Influence of the Methods of the Component Activation of Polymer Composites Based on Polytetrafluoroethylene and Carbon Fiber on the Operational Properties

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Abstract. The article presents the dependence of the physical-mechanical and tribological characteristics on the manufacturing technology of polymer composite materials based on PTFE of PN grade and carbon fibers of UVIS-AK-P brand produced by OOO UVIKOM. Modification of polytetrafluoroethylene with a carbon filler provides low friction coefficient, and the wear resistance of composites increases by 77–2024 times in comparison with an unfilled polymer. The technological method of introducing filler through a concentrate applied in the present work has resulted in an improvement of the operational characteristics of composite materials compared to the initial polymer. Various technological approaches based on the methods of joint mechanical-chemical activation of components and milling of a polymer mixture, which contribute to an increase in operational characteristics, have been considered. The dependence of the operational properties of composite materials on the amount of filler in the polymer mass has been analyzed.

1. Introduction

At present, one of the main reasons for product failure in cold climates is low frost and wear resistance of materials used in mechanical engineering. Polymer composite materials (PCM) based on polytetrafluoroethylene (PTFE) are promising materials for friction units due to the wide operating temperature range and low friction coefficient. PTFE-based composites are widely used in the oil and gas industry as sealing materials. Application of such materials in the Arctic requires a specific brand of PTFE, which can be used at low temperatures [1-3].

Table 1 presents the characteristics of well-known brands of PTFE.
Table 1. Characteristics of PTFE brands.

| PTFE brand                  | Tensile strength | Elongation at break | Operating range             |
|-----------------------------|------------------|---------------------|----------------------------|
| Fluoroplast-4 of PN grade   | minimum 25.0 MPa | minimum 350 %       | From minus 269 °C to plus 260 °C |
| Fluoroplast-2M of B grade   | minimum 52.9 MPa | minimum 410 %       | From minus 60 to plus145 °C  |
| Fluoroplast-2M of 1 grade   | minimum 40.0 MPa | minimum 350 %       | From minus 60 to plus135 °C  |
| Fluoroplast-3 of B grade    | minimum 30 MPa   | minimum 75 %        | From minus 195 to plus125 °C |
| Fluoroplast-32 of B grade   | minimum 26 MPa   | minimum 220 %       | From minus 60 to plus 200 °C |

Table 1 shows that PTFE of PN grade is the most promising for operation at low temperatures.

The main disadvantages of PTFE include a high coefficient of linear thermal expansion, low wear resistance and the ability to deform under normal conditions even under light loads. Thus, it is promising to use carbon fillers-modifiers of various dispersion and particle shape [4-6].

There are two main problems in the development of any polymer composites, especially the ones based on PTFE, which are characterized by inertness and high melt viscosity. The final properties of the materials to be produced depend on their solution:

- ensuring uniform distribution of the filler throughout the matrix volume;
- ensuring high adhesion of fillers with a polymer matrix.

PCM properties directly depend on the distribution of the filler in the polymer matrix. Uneven distribution of the filler in the polymer matrix causes the formation of agglomerates, which are stress concentrators in the composite volume and lead to premature destruction of the material. Thus, filled composites are inferior in terms of deformation and strength properties to the matrix polymer.

The present paper is aimed to study the dependence of the physical-mechanical and tribological properties of polymer composite materials based on PTFE and carbon fibers of the UVIS-AK-P brand on the method of mixing components and the filler content in the concentrate.

2. Objects and methods of research

Commercially manufactured polytetrafluoroethylene (PTFE) of PN grade, which is characterized by the increased frost and heat resistance, was selected as a polymer matrix. However, PTFE without filling is rarely used due to its low strength, wear resistance and high creep under load. To eliminate these shortcomings and to improve the properties of PTFE, various fillers are used, and carbon fibers occupy a special place among them.

Carbon-based fibrous activated material of UVIS-AK-P brand with a diameter of 5-8 microns and a length of 50-300 microns was used as a filler for PTFE on the basis of hydrated cellulose carbon fiber produced by OOO Scientific and Production Center UVICOM (Russia).

To improve the dispersion quality of the filler agglomerates and the filler mixing in the polymer, as well as to increase the adhesive interaction of the inert hydrophobic PTFE with the hydrophilic surface of the carbon filler, two methods of mixing the polymer with filler were used in the course of the work:

- Standard mixing of the required amount of CF with half of the polymer mass (50%) in a blade-paddle mixer. Then, the method of joint mechanical activation of the PTFE+CF powder composition was applied at a rotation speed of the planetary mill drums equal to 400 rpm. The rest of the polymer mass (50%) was introduced afterwards and mixed in a paddle mixer.
- standard mixing of the required amount of CF with part of the polymer mass (50%) in a paddle mixer. The rest of the polymer mass (50%) was introduced afterwards and the resulting powder composition was put through a laboratory mill.
Figure 1 demonstrates the manufacturing technologies of PCM based on PTFE and carbon fibers of UVIS-AK-P brand.

![Diagram of manufacturing processes](image)

**Figure 1.** Technologies for manufacturing PCM samples: a – Composites obtained by joint mechanical activation in a planetary mill; b – Composites obtained by additional pressing in laboratory mill.

The mechanical properties of PCM (tensile strength; elastic modulus, elongation at break; compressive strength) were determined according to GOST 11262, GOST 9550 and GOST 4651 on a UTS-20K testing machine (UTS-Test systeme GmbH, Germany) at a temperature of 23 ± 2°C. Tribological characteristics, such as the mass wear rate and the friction coefficient, were investigated by the standard method (GOST 11629–75) on the multifunctional friction testing machine CETRUMT-3. The friction scheme is “finger – disk”, the sample is a cylinder with a radius of 5 mm, the counter body is made of 45# steel with a hardness of 45–50 HRS and a roughness of R = 0.06–0.08 µm at a specific pressure of 160 N and a sliding speed of 96 rpm. The test time was 3 hours. Creep was determined according to GOST 18197-2014 “Plastics. Determination of tensile creep”.

3. Discussion of results

Previous studies [7,8] have revealed the promising use of UVIS-AK-P carbon fibers as a filler for PTFE. These studies consider formulations of PTFE + 1, 3 and 5 wt.% UVIS-AK-P, where a composite with CFof5 wt.% content obtained using the joint mechanical activation technology demonstrates the best results. The wear resistance of the composite is increased by 2024 times, compressive strength by 34%,
modulus of elasticity by 9%, and elongation by 16% compared to the virgin polymer. The present paper considers PTFE + 7 and 10 wt.% UVIS-AK-P formulations to continue the study of the influence of manufacturing technologies of PCM on operational its properties.

The results of the study of the stress-strain properties of PTFE and composites based on it are given in Table 2.

Table 2. Dependence of physical-mechanical properties on UVIS-AK-P concentration and production technology of PCM.

| Content           | Production technology of PCM | σₜ, MPa | εᵦᵣ, % | E, MPa | Compression strength |
|-------------------|-----------------------------|---------|---------|--------|----------------------|
| PTFE              | -                           | 20      | 304     | 469    | 14 25                |
| PTFE +5wt.% UVIS-AK-P | Standard                  | 13      | 117     | 507    | 16 26                |
| PTFE+5wt.% UVIS-AK-P | Mechanical activation 400 rpm | 20      | 354     | 514    | 20 31                |
| PTFE+5wt.% UVIS-AK-P | Compression treatment in laboratory mill | 17      | 192     | 489    | 21 35                |
| PTFE+7wt.% UVIS-AK-P | Mechanical activation 400 rpm | 12      | 113     | 378    | 14 25                |
| PTFE+7wt.% UVIS-AK-P | Compression treatment in laboratory mill | 13      | 113     | 582    | 17 29                |
| PTFE+10wt.% UVIS-AK-P | Mechanical activation 400 rpm | 8       | 34      | 273    | 12 22                |
| PTFE+10wt.% UVIS-AK-P | Compression treatment in laboratory mill | 12      | 55      | 531    | 14 26                |

Note: σₜ - tensile strength; εᵦᵣ is the relative elongation at break; E is the modulus of elasticity at break

According to the table, the stress-strain characteristics decrease with an increase of CF content in the polymer. This can be explained by the formation of a loose porous structure of PCM. The main disadvantage of fluoroplastic composites is still the loose porous structure of the material, especially when the filler content is exceeded (starting at 5 wt.% and above) since carbon fibers have a porous structure. Technological method of mechanical activation in the form of milling PCM powder mixture is used to reduce the porosity of the composites. The work [9] shows that a similar method leads to an increase in the strength characteristics of highly filled composites based on PTFE and a decrease in porosity. As it can be seen from the table, this technological method leads to an increase in the modulus of elasticity and compressive strength of PCM compared with composites obtained using the technology of joint mechanical activation of components.

Table 3. Dependence of the porosity of composites on PCM production technology.

| Composition         | Production technology of PCM | Density, g/cm³ | Porosity, % |
|---------------------|-----------------------------|----------------|-------------|
| PTFE                | -                           | 2,17           | 8,1         |
| PTFE +5wt.% UVIS-AK-P | Standard                  | 2,02           | 14,4        |
| PTFE +5wt.% UVIS-AK-P | Mechanical activation 400 rpm | 2,03           | 13,8        |
| PTFE +5wt.% UVIS-AK-P | Milling treatment          | 2,06           | 12,5        |
| PTFE +7wt.% UVIS-AK-P | Mechanical activation 400 rpm | 1,92           | 18,4        |
| PTFE +7wt.% UVIS-AK-P | Milling treatment          | 1,98           | 15,9        |
| PTFE +10wt.% UVIS-AK-P | Mechanical activation 400 rpm | 1,93           | 18,2        |
| PTFE +10wt.% UVIS-AK-P | Milling treatment          | 1,99           | 15,4        |
Based on the density values of the developed composites, their porosity was evaluated depending on the production technology and CF concentration.

According to the table, milling PCM powder mixture leads to a decrease in porosity. The porosity of the composite containing 5 wt.% CF has decreased by 9% after milling. The porosity of the composites containing 7 and 10 wt.% CF has decreased by 15% and 18% compared with composites obtained using joint mechanical activation of the components.

It is known that one of the most important characteristics of fillers that determines the structure and properties of PCM is the ability of powdered and fibrous particles to pack in a given volume. It is numerically expressed by the coefficient of maximum filling of the volume with filler or the critical content of filler in PCM (γmax). For most fillers, γmax is defined as the ratio of packed density to the true density of the filler. It has been established that γmax for the UVIS-AK-P brand is 0.09 vol.% and that corresponds to 7 wt.% UVIS-AK-P when it is introduced into the volume of PTFE. It is known that when the filler concentration approaches its maximum critical volumetric content φm, the so-called “reversibility” of the reinforcing action of fillers is observed in the composite. That is, large internal over voltages arise in the matrix of a highly filled composite during deformation, which causes a decrease in the composite strength when the UVIS-AK-P concentration exceeds 5 wt.% [9,10].

The results of the study of the tribological characteristics of PTFE and composites based on it are shown in Fig. 2.

![Figure 2. Tribological parameters of the composites depending on the filler content and PCM production technology: a) mass wear rate; b) friction coefficient.](image)

According to Fig. 2, when using the method of joint mechanical activation, an increase in UVIS-AK-P content in the PTFE matrix leads to a 54-times decrease in wear resistance compared to a composite with a content of 5 wt.% CF, while a decrease in PCM friction coefficient is observed. This may be explained by the formation of a protective shield of carbon fibers on the friction surface and their orientation along the sliding direction. When using milling technology, wear resistance is increased by 4 times compared with composites obtained using joint mechanical activation of components in a planetary mill. This may be due to a decrease in the porosity of these composites, which gives a positive effect on increasing strength and wear resistance.

4. Conclusion
As a result of the studies, the efficiency of using carbon-based fibrous activated material of UVIS-AK-P brand based on hydrated cellulose carbon fiber manufactured by OOO Scientific and Production Center UVICOM (Russia) as a PTFE filler for producing wear-resistant composites is shown.

Technological methods of introducing UVIS-AK-P into a polymer matrix have been developed to improve the physical-mechanical and tribological properties of PCM. It has been established that the
introduction of UVIS-AK-P to 7 and 10 wt.% leads to a decrease in the stress-strain and tribological characteristics when using the technology of joint mechanical activation in a planetary mill. The application of the technology of milling powder composition leads to an increase in the stress-strain properties of PCM. The wear resistance of the composites is increased 4 times in comparison with composites with 7-10 wt.% of CF content obtained using the joint activation of components in a planetary mill.

Thus, various technological approaches have been developed based on the methods of joint mechanical-chemical activation of components and mill rolling of the polymer mixture contributing to improved operation characteristics.

5. References

[1] Kobzev D E, Baronin G S, Dmitriev V M 2012 Intensification of solid-phase plunger extrusion of nanomodified high density polyethylene by ultrasonic treatment Materials Science 4 pp 37–40
[2] Shanfu Lu, Ruijie Xiu, Xin Xu [et al.] 2014 Polytetrafluoroethylene (PTFE) reinforced poly(ethersulphone)–poly(vinyl pyrrolidone) composite membrane for high temperature proton exchange membrane fuel cells Journal of Membrane Science Vol 464 pp 1–7 DOI: 10.1016/j.memsci,2014,03.053
[3] Ghalmi Z, Farzaneh M 2014 Durability of nanostructured coatings based on PTFE nanoparticles deposited on porous aluminum alloy Applied Surface Science Vol 314 pp 564–569 DOI: 10.1016/j.apsusc,2014,05.194
[4] Boldyrev V V, Ohlopkova A A, Popov S N, Petrovaidr P N Fundamentals of mechanical activation, mechanochemistry and mechanochemical technologies (Novosibirsk: Publ. house of SB RAS) 343 p
[5] Mashkov J K, Ovchar Z N, Bajbarackaja M J, Mamaev O A 2004 Polymeric composite materials in tribotechnology (M.: OOO Nedra-Biznescentr) 262 p
[6] Soklova M D, Davydova M L, Shadrinov N V 2011 Processing to increase the structural activity of xerolite in polymer-elastomer composites Int. PolymerSci. And Technol vol 38 5 pp 25-29
[7] Petrova P N, Markova M A, Gotovceva M E 2017 Development of tribotechnical materials based on polytetrafluoroethylene and carbon fibers of UVIS-AK-P brand Scientific and Technical Journal ISSN 1994-6716 Material Science Issues 4(92) pp 90-100
[8] Markova M A, Gotovceva M E 2017 Investigation of composites based on PTFE and carbon fillers Scientific peer-reviewed electronic journal ISSN 2413–9858 The journal of Science and Education of North-West Russia vol 3 16 p
[9] Prushak D A, Mihajlova L V, Voropaev V V 2011 Technology of tribological and sealing composite materials based on polytetrafluoroethylene Mining mechanics and mechanical engineering 3 pp 19-31
[10] Rambidi N G, Berezkin A V 2009 Physical and chemical foundations of nanotechnology (M.: FIZMATLIT) 456 p

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