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Study of influence of carbon fibers and zeolite on mechanical and tribological properties of PTFE

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ABSTRACT

One of the modern problems in Arctic development is the performance of equipment in extreme operating conditions. Polymer materials are widely used in machine applications and exposed to climatic influences. Polytetrafluoroethylene (PTFE) is distinguished by its performance in a wide temperature range and resistance to aggressive media. Its disadvantage is its low wear resistance. This work presents the study of the effect of combined fillers on the properties of PTFE. Carbon fibers, mechanically activated zeolite, ultradispersed polytetrafluoroethylene were used as fillers. The introduction of combined fillers into PTFE leads to a significant improvement in the tribological properties of materials. Polymer composites showed high wear resistance (k = 0.61-0.99 × 10^{-6} $mm^3/N \cdot m$) while keeping the coefficient of friction at the level of the initial polymer. The structural investigations of polymer composite material were carried out using XRD, SEM, and IR-spectroscopy. The degree of crystallinity of the composites was increased relative to the initial polymer. Structural studies by SEM and IR spectroscopy of the worn surfaces of the composites showed the formation of wear-resistant secondary structures which improved the wear resistance of materials.

KEY WORDS: Polytetrafluoroethylene, polymer composite materials, carbon fibers, zeolite, wear resistance.

INTRODUCTION

Currently, polymer composite materials (PCM) are widely used in various friction units of machines and equipment due to the ease of manufacture of products, lightweight, corrosion resistance, and do not require maintenance (Friedrich, 2018). Of interest are studies aimed at developing polymer materials that are used in the Arctic. It is known that the equipment productivity in winter decreases by an average of 1.5 times, and the productive resource - by 2–3.5 times (Okhlopkova, et al., 2019). Polytetrafluoroethylene (PTFE) has a wide working temperature range, high chemical resistance, and low coefficient of friction. Due to these properties, PTFE can be used as plain bearings, O-rings, gaskets, etc. (Dhanumalayan, et al., 2018). The disadvantages of PTFE include low wear resistance and creep, which limit its use. To eliminate the disadvantages, various fillers are introduced into PTFE: dispersed particles, fibers, and their combinations (Conte, et al., 2012). Recently, when developing PCM for tribotechnical purposes based on PTFE, combined fillers containing carbon fibers and glass fibers together with various dispersed particles have been used (MoS_2, graphite, bronze) (Song, et al., 2016, Conte, et al., 2012).

Previous studies showed that the introduction of carbon fibers mixed with kaolin/vermiculite and ultradispersed polytetrafluoroethylene made it possible to significantly improve the wear resistance of the PTFE compared to PTFE-composites containing only fibers (Vasilev, et al., 2019). It was shown that the secondary structures are formed on the friction surface during the wear of PCMs, contributing to an increase in the wear resistance of materials.

Sleptsova S.A. and co-authors investigated the properties of PCM based on PTFE filled with mechanically activated layered silicates (Sleptsova, et al., 2018, Sleptsova, et al., 2019). It can be seen from their works that the tribotechnical properties of PCM based on PTFE filled with natural silicates depend on the type of layered silicate. The coefficient of friction of composites based on PTFE with vermiculite is higher compared to composites containing bentonite (Sleptsova, et al., 2018, Sleptsova, et al., 2019). Thus, by varying the type of layered silicate, it is possible to change PCM tribotechnical properties based on PTFE. In this work, together with the reinforcing carbon fiber, we used a natural filler - zeolite. It is known that natural zeolites, due to their heat resistance, easy availability, and low costs are used to modify polymers (Petrova, et al., 2018).

The aim of this work is to study the effect of carbon fibers together with zeolite and ultradispersed polytetrafluoroethylene (Forum) on the properties and structure of PTFE.

EXPERIMENTAL

The polymer matrix was represented by PTFE brand PN-90 (GaloPolymer, Russia) with a 46–135 μm mean particle size. As a fiber filler, modified discrete Belum carbon fibers (CF) of (OAO Svetlogorsk-Khimvolokno, Belarus) were used. The mean width of CFs was 8–10 μm and the fiber length varied from 50 to 500 μm. CF were modified plasmochemically in organofluorine compounds; the technology of modification was developed in the Belyi Metal-Polymer Research Institute, National Academy of Sciences of Belarus (Shelestova, et al., 2003). As a disperse filler, we used a clay mineral represented by zeoilite (Zt) from a deposit in Republic of Sakha (Yakutia), Russia, whose approximate chemical composition was $M_2/nOAl_2O_3{\cdot}xSiO_2{\cdot}yH_2O$ and mean specific surface was 15 m^2/g (Gogoleva, et al., 2014).

The physical and mechanical characteristics of PTFE and PCM were determined according to the GOST 11 262–2017 (Plastics. Tensile test method, ISO 527-2:2012) and GOST 4651–2014 (Plastics. Compression test method, ISO 604:2002) on the Autograf AGS-J universal testing machine (Shimadzu, Japan). The densities of the PTFE and PCM samples were determined according to Russian standard GOST 15139-69 (Plastics. Methods for the determination of density (mass density)). Distilled water was used as the media.

Tribological tests were carried out under a pin-on-disc configuration on a UMT-3 (CETR, USA). The coefficient of friction PTFE and PCM were determined according to Russian standard GOST 11629-2017 (Plastics. Method for determination of friction coefficient). The counter body was a #45 carbon-steel disk with a hardness of 45–50 HRC. We used a normal loading force of 160 N, an average sliding speed of 0.2 m/s, and a test duration of 3 h. The test specimens were cylinders with diameters of 10.0 ± 0.2 mm, and heights of 20 ± 1 mm. The specific wear rates (*k*) was determined using the equation: $k=V/F_N \cdot d$, where F_N, N - normal load; d, m - is the sliding distance; V, mm^3 - is the volume loss.

The crystal structure of the PTFE and its PCMs was determined using X-ray powder diffractometry (XRD; ARL X'Tra, Thermo Fisher Scientific, Switzerland) with a CuK_α (λ = 0.154 nm) radiation source. The degree of crystallinity was estimated from the ratio of the areas of reflections corresponding to amorphous and crystalline regions. WinXRD software (v. 2.0-6, ThermoFisher, Switzerland) was used for data analysis. The worn surface of the initial PTFE and PCM were characterized using scanning electron microscopy (SEM; JSM-7800F LV, JEOL, Japan). IR spectra of the specimens were recorded on a Varian 7000 FT-IR Fourier spectrometer (Varian Company, USA). The spectra were recorded using an attenuated total reflection (ATR) adapter in the range of 550–4000 cm^{-1}.

RESULTS AND DISCUSSION

Table 1 shows the results of a study of the mechanical characteristics and the degree of crystallinity of PTFE and PCM, depending on fillers content and composition.

Table 1. Mechanical properties and degree of crystallinity of PTFE and PCM

Sample	Tensile strength, MPa	Elongation at break, %	Compressive strength at 10%, MPa	Crystallinity, %	ρ, g/cm^3
Initial PTFE	20	320	15	55	2.16
PTFE+1 wt.% CF+1 wt.% Zt	19	374	16	56	2.17
PTFE+3 wt.% CF+1 wt.% Zt	18	367	17	63	2.16
PTFE+5 wt.% CF+1 wt.% Zt	18	305	19	59	2.16
PTFE+8 wt.% CF+1 wt.% Zt	14	260	22	62	2.11
PTFE+10 wt.% CF+1 wt.% Zt	13	220	23	61	2.08
PTFE+1 wt.% CF+1 wt.% Zt+1 wt.% Forum	20	311	16	56	2.18
PTFE+3 wt.% CF+1 wt.% Zt+1 wt.% Forum	18	301	17	64	2.17
PTFE+5 wt.% CF+1 wt.% Zt+1 wt.% Forum	18	296	19	64	2.16
PTFE+8 wt.% CF+1 wt.% Zt+1 wt.% Forum	16	255	21	68	2.12
PTFE+10 wt.% CF+1 wt.% Zt+1 wt.% Forum	14	225	22	68	2.08

As can be seen from Table 1, when the content of fillers in PCM is about 1-5 wt.% CF with additional content of Zt and Forum (1 wt.%), the tensile strength and elongation at break remain at the level of the initial polymer. The preservation of PCM deformation-strength properties is since the carbon fibers were modified by plasma-chemical treatment, due to which the fibers have the higher adhesive ability (Grakovich, et al., 2019). The deformation-strength properties of PCM with a high content of fillers (8-10 wt.% CF) slightly decrease, which is possibly associated with the formation of defect regions in the material's structure. The compressive strength of PTFE/CF/Zt and PTFE/CF/Zt/Forum with an increase in CF content from 1 to 10 wt.% increases by 53% and 47% relative to the initial polymer, respectively. A significant increase in PCM's compressive strength indicates the reinforcement of the polymer matrix, which is associated with the content of short fibers, which are reinforcing fillers (Ronghao, et al., 2017).

Figure 1 shows the results of X-ray diffraction patterns of initial PTFE and PCM.

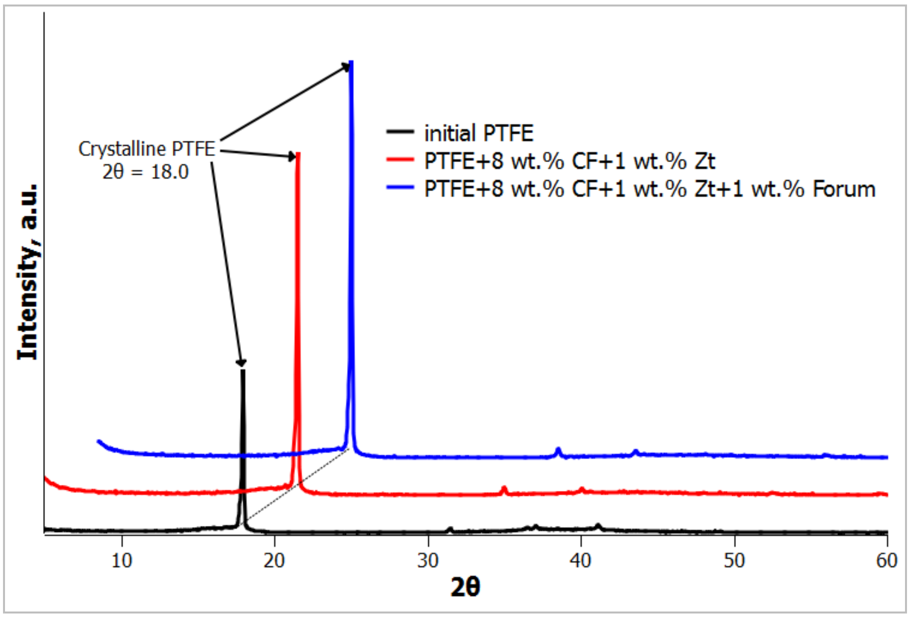

Figure 1. X-ray diffraction patterns of initial PTFE and PCM

As can be seen from Figure 1, the composites exhibit an intense diffraction peak at 2θ = 18 °, which corresponds to the polymer's crystalline phase; no other peaks were found in the composites (Yuan, et al., 2016). Moreover, the intensities of the diffraction peak of crystalline PTFE at 2θ = 18 ° increased with increasing filler content, which indicates an increase in the degree of crystallinity of PTFE (Table 1).

Table 2 shows that the degree of crystallinity of PCM increases with the introduction of fillers. The degree of crystallinity of the composites PTFE/CF/Zt is higher than the initial PTFE by 1-8% and PTFE/CF/Zt/Forum is by 1-13%, respectively. This indicates that the additional introduction of the filler - Forum contributes to an increase in the degree of crystallinity of the polymer. The density of PCM monotonously decreases with an increase in the content of fillers. The decrease in density is due to the lower density of carbon fibers (1.45 g/cm^3) compared to PTFE (2.16 g/cm^3), as well as the loosening of the supramolecular structure (Vasilev, et al., 2019).

Figure 2 shows the results of a study of the tribological properties of PTFE and PCM, depending on the content and composition of fillers.

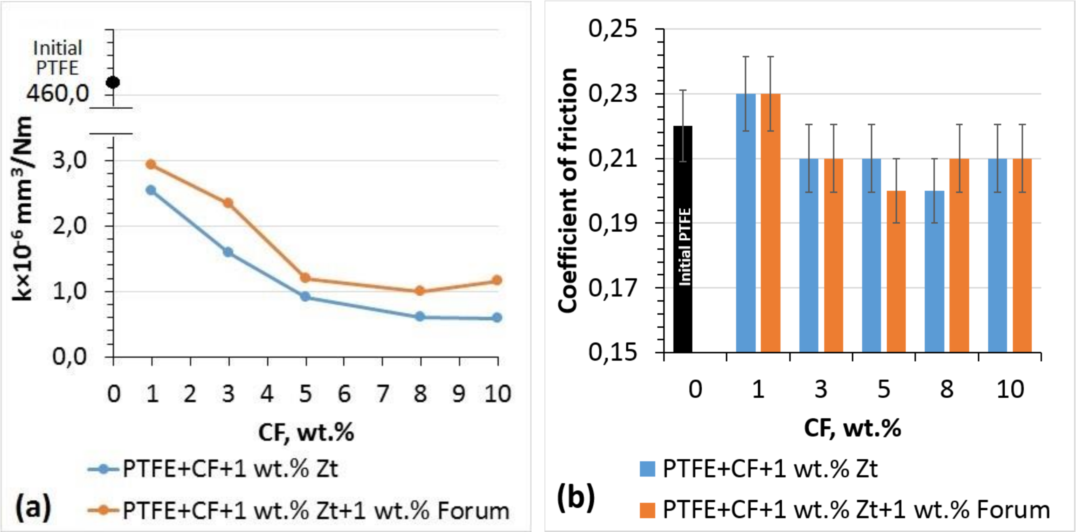

Figure 2. Tribological properties of PTFE and composites: a) specific wear rate *k*; b) coefficient of friction

As is seen from Figure 2 (a), the introduction of combined fillers into PTFE significantly increased the wear resistance compared to the initial polymer. The wear rate of the initial PTFE is ~462 10^{-6} mm^3/N•m, and the coefficient of friction is ~0.22. It can be seen that the PCM wear rate depends on the CF content: PTFE/CF/Zt is in the range of 2.53-0.61×10^{-6} mm^3/N•m, and PTFE/CF/Zt/Forum is in the range of 2.93-0.99×10^{-6} mm^3/N•m. Composites containing CF/Zt show lower *k* values than PCM containing CF/Zt/Forum. Adding 1 wt.% Forum to PTFE /CF/Zt increases the wear rate by about 14-40%.

As seen from Figure 2 (b), the coefficient of friction of the composites PTFE/CF/Zt and PTFE/CF/Zt/Forum showed the same values regardless of the CF and Forum content. The coefficient of friction of the composites is comparable with the results of the initial PTFE and is in a relatively narrow range, i.e. 0.19-0.23.

Investigations by the IR spectroscopy method after friction of PTFE and PCM have been carried out (Figure 3). The IR spectra of the initial PTFE and composites before and after friction revealed characteristic intense absorption bands related to the main chain's links (-CF_2-).

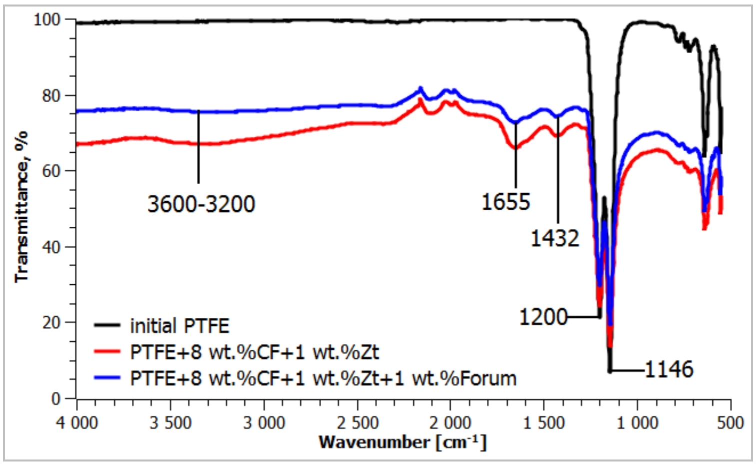

Figure 3. IR spectra of the initial PTFE and composites

As can be seen from Figure 3, in the IR spectra of the composites after friction, new peaks appear in the range of 3600-3200 cm^{-1}, ~1655 cm^{-1}, and ~1432 cm^{-1}, which were not found in the initial PTFE. Peaks in the region of 3600-3200 cm^{-1} are attributed to hydroxyl groups, and peaks in the region of ~1655 cm^{-1} and ~1432 cm^{-1} are attributed to functional groups of carboxyl groups (Pitenis, et al., 2015). Thus, these peaks are related to oxygen-containing compounds, which indicate the occurrence of tribochemical reactions. It is known that the formation of these peaks in PTFE indicates the formation of a strong transfer film, which is one of the reasons for improving the wear resistance of PCM (Harris, et al., 2015).

Figure 4 shows the results of studying the friction surface of PCMs depending on the filler's composition.

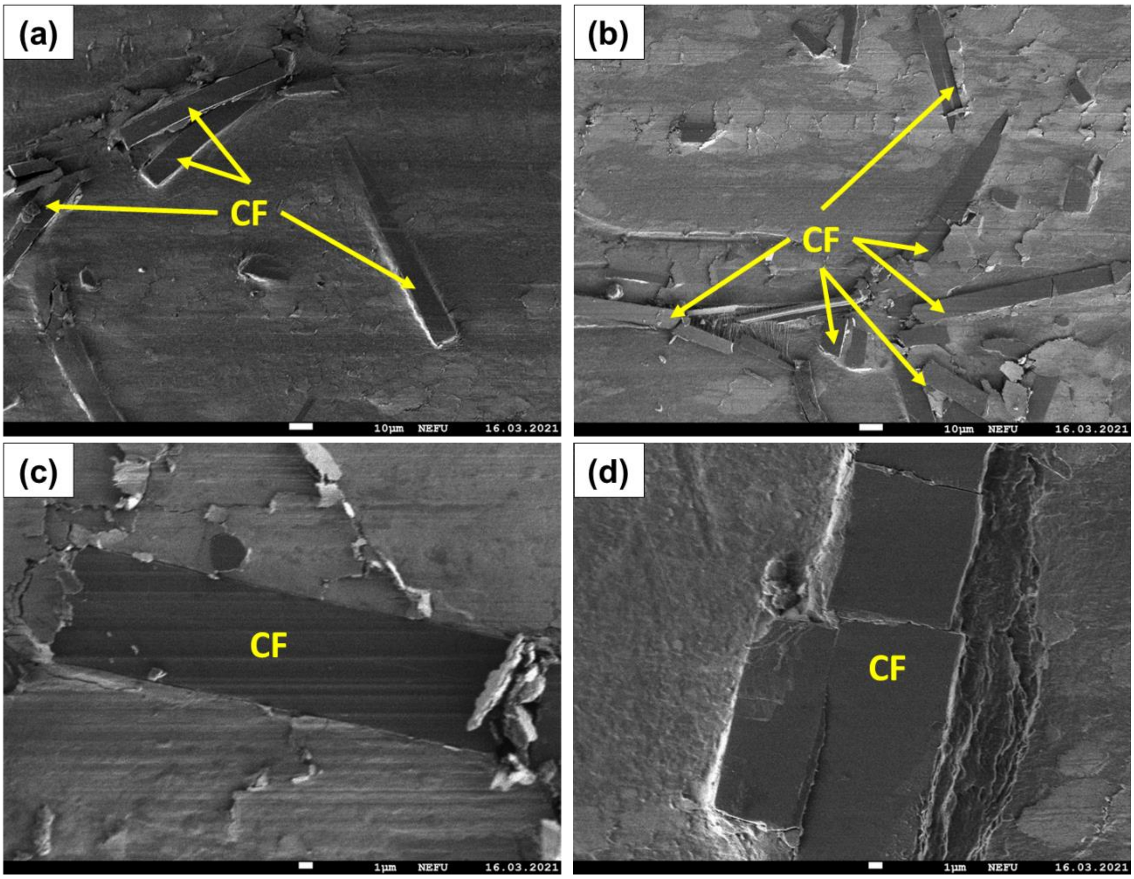

Figure 4. SEM images of the PCM: a) PTFE/CF/Zt (×500); b) PTFE/CF/Zt/Forum (×500); c) PTFE/CF/Zt (×3000) and d) PTFE/CF/Zt/Forum (×3000)

As seen from Figure 4, on the worn surface of the PCM, fibers are irregularly oriented. It is known that the fibers become microprotrusions on the friction surface, which protect the surface layer of PCM from destruction (Ohlopkova, et al., 2016). Figure 4 (c) and (d) show that the fibers are also subject to wear, and secondary structures are revealed between the fibers. A similar structure on the worn surface was previously identified in composites containing CF/kaolin and CF/vermiculite (Vasilev, et al., 2019). The formation of such structures is associated precisely with the content of layered silicates and is not observed on the PTFE/CF friction surface (Vasilev, et al., 2018). The results of tribological studies have shown that the wear resistance of PTFE with the introduction of carbon fibers with layered silicates (vermiculite, kaolin, and zeolite) is generally at the same level. However, composites containing CF/Zt and CF/Zt/Forum have a lower friction coefficient compared to composites containing CF/kaolin, CF/kaolin/UPTFE, and CF/vermiculite. Thus, in this work, it is shown that the introduction of zeolite with CF into PTFE leads to an increase in the wear resistance of PCM while maintaining a low coefficient of friction.

CONCLUSIONS

In this work, the effect of mixing of carbon fibers with zeolite and Forum on the structure, mechanical and tribological properties of PTFE is considered. It is shown that the introduction of CF/Zt and CF/Zt/Forum in PTFE increases the compressive strength, and deformation-strength characteristics depend on the CF content. The degree of crystallinity of PCM increases with the introduction of fillers, and the density decreases. Developed PCM is characterized by high wear resistance ($k = 0.61\text{-}0.99 \times 10^{-6}$ $mm^3/N\bullet m$) while maintaining the friction coefficient at the level of the initial PTFE. The results of structural studies have shown that discrete surface from fibers and secondary structures is formed on the worn surface, protecting the friction surface from destruction. Due to PCM's improved properties based on PTFE, it can be used as parts and assemblies of machines operated in extreme conditions.

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