+ 4.8 wt% serpentine + 0.2 wt % NS; 5) PTFE + 4.5 wt% serpentine + 0.5 wt % NS; 6) PTFE + 4.0 wt% serpentine + 1.0 wt % NS.

4. Conclusion

It is shown that layered silicates with a crystal lattice structure of the type 1: 1 are more active modifier PTFE compared with other layered silicates. Using a serpentine possessing such structure allowed us to obtain a polymer-silicate composites intercalated nanostructure. These nanocomposites have high levels of mechanical and tribological properties.

Acknowledgement

This work was supported by the Ministry of Education and Science of the Russian Federation, state assignment no. 11.512.2014/K

S- serpentine; F- phlogopite. The silicate content was varied from 1 to 7 wt. %, the SNh content was 0.2 wt.%; 0, 5 wt.% and 1 wt. %.

References

[1] M. Alexandre and P. Dubois, Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials, *Materials Science and Engineering R: Reports*, **28**, no. 1, 1–63, (2000).

[2] S. Sinha Ray and M. Okamoto, Polymer/layered silicate nanocomposites: A review from preparation to processing, *Progress in Polymer Science (Oxford)*, **28**, no. 11, 1539–1641, (2003).

[3] T. J. Pinnavaia, Intercalated clay catalysts, *Science*, **220**, no. 4595, 365–371, (1983).

[4] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi, and O. Kamigaito, Synthesis of nylon 6-clay hybrid by montmorillonite intercalated with ε-caprolactam, *Journal of Polymer Science, Part A: Polymer Chemistry*, **31**, no. 4, 983–986, (1993).

[5] K. Yano, A. Usuki, and A. Okada, Synthesis and properties of polyimide-clay hybrid films, *Journal of Polymer Science, Part A: Polymer Chemistry*, **35**, no. 11, 2289–2294, (1997).

[6] V. A. Gerasin, F. N. Bakhov, N. D. Merekalova, Y. M. Korolev, H. R. Fischer, and E. M. Antipov, Structure of surfactant layers formed on Na+ montmorillonite and compatibility of the modified clay with polyolefins, *Vysokomolekularnye Soedineniya. Ser.A Ser.B Ser.C - Kratkie Soobshcheniya*, **47**, no. 9, 1650–1651, (2005).

[7] AS. Vorontsov and VA. Liopo, Avdeichik SV, Kozello AV: Aggregation processes of dispersed particles of polymeric matrices modifiers, *Gorn. Mekhan. Mashinostr*, **4**, no. particles, 81–85, (2011).

[8] YeG. Avvakumov, (2009)., Gusev AA: Mechanical methods of activation in processing of natural and technogenic raw materials Novosibirsk: Geo, .

[9] K. Nakanishi, *Infrared spectra and structure of organic compounds. Practical Guidance*, Wiley, New York, 1965.