THE RESULTS OF THEORETICAL AND EXPERIMENTAL STUDIES OF TRIBOTECHNICAL PURPOSES COMPOSITES ON THE BASIS OF EPOXY COMPOSITE MATERIAL

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The results of theoretical and experimental studies of tribotechnical purposes composites on the basis of polytetrafluoroethylene (PTFE) and epoxy composite material with fillers of different chemical nature are given. The results have been obtained that prove that the introduction of carbon fiber of optimum length ensures the formation of a composite structure in which the fibers are evenly distributed and have sufficient surface energy to increase adhesion strength. It has been established that depending on the parameters of mechanical activation (the number of revolutions of the working organs of the mill, activation time), an ordered spherulite supramolecular structure of PTFE with an increased heat resistance on (293-353) K is formed. No marked fracture of the molecular chain of the polymer has been observed, but the concentration of free CF2 groups to (4-8) times. For the first time, the conditions for obtaining self-organized structures on the tribological surfaces were determined by the stepwise growth of the frictional load (gradual increase in the slip rate for a constant specific load or a gradual increase in the specific load at a steady slip rate).

KEYWORDS

Polymer composites; adhesion; molding; thermal vacuum technology; mechanical properties

1 INTRODUCTION

One of the trends in the development of modern machines, equipment is the increasing use of composite materials for their production. This allows the material to be reduced in design without losing the required strength and rigidity characteristics. The purpose of creating a composite material is to combine similar or different components to obtain a material with new specified properties and characteristics that are different from the properties and characteristics of the original components. At present, polymer- composite materials (PCM) are the most promising materials for the automotive and other industry. Most of the properties of the resulting PCM are higher than the properties of the original components [Jurko 2016, Panda 2011 and 2016]. With the advent of such materials, it became possible to selectively select the properties of composites necessary for the needs of each specific field of application. They provide not only the replacement of metals and alloys, but also increase the reliability and durability of parts of friction units. Products from modern PSM can work in chemically active media, a wide range of loads and sliding speeds.

The development of composite materials production based on thermoplastic or reaction able polymers should be grounded on scientific principles of polymers technology, applied materials science and physical and chemical mechanics of composite structures [Asadi 2016, Panda 2017, Bijwe 2012, Todic 2011, Buznik 2012]. Selecting the type of polymer matrix is conditioned by tribo-units operating conditions, loading and high-speed modes that further determine the technological principles of formation of polymer composites structure. Differences in technology for obtaining polymer composites are mainly conditioned by the structure of macromolecular chains of the polymer matrix and by the formation of links between the segments of macromolecules. Substantiated mode parameters of matrix and fillers preparation process and formation of filled composition affect the level of physical, mechanical and tribotechnical characteristics of polymer composites. One of the materials that has frost resistance, chemical inertness, high thermal resistance, low adhesive resistance and low friction coefficient is polytetrafluoroethylene (PTFE) [Budnik 2015]. Along with the advantages, PTFE has several disadvantages: low wear resistance, high linear thermal expansion coefficient and high deformability [Budnik 2015]. These disadvantages are eliminated by the introduction of various modifiers into the matrix of PTFE [Budnik 2013]. Replacement of traditional tribomaterials in friction units of industrial equipment [Eremin 2014] mainly consists in developing carbon fiber reinforced polymer (CFRP) on the basis of polytetrafluoroethylene containing modified fillers or epoxy composite materials containing powder products based on copper. For a long time, the growth of PCM development technologies was based primarily on empirical researches that were connected with the complexity of interphase interactions in multicomponent polymer systems and with their determining influence on the properties of polymer composites. The combination of theoretical studies of structural and phase transformations with experimental researches allows formulating the scientifically grounded approach to the forecasting and targeted adjustment of polymer composite properties.

Identifying the influence regularities of fillers, chemical and technological factors on the formation processes of composites with deepening the scientific ideas about the formation structure, studying their physical, mechanical and tribotechnical characteristics, allows control of the properties of polymer composites, that is one of the important problems of contemporary polymer materials science [Liu 2018]. The implementation of matrix and fillers modification methods and application of composites formation technology [Khoshnevis 2018] on the basis of polymers under the influence of external physical fields solves the important scientific and technical problem of polymer composites development and it defines the relevance of this research direction.

The aim of this work is to generalize the results of studies of the impact of technological factors on physical, mechanical and operating properties of polymer composite materials and to optimize technological process parameters. The results of the scientifically grounded solution of these tasks allow creating controlled technology for obtaining polymer composite materials and they provide consumers with the forecasted properties of composite materials on the best world analogues level.

2 EXPERIMENTAL PART

2.1. Materials and Methods

Polytetrafluoroethylene is a high-molecular composition, molecules of which consist of a large number of identical atomic groups $(-CF_2-)$ with: $(-CF_2-CF_2-)_n$ chemical bonds. Tetrafluoroethylene is a primary monomer for PTFE.

The resulting polymer is a loose, fibrous and cloggy white powder [6]. On the basis of experiments, it was found out that PTFE used for these studies is the most relevant for the requested requirements (Table1).

Table 1. Characteristics of polytetrafluoroethylene (PTFE)

Appearance	White powder, which easily lumps without visible impurities
Mass fraction of moisture, %, not more than	0.02
Density, kg/m^3, not more than	2180–2210
Breaking strength non-hardened sample, MPa, no less than	15–26
Relative elongation at break of non-hardened sample, %, no less than	150–350
Dielectric strength, kV/mm, not less than	50–60
Average particle size, μm	100–80 (it is not normalized)

Hydrated cellulose carbon fiber (CF) obtained by chemical processing in an aqueous solution of fire-retardants $Na_2B4O_7\cdot 10H_2O+(NH_4)_2HPO_4$ and annealing at temperatures 723 ± 20 K in natural gas CH_4 environment was used as the main fiberfill.

Epoxy resin is high-viscosity transparent liquid, which is structured at normal and elevated temperatures without external pressure [Buketov 2016]. Hardener polyethylenepolyamine – PEPA was applied for structuring epoxy compositions. The basic physical and chemical properties of the resin and forester are presented in Table 2.

This hardener is intended for solidification of epoxy resins at room and reduced temperature in a high humidity. Epoxy polymers are used widely for manufacturing components of the frictional unit.

These materials are endowed with many important properties, such as high adhesion to metals and other materials, mechanical strength, insignificant shrinkage and water permeability, vibration- and soda-resistance, high electric insulating properties. The introduction of special additives to epoxies increases the hardness, loading capacity and wear resistance.

Table 2. Physico-chemical properties of the resin of the brand ED-20 and PEPA cement

Name of the indicator	Value of the indicator	
	Epoxy resin of the brand ED-20	PEPA
Density, g/cm^3	1.16-1.20	0.95-1.05
Molecular weight	390-430	230-250
Content of epoxy groups,%	20.0-22.0	–
Content of volatile substances, %	0.8	–
Relative viscosity at a temperature of 25°C	65	–
Dynamic viscosity at 25 °C, Pa·s	12-25	–
Total chlorine content, %	0.8	–
The content of chlorine ion	0.005	–
Mass fraction of total nitrogen, %	–	30
The content of hydroxyl groups,	1.7	–
Water content	–	–

Composite materials based of epoxy resins used for the manufacture of details for the frictional units, which are working in corrosive medium and in vacuum for the temperatures -100…+200 °C, in water, gas and in other environments. Nowadays polymer self-lubricating materials – tribopolymers are designed and used [Berladir 2016].

In the work complex of ingredients was used as filler, which was aimed at enhancing the durability of tribo-units.

The graphite is natural mineral based on carbon. It is effective hard grease in the polymer system because graphite has a high thermal and electrical conductivity. Hardness on a Moths scale of graphite is 1, density – 2090-2230 kg/m^3. Introduction of graphite in epoxy composite materials increases the stability of dimensions, antifriction characteristics, thermal and electrical conductivity [Dyadyura 2016, Lv 2011]. The graphite improves tribotechnical characteristics of composite materials without a substantial decrease of cohesive strength. Large lamellar graphite (0.1-1.0 mm) was applied in the work.

In the work, powder of pure copper (Cu) was used, which was fire-safe, blast-resistant and nontoxic, did not contain unconnected inclusions and lumps. The apparent density of the powder was 1250-1900 kg/m^3. Hardness on a Moths scale was 2.5-3. The powder of copper is chemically little active. The dimensions of copper particles copper are 30-100 μm.

The powder of oxide copper (CuO) was used in the work. The density of CuO is 6310 kg/m^{3,} the temperature of melting – 1447 °C. Crystals of powder oxide copper are quite stable in normal conditions, almost soluble in water, alcohol, but soluble in acids. The medium diameter of particles powder oxide copper is 60-80 μm.

2.2. Methods of research of properties and structure of composites

To ensure high structural strength and to determine the influence of temperatures, mechanical, thermophysical and chemical methods of research and methods for determining the degree of structuring composite systems were used.

Tensile strength and relative elongation at break were carried out on ring samples ∅50x∅40 and 10 mm high using rigid semi-disks according to ASTM D3479 / D3479M. The tests were carried out at the universal testing machine (Hegewald & Peschke) at speed moving grips of 10 mm / min and load of 1 kN. Tensile strength (σ) in MPa is calculated by the formula (1):

$$\sigma = \frac{F}{2 \cdot h \cdot h_1} = \frac{F}{2 \cdot A} \tag{1}$$

where F is the tensile force; h is radial thickness of the ring's wall; h_1 is axial height of a circular sample and A is the nominal cross-section of the specimen. Relative lengthening (δ) in % is calculated by the formula (2):

$$\delta = \frac{\Delta l}{l_0} \cdot 100\% \tag{2}$$

where Δl is change of the estimated length of the sample at the time of the break; l_0 is initial calculated design length.

The error of measurement of the load is not more than 1% of the measured value, determination of geometric sizes - no more than 0.05 mm. For the result of the test, the average of the arithmetic mean of the three values, the difference between which should not exceed the permissible difference, is equal to 15% in determining the strength and 30% in determining the relative elongation at break, from the calculated mean arithmetic value.

2.3. Definition of tribotechnical characteristics

The study of the intensity of wear was carried out on a Universal friction machine 2070 SMT-1 under the scheme of partial insertion – shaft in accordance with ASTM D1894.

The opposite element was a roller ø48 mm made of steel 1045 (ANSI/SAE) (HRC 45, *Ra* 0.72 microns). Partial insert was made from the investigated material. The partial insertion sector was 16 mm in width from ø80 to ø60 mm and 9 mm high. Intensity of wear (I) mm^3/ (N·mm) is calculated by the equation (3):

$$I = \frac{V}{F_n \cdot L} \tag{3}$$

where V is the volume of worn material; F_n is normal load; L is the friction path.

In estimating the intensity of wear, the mean square error did not exceed 5%. The temperature in the contact zone «PCM − opposite element» was determined by the infrared thermometer (pyrometer) by the professional CEM DT-8867H.

The roughness of the surfaces of the studied composites was measured according to ISO 4287 and ISO 16610-21 using the Nanovea ST400 Profilometer.

2.4. Investigation of physical and chemical properties of PCM

Investigation of the physico-chemical structure of composites was carried out by methods of electron microscopy, Differential thermal analysis (or DTA), thermogravimetric analysis or thermal gravimetric analysis (TGA), X-ray diffraction analysis (XRD analysis or XRPD analysis) and infrared spectroscopy (IR spectroscopy).

2.4.1. Electron microscopic research.

The study of the supramolecular structure of the activated PTFE powder, fillers, PTFE composites, and the structure of the composites before and after friction was carried out using a high-resolution scanning electron microscope TESCAN MIRA 3 LMU.

2.4.2. Differential-Thermal (DTA) and Thermogravimetric (TGA) analysis.

Thermographic examinations of PTFE specimens [Brostow 2016] were carried out on the derivative "Thermoscan-2". The research was carried out in the temperature range ΔT = (298-873) K, using quartz crucibles for specimens of volume V = 500 mm^3. During the study, the rate of rise of the temperature was υ = (5-10) deg/min, while Al_2O_3 (m = 0.5 g) was used as the reference substance, the weight of the test sample was m = 0.3 g. The temperature error was ΔT = ± 1 K. The accuracy of the determination of thermal effects is 3 J/g. The installation is designed to determine the temperature and estimate the heat of phase transitions and other processes associated with the release or absorption of heat, as well as to determine the temperature and the amount of weight loss of the sample during heating. The change in the heat content of a substance with a change in temperature is recorded on the basis of measuring the temperature difference in the sample under study and in a standard in which no transformations occur in the temperature range studied. The change in the weight of the sample with a change in temperature is determined using an electronic system of continuous weighing. The accuracy of determining the change in sample mass is Δm = 0.02 g.

2.4.3. X-ray structural analysis.

The research of the structure of the materials is performed on the automated diffractometer DRON-4-07 [Jose 2012]. In the study of the structural parameters of the matrix PTFE, the radiation Cu Kα (wavelength 0.154 nm), Bragg-Brentano focusing ϑ-2ϑ (2ϑ - Bragg angle) was used. The values of current and voltage on the X-ray tube were 20 mA and 40 kV. Sampling was carried out in step-by-step mode (exposure - 3 s), the range of angles 2ϑ from 16 ° to 20 °.

The study of composite structures was carried out in Co Kα radiation (wavelength 0.179 nm), Bragg-Brentano focusing ϑ-2ϑ (2ϑ - Bragg angle). The values of current and voltage on the X-ray tube were 20 mA and 40 kV. Sampling was carried out in continuous recording mode (speed 1 º / min), range of angles 2ϑ from 10 ° to 55 °.

Experimental results were transmitted directly to the DifWin-1 trial software package for pre-processing. The preliminary treatment was to smooth out the spectrum, remove the background, remove the halo from the amorphous component and select the peaks from the crystalline.

The calculation of the average size of the coherent scattering regions (OCR, crystallites) was performed after subtraction from the peak of the Kα2-component using the Sherrer formula [Kumar 2010, Conte 2013] (4):

$$L = \frac{\lambda}{\beta \cdot \cos\theta} \tag{4}$$

where λ is the wavelength of the X-ray radiation Co Kα, β is the physical extension of the peak (obtained after subtracting the instrumental extension from the experimental one).

To evaluate the degree of crystallinity (DC, [Masuelli 2013]), the program used to analyze and display the Origin (OriginLab, originlab.com) data. With this program, the total areas of amorphous halo and crystalline peaks were calculated without subtracting the Kα2-component in the latter case (5):

$$DC = \frac{S_{cryst}}{S_{cryst} + S_{amorh}} \tag{5}$$

where S_{cryst} is the total area of the peaks that belong to the crystalline component, S_{amorph} is the total area of amorphous halo.

2.4.4. IR spectroscopy

Infrared spectra of PTFE were recorded on a spectrophotometer Specord 75-IR in the range of wave numbers (400-4000) cm^{-1}. As a comparison band, the absorption band of CF$_2$ PTFE groups at 1206 cm^{-1} was used. The relative error in determining the optical density in a series of three measurements was ~ 20%.

Fisher's criterion was used at a significance level of $\alpha = 0.05$ to assess the quality of research results. The validity of the estimation of the coefficients of the model is checked using Student's criterion with a confidence probability of 0.95 and degrees of freedom $\nu_1 = 5$ and $\nu_2 = 9$. The value of the sample correlation coefficient was 0.962 - 0.988, the determination coefficient being 94.5%. The average relative error of approximation does not exceed 5%.

2.5. Investigation of physical and chemical properties of PCM

Despite all the unique features of PTFE, it has a number of properties that limit its use as tribotechnical material. These include [Trabelsi 2016, Aly 2012, Yuan 2018]:

– the load on the creep at high tensile strength of PTFE, which occurs at 3 MPA load when stretched under normal temperatures;

– high thermal expansion coefficient PTFE under normal temperatures that abnormally varies at temperature range of structural phase transitions (280-310 °C);

– low resistance of epoxy polymers to dynamic loads;

– low thermal conductivity of polymer (10-50 times less than in metals);

– low durability polymer in conditions of dry friction, especially at high sliding velocity.

The heat released in the friction zone due to low thermal conductivity, encourages raising the temperature on the surface friction. As a result, the physical and chemical processes that reduce the strength and stiffness of the polymer are intensified and the linear sizes are greatly increased, which can eventually lead to the destruction of the friction unit. Thereby it is necessary to use physical and chemical methods of PTFE modification. The review of literature and patents [Shen 2015, Ye 2013] is a low potential of traditional technological approaches to PTFE based on PTFE. However, various advanced technological methods, which will allow receiving composite materials and products with the necessary operational properties, can be implemented. This is the synthesis of polymer matrices of various composition and structure [Park 2012]; composition of polymer and oligomeric mixture with different levels of interaction [Haidar 2017, Mnif 2013]; modification of matrix of different origin in the direction of restructuring and structural interaction of energy influence [Ruiz 2011]; modification of the matrix of adding activators of various sizes, shapes and properties [Smith 2014]; the formation of nano-phase matrices with different characteristics [Shelestova 2015]. It should be noted that the industrial implementation of these technologies is associated with significant energy, material and labor expenses and that it requires the managerial study of the price-quality relationship. Modification of epoxide polymers is carried out in order to increase thermal stability through the introduction of polysiloxanes, in particular, silicon organic lacquer of KO-921 brand, which is characterized by high stability of silicone skeleton, aromatic and aliphatic components at elevated temperatures in an approved condition [Harris 2015, Stepashkin 2014].

In this case, it was important to assess the effect of modifier on adhesive and strength characteristics of epoxide polymer since adhesion is the determining parameter for the formation of coatings on metallic surfaces. It was found out that introduction of the modifier over 70 mass fractions sharply worsened physical and mechanical properties of epoxy silicon organic polymer, so this content was accepted as a boundary limit. Introduction of the hardener in amounts of 11 and 13 mass fractions leads to the significant decrease of adhesion strength of epoxide matrix (24.1 MPa and 21.0 MPa respectively) (Figure 1).

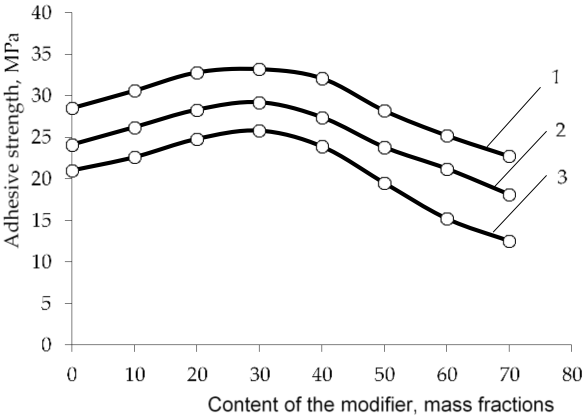


Figure 1. The effect of KO-921modifier on adhesive strength of epoxy polymers with PEPA hardener content: 1-12 mass fractions, 2-13 mass fractions, 3-11 mass fractions

The content of PEPA in an amount of 11 mass fractions is insufficient for full extent running of the polymerization reaction, as evidenced by the lowest content of gel fraction ($G = 90.2$ %) in the matrix, and at the higher content of the hardener, the defective structure with high internal tensions (0.61 MPa) is formed. This characteristic determines the content of the insoluble part of the reactoplast, in which the chemical connections between the components of the system were formed. Determined by the equation for content of gel-fraction G (6):

$$G = 100\% - \frac{\left(m_0 - m_1\right)}{m_1} \cdot 100\% \qquad (6)$$

where m_0 is sample mass before extraction, m_1 is sample mass after extraction.

Increase of adhesive strength of epoxy polymers is observed with the introduction into the composition content the modifier in the range of 10-30 mass fractions, which is connected with the decrease of internal tensions in the value of 1.9-2.1 times due to the increased segment mobility of macromolecules of epoxide matrix with the modifier introduction. The introduction of silicone organic lacquer in the amount of 30 mass fractions leads to the occurrence of peaks in curves at different concentrations of the hardener.

The highest value of adhesion strength ($\sigma_a = 33.9$ MPa) was obtained with the introduction of PEPA in the amount of 12 mass fractions through the optimal balance between the degree of structuring ($G = 91.8$ %) and the value of internal tensions ($\sigma = 0.24$ MPa).

Introduction of the modifier in the amount of more than 30 mass fractions on 100 mass fractions of epoxide basis leads to the sharp decrease of the strength characteristics of obtained polymer because of the excessive content of poly(methyl phenyl siloxane) (PMPS), which slows the structure-forming processes. It was experimentally defined that the content of gel fraction is reduced to 1.5-2.1 % with the high content of the modifier ($g \geq 30$ mas.ch.) since the formation of the maximum amount of cross-linking units at 160 °C temperature is not possible because of the low running speed of chemical reactions [Aderikha 2017, Onodera 2014]. In addition, silicon organic modifier in an amount of more than 30 mass fractions raises the structure defectiveness, as evidenced by 11.2 % growth of the internal tensions value in the epoxy silicon organic polymer.

Modifier introduction reduces the structuring degree of epoxy polymers proportionally to the additive content, as evidenced by the 3.4 - 3.9 % content decrease of the gel fraction in the system. The high values of the structuring degree in 13 mass fractions content of the hardener are connected with the formation of a maximum amount of possible chemical bonds, and low values indicate the insufficient amount of PEPA (11 mass fractions) for the polymer structuring.

Modifier with concentrations up to 10 mass fractions, 30 and 40 mass fractions for epoxy silicon-organic polymers containing 11, 12, 13 mass fractions of PEPA respectively, leads to the decrease of the value of internal tensions (Figure 2).

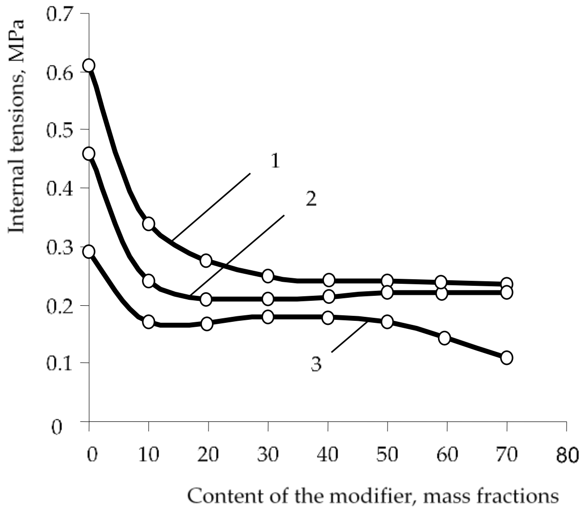


Figure 2. The effect of KO-921 modifier on adhesive strength of epoxy polymers with PEPA hardener content: 1-12 mass fractions, 2-13 mass fractions, 3-11 mass fractions

This is explained by the formation of the spatial and structural net of polymer with raised segment mobility of macromolecules, capable of relaxation. It was reported that subsequent increase of the modifier content up to 70 mass fractions for the polymers with PEPA (12 mass fractions) was accompanied by the 11.2 times growth of the researched characteristic. In polymers containing 11 mass fractions hardener initially the growth ($\sigma = 0.18$ MPa) for concentrations of the 30...40 mass fractions modifier, and then value decrease of internal tensions in 1.6 times by the modifier content of 70 mass fractions are observed.

Hence, it was experimentally determined that the optimal PEPA hardener content, necessary for the maximum structuring of epoxy silicon organic polymer, is 12 mass fractions per 100 mass fractions of epoxy. It was also found out, that the highest adhesion strength and the lowest internal tenses thermally treated at 160 °C had epoxy silicon-organic polymers with modifier of the concentration of 30 mass fractions.

3 RESULTS AND DISCUSSIONS

The surface of CF is generally inert [Wang 2017]. The PTFE composition of CF represents a complex heterogeneous system with phase-distribution surfaces. Physico-chemical processes in the boundary layers during the formation of the composition contribute significantly to the formation of the structure and, consequently, to the main operational properties of such compositions [Utracki 2014]. Formation of reaction surfaces of PTFE-matrix and CF is an important scientific and practical task, and its solution guarantees the planned properties of the composite are obtained and reproduced.

Modification of the carbon fiber surface by various methods is proposed to provide a technological combination of carbon fiber with a polymer matrix in PTFE-based antifriction composite materials [Vail 2011]. Such processing of the filler allows enhancing the characteristics of composites, which are mainly dependent on adhesive bonding of carbon fiber and PTFE matrix [Venkateswarlu 2014].

The study showed that the most common method for modifying the carbon fiber surface to improve the adhesion of PTFE to CF is the thermal oxidation of the surface of the fibers. Thermo-oxidation treatment of the CF surface leads to an increase in the surface area and multi-molecular adsorption [Yan, Y. 2011]. The features of the thermal (before grinding) and thermomechanical (during milling) modification of the surface of the fiber by the results of experiments were studied.

The most effective thermal and thermomechanical modification was observed at a temperature of 400 °C. This is a result of a change in the supramolecular structure, due to the increased flexibility of the PTFE macromolecules. The increase in strength by 50% and durability more than twice is observed for CFRP containing CF after thermomechanical modification. The mechanical modification was carried out in a vacuum (p = 73.33 kPa) in order to enhance the energy effect when milling CF. It was found that the strength of CFRF containing fibers, modified in a vacuum, increases by almost 50%, and wear resistance increases by 100% when crushing KF in a vacuum (Table 3).

Table 3. Physical and mechanical properties of CFRP depending on the conditions of grinding fiber (grinding time 15 min, vacuum p = 550 ± 10 mm Hg)

Parameter	Control	Rotation speed of working min^{-1}			
		7000		9000	
		Environment			
		Air	Vacuum	Air	Vacuum
Tensile strength MPa	15.0	20.0	22.0	21.0	22.5
Wear intensity I·10^{-7} m^3/(N·mm)	12.5	7.0	6.0	7.1	6.5

Synergistic approach to the issue of increasing the strength of composites was widely used, therefore, a study was conducted on the combined effect of thermomechanical processing and vacuum processing CF on the physical, mechanical and tribotechnical properties of CFRP.

As shown in Table 3, with thermomechanical modification of fibers at 400 °C for 15 minutes in a vacuum (p = 73.33 kPa), as compared to the unmodified sample, the strength of the CFRP increases by more than 75%, and wear resistance increases by more than three times.

After a series of experiments was analyzed and the effectiveness of the influence of different technological methods on composite properties was demonstrated, it turned out that the technology of thermal vacuum CF, which allowed to increase the strength of PTFE composite by 18-22%, and its wear resistance of 20-25% was most effective; all of them represented practical interests for industry.

The glue epoxy capacity is much higher compared to thermoplastics, so no preparative activation of fillers is required. Therefore, it is advisable to perform a powder drying operation to remove moisture at a temperature of 100 °C for 1 hour, which increases the mechanical properties to 30-40%.

The perfection of the carbon filler method is possible due to the successive grinding of KF in the presence of PTFE powder, which allows binding of fibers in the UHFS agglomerate. Such a high-quality and chemically reactive carbon filler increases the strength and resistance to wear of PTFE-composite. Scanning electron microscopy is used to study the CF structure obtained in situ. As photomicrography shows a layer with a high content of PTFE on the CF surface (Figure 3).

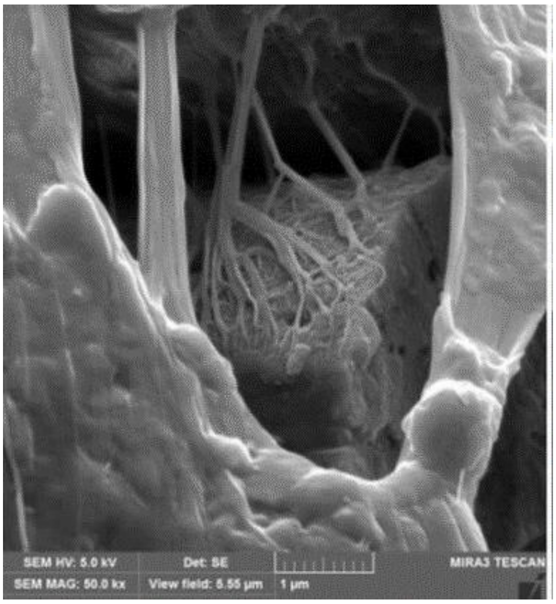
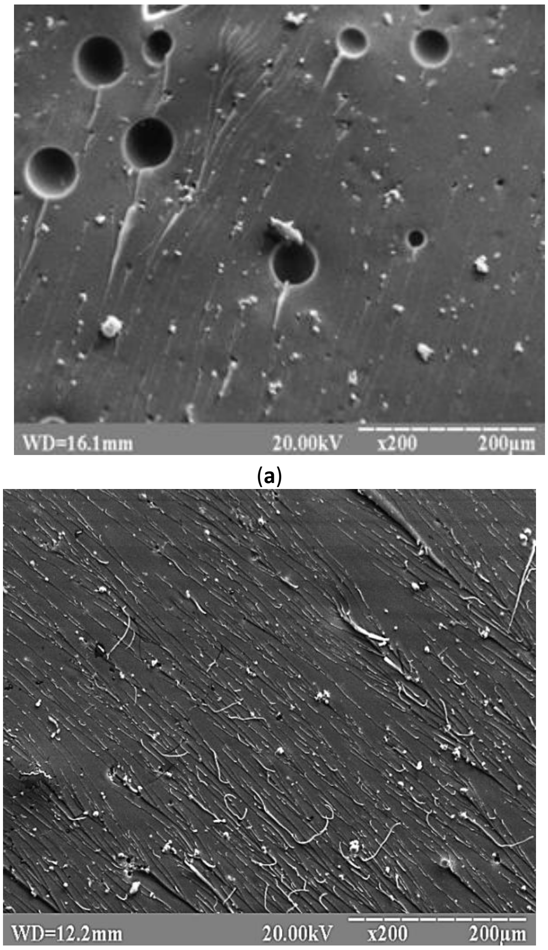


Figure 3. REM - micrograph of the surface of CF modified by technology in situ (x10000)

The analysis of the compositions with CF prepared according to the above-mentioned decision and the known technological process shows that the compositions based on PTFE with this filler increase the tensile strength by 10-20% and resistance to wear by 17-40%.

Improvement of the operational properties of the composite due to the developed scientific and technological method lies in the mechanical combination of fine (powdered) KF with powder PFTE. This results in the formation of a dispersed composite product before the formation of the warehouse as a whole. At the end of the formation, the composition will consist of three fractals. The first fractal is the fraction of CF particles attached to the PFTE powder; the second is more CF, coated with PFTE (Figure 3), the third is the unbound mass of the PTFE matrix. In accordance with the theory of percolation, the structure of a polymer composite is a necessary prerequisite for the creation of an infinite filler cluster (CF) in a polymer matrix (PTFE). Thus, the thermodynamic coupling of small particles of fiber with the necessary and sufficient volume of PTFE powder results in a more reactive filler with higher thermodynamic compatibility than a mixture of mechanical components in similar proportions.

Operation of mechanical mixing at an initial stage of epoxy composites formation is necessary for equal distribution of filler particles and hardener macromolecules in a composite volume. Thus the frequency of rotation of the mixer tool should be minimal in order to avoid epoxy composition heating, as an intensification of structuring processes with the local formation of physical and chemical bonds takes place, that would lead to the impairment of mechanical and operating characteristics. 5 minutes of ultrasound treatment of composition is reasonable, which at micro level provides mixing of the components and improves the system lyophilicity, leads to the greater number of links between the active groups on the filler particles surface and formation of polymer component macromolecules. On fracture fractogram of epoxy composite filled with highly dispersed iron particles, the composition of which was not treated by external physical fields pores of different diameters (10-50 μm) were detected (Figure 4 a).



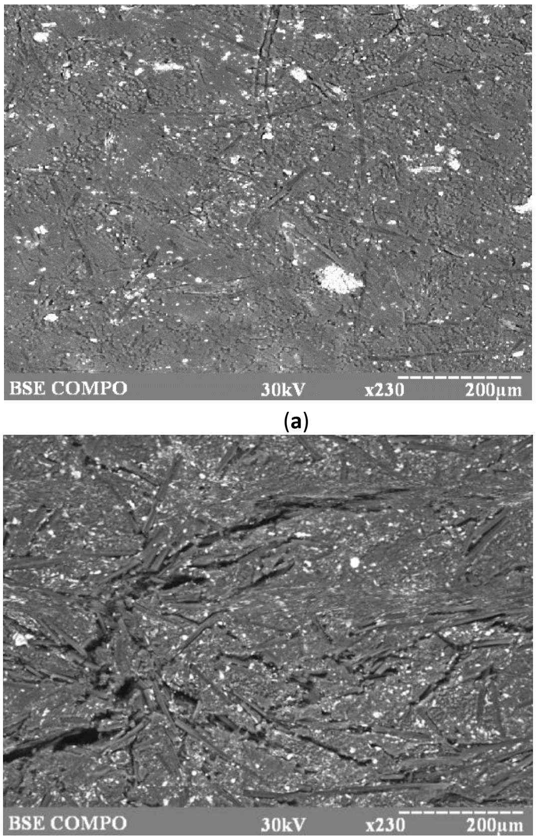
(**a**)

(**b**)

Figure 4. Fracture fractograms of epoxy composites filled with iron dispersed particles: (**a**) without treatment; (**b**) ultrasound treatment of composition (×200)

Epoxy composites surface after treatment of composition at the stage of ultrasound treatment (Figure 4 b) is characterized by a large number of distinct microscopic chipping lines, which have significant branchings that define the system structuredness of high tension state. In epoxy composites, the compositions of which were treated by ultrasound, the minimal value of residual tensions (σ = 0.48 MPa) was fixed at the small filling degree of the system (6-10 mass fractions) of highly dispersed powders. Ultrasonic waves enhance the uniformity of the location of the particles in the epoxy polymer matrix and provide the segments fixation of the matrix macromolecules in the particles external surface layers.

The research results showed that surface micro defects can appear in CFRP during product manufacturing, which can develop into destroying cracks (Figure 5a and Figure 5b).



(**a**)

(**b**)

Figure 5. Electron photomicrographs of CFRP [20]: (**a**) before; **(b)** exposition in water (x230)

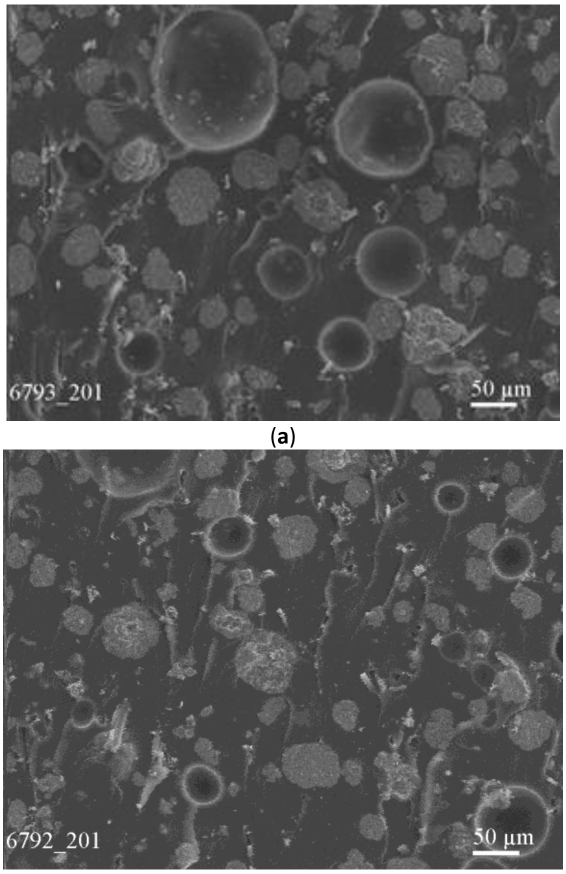
Analysis of data showed that the absorption of moisture from the composite with KF should be regulated by the formation technology determining the structure, properties and durability of the composite material. With the help of the technology, it is possible to control the absorption of moisture of the composite and to maintain the operational properties. It is a choice of optimum conditions of formation; pre-treatment of CF with PTFE particles; introduction of technological auxiliaries in CFRP.

The complexity of formation of epoxy composites is connected with the presence of air bubbles in the structure, which enter the composition during the mixing operation and remain in the system due to high viscosity. The presence of these defects also increases the water absorption and reduces mechanical characteristics, which leads to the loss of composite durability. From Figure 6a and Figure 6b it is evident that fraction fractograms of epoxy composite material have a smooth surface since they are absent of sharp drops of relief.

Because of the presence of a minor ledges on the surface, it can be assumed, that the development of the crack passes through the boundary partition of fiber and matrix. This can be explained by the higher cohesive strength of the epoxy composite components than the adhesive strength of the polymer matrix with carbonaceous fiber.

Parallel lines of chipping on surfaces point to the uniform distribution of residual tensions in epoxy composite material, which is presumably related to the uniform distribution of tensions in the material, since conduct of the thermal processing at elevated temperatures (60 °C) leads to the local cross-linking of composite epoxy areas, formed under pressure. Fracture passes through areas with predominant micro-pores location.

In the material formed under the pressure of 150 MPa, the size of micro-pores is 40-150 microns, and under the pressure of 300 MPa it is 25-100 μm. Thus, the formation of epoxy composites at the higher pressure of pressing reduces the number of pores and their size in the highly filled system, while enhancing its strength and viscosity, what is a significant point in development of tribotechnical function materials.



(**a**)

(**b**)

Figure 6. Fracture fractograms of epoxy composite material formed under the pressure of: (**a**) 150 MPA; (**b**) 300 MPa

Formation of epoxy composites is conducted by the following optimal mode of pressing:

– the compaction pressure - 300 MPa;

– the speed of pressing the billet - 1 m/min;

– the holding time of compaction under the pressure - 60 min.

The lifetime of composite parts depends on the effect of heat during the production process. Insufficient information and summary data on the influence of thermal effects on the properties of polymeric materials makes the choice of optimal regimes for the production and heat treatment of PTFE composites more complicated. The technology of thermal processing of PTFE-composites is a thermal process of impact on the material that starts with drying of the initial material and ends with cooling of the heat-treated product. The main type of heat effect is PTFE, and its composition is sintering, which lies in heating the semi-finished product to 360-380 °C, at this temperature (1 hour per 1 mm thickness) and quick cooling within the temperature range from 327 ° C to 350 °.

It is the time of material exposure during quenching that has a significant effect on the properties of end products. This is the result of the change in the structure of the polymer macromolecule configurations and the increase in the number of straight sections that become centers of crystallization with PTFE cooling.

Thus, the technological modes of heat processing define the degree of crystallization and, as a result, they define the physicomechanical properties of the material. The crystallinity degree of the sintered PTFE ranges from 50 to 70 % and it depends on the molecular weight and the cooling rate. The majority of PTFE mechanical properties worsen with the increase of the crystallinity degree. During sintering of billet material at the stage of fusion of particles of polymer and carbon fiber filler, the chemical, physico-mechanical, physico-chemical and electrical properties of the future product are formed in the composite. After an application of cascade heat treatment mode on composite during sintering, which includes heating at different rates and different time exposures with slow cooling, a shift of alternate disordered orientation and structure stabilization on the molecular level take place.

The orientation of fragments of molecules allows forming a more homogeneous supramolecular structure and stable composite properties throughout the volume. As a result, the strength characteristics and wear resistance of the composite are increased.

The cascade mode of sintering with hourly exposure at each stage of the cascade eliminates the uncompensated formation tension and provides a complete structural transformation in the composite volume during the transition through the characteristic temperature points of phase transformations preventing the damage to the composite integrity when cooled (cracking) and the formation of the necessary correlation of the phases of the polymer matrix. All of them allow forming the structure of CFRP with high homogeneity and stable properties of the composite. This leads to an increase in the strength and wear resistance of the composite (25 and 50% respectively) and can be recommended for the production of general and antifriction building materials suitable for high temperatures, as well as in chemically active environments.

Thermal processing of epoxy composites consists in the thermal effect on composition located in the matrix pressform at a temperature of 40 °C, and the main handling of products after their removal from the pressform. Optimization of the hardening temperature and time mode is important technological stage in the ECM development, since insufficient time of structuring at low temperature does not ensure the formation of optimal amount of physical and chemical links between the matrix and the filler particles, and at high temperature the reduction of physical and mechanical characteristics of the material takes place due to the destruction of bonds in the composite as a result of thermal destructive processes and an increase of internal tensions.

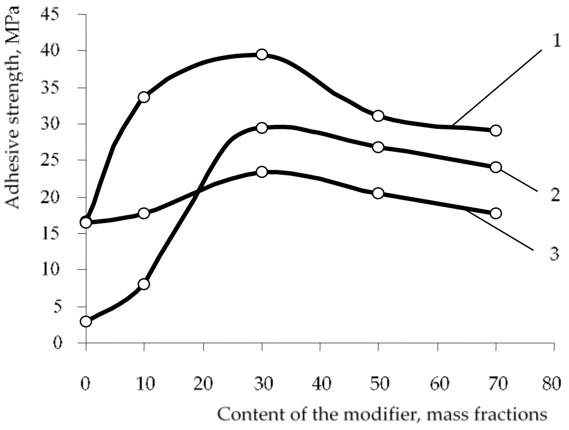


Figure 7. The effect of KO-921 modifier on adhesive strength of epoxide matrix at final thermal treatment temperature: 1-210 °C, 2-240 °C, 3-180 °C

In works it is noted that it is appropriate to conduct the process of hardening the ED-20 epoxy in presence of PEPA at the maximum final temperature of 160 °C. However, this temperature is insufficient for complete polycondensation of silicon organic compounds, the thermal hardening of which takes place within the temperature range of 20-250 °C.

The highest values of adhesive strength (σ_a = 39.2 MPa) were obtained for epoxy silicon-organic polymers, thermally treated at 210 °C, that registered the lowest internal tenses (0.17 MPa) (Figure 7).

Thermal treatment at 180 °C does not provide sufficient thermal effect on the structuring processes in the presence of silicon-organic additive, and a high temperature of 240 ºC leads to the initiation of thermal destructive processes. It was determined that the temperature of 210 °C is optimal for epoxy silicon-organic polymers, since in this thermal processing mode the high mobility of conglomerates of matrix macromolecules is achieved, that leads to the reduced internal tensions of the system and provides the highest structuring degree of the composite (*G* = 94.2 %) in comparison to the other modes, as evidenced by the deterioration of physical and mechanical properties of the epoxy organic silicon matrix processed at 240 °C. It was determined that the highest structuring degree of thermally treated (210 °C) epoxy silicon organic polymer was obtained by slow heating of the material at the rate [43, 44, 50] of 7 °C/min during 4 hours. During the heating rate of 42 °C/min the maximal hardening takes place after 5 hours. It is connected with the fact that with rapid heating the part of epoxy matrix remains in the unstructured state through the local kinking of cross-links that blocks the structure-forming process. Heating over five hours is unreasonable [44, 45] as the growth of the researched characteristic is not observed [51].

Optimal structural and mechanical characteristics are obtained at the stepped heating for 24 hours at 20 °C; 1 hour at 60 °C; 1 hour at 120 °C; 1 hour at 180 °C; 4 hours at 210 °C as it provides the most complete structuring (*G* = 94.3 %), as at slow heating, and creates conditions to reduce internal tensions (0.18 MPa), because the three-dimensional net formation takes place uniformly with the adequate lead time for the conformational changes.

Epoxy silicon-organic polymers containing KO-921 modifier with 30 mass fractions per 100 mass fractions of epoxy have the highest structuring degree and the lowest internal tensions. It was determined that additional high-temperature thermal processing of systems, that consisted of a stepped heating to the final temperature of 210 °C is optimal for the developed materials, whereas the maximal growth of physical and mechanical characteristics of the composite was observed.

4 CONCLUSIONS

The research results defined operation modes of process equipment: after the processing, the PTFE-composites increased service properties compared to the basic ones, and they can be most effectively used for the following industrial applications:

– energy impact on uncompounded PTFE results in an increase of parameters of deformation and strength characteristics (breaking strength by 2.6 times, breaking elongation by 4.3 times) while high tribotechnic characteristics are preserved. Modification of reaction capable polymers consists in the introduction of substances that are able to form additional physical and chemical links in polymer net and to increase system to relaxation. Thus, the introduction of PEPA hardener (12 mass fractions) and KO-921 organic silicone lacquer (30 mass fractions) provides 15% increase of adhesive strength and it reduces the internal tensions by 1.9–2.1 times.

– thermal and vacuum technology of modification of CF, which allowed increasing the strength of PTFE - composite by 18-22%, and its wear resistance, was the most effective at 80%.

The technology of forming polymeric composites on a thermally reactive basis does not involve special operations related to the use of physical fields for activating components because of their high reactivity.

– in the course of the production of PTFE with CF with the use of two-stage mode, the level of strength characteristics of carbon plastics is increased by 45% compared with the control sample, and wear resistance increases by 80%. The efficiency of physical fields is evident at the stage of mixing the components of the polymer composition. The adhesive strength of epoxy polymers as a result of the ultrasound treatment of the composition increased 1.7 times compared to an untreated epoxy system, and 1.5 times in comparison with epoxy polymers, the compositions of which were processed by an electromagnetic field. The application of ultrasonic treatment provides a higher degree of homogeneity of the system due to the intensification of interactions between the components and decrease of the system defectiveness as a whole.

– the optimal moulding modes were determined, which provide stable phases interaction of PTFE-matrix with CF with minimal moisture absorption (less than 15–25 % in comparison with the analogue) and high-service properties (compression strength is higher by 15–25 %, resistance to wear is higher by 40-45 %). It is appropriate to perform the formation of epoxy composites at a compaction pressure of 300 MPa, thus providing a reduction in the number and size of micro-pores in the highly filled system and increasing the strength and dynamic viscosity, which is an essential aspect of the development of materials with tribotechnical function.

– cascade mode of sintering of PTFE-composite allowed obtaining PCM, which was characterized by increased strength and resistance to wear (25 and 50 % respectively) in comparison with the analogue. High mechanical characteristics of the modified epoxy composites were obtained by the stepped heating mode at the final temperature of 210 °C, thus providing the complete structuring (G = 94.3 %), as at slow heating, and creating conditions for a decrease in the internal tensions (0.18 MPa).

Therefore, the primary targets for future development have to be the application of hybrid composites (fibres with low cost must be used where possible, while aramid and carbon fiber should be used only where they are needed for the admission of damage or the reasons hardness), assessment of highly automated and rapid production processes, including intellectual preforms or semi-finished products, as well as full use of the potential for composites integration of parts.

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