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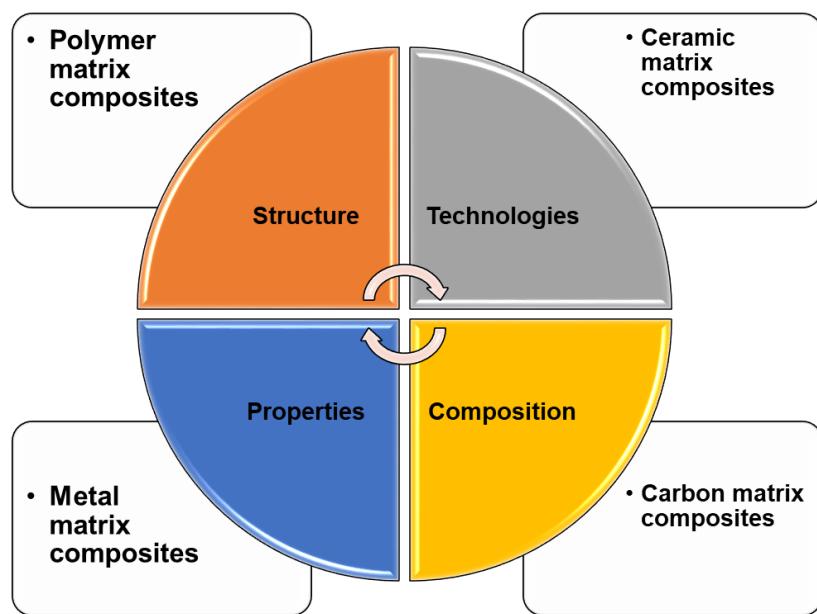
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Polymer Composites for Automotive Sustainability.

Polymer Bearing Solutions for Lubricated Applications.



Creation of high-tech equipment, a significant acceleration of progress made by science and technology and the implementation of resource-saving technologies require the development of new materials in the parts of machines working with slip friction and have a low coefficient of friction. The monograph presents the results of theoretical and experimental studies of polymer composite materials (PCM) on the basis of polytetrafluoroethylene (PTFE). Polytetrafluoroethylene has been studied with fillers of different chemical nature in order to form a perfect structure and the required level of operational properties of fluoroplastic composites. An important aspect here is the objective assessment and analysis of the influence of fillers on the structure and physical and mechanical properties of PCM. The development of composite models and prediction of operating characteristics of antifriction materials using PTFE on their basis was studied. Promising in this respect are polymer composite materials (PCM) based on polytetrafluoroethylene (PTFE) due to its unique operational properties - the lowest coefficient of friction among polymers, high chemical inertia, thermal and cold resistance. However, low wear and thermal conductivity, high coefficient of thermal expansion and creep limit the possibilities of its application in its pure form. The technical progress leads to the complication of the use of PCM, in which they no longer meet the necessary requirements. This causes the need for new macromolecular substances or the modification of already existing polymers. First, it requires large material costs (for the synthesis of new polymers and the creation of new technological productions). The second is more economical and promising. Technically, it can be implemented by modifying polymers. In the case of PTFE it is advisable to modify the polymer by mechanical activation, which is related to the low energy and metal capacity of the equipment, the simplicity and safety of the process, as well as the possibility of introducing the corresponding functional fillers. The influence of modes of mechanoactivation processes in the technology of preparation of ingredients on the structure and properties of composites is insufficient. The problem of increasing the efficiency of composite sealing elements of friction units and increasing the life of their operation remains unresolved.

Therefore, the study of the specific features of the activation and modification of the matrix and fillers, the development of the principles of obtaining tribo-technical composites based on PTFE is an actual task of the technology of polymer and composite materials, which is an important scientific and technical problem.

The information provided may also be useful to engineers and technical staff in technical practice organizations that are producers of ensuring series production and production of spare parts in the automotive and other demanding industries. Monograph is also based on its own experience and discussions with various companies and organizations, such as Poltava-GasVydobuvannya Gas Production Division (GPD) (Poltava, Ukraine), "Sumy NPO" PJSC (Sumy, Ukraine), Concern «NICMAS» (Sumy, Ukraine) and so on.

The monograph provides a comprehensive presentation of information from data collection to assess them and issuitable and useful also for university teachers, students of technical faculties who are interested in new approaches and trends in this area. The monograph was supported by grant KEGA.

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Anton PANDA, Konstantin DYADYURA:

POLYMER COMPOSITES FOR AUTOMOTIVE SUSTAINABILITY. POLYMER BEARING SOLUTIONS FOR LUBRICATED APPLICATIONS

Abstract:

Creation of high-tech equipment, a significant acceleration of progress made by science and technology and the implementation of resource-saving technologies require the development of new materials in the parts of machines working with slip friction and have a low co-efficient of friction. The monograph presents the results of theoretical and experimental studies of polymer composite materials (PCM) on the basis of polytetrafluoroethylene (PTFE). Polytetrafluoroethylene has been studied with fillers of different chemical nature in order to form a perfect structure and the required level of operational properties of fluoro plastic composites. An important aspect here is the objective assessment and analysis of the influence of fillers on the structure and physical and mechanical properties of PCM. The development of composite models and prediction of operating characteristics of antifriction materials using PTFE on their basis was studied. Promising in this respect are polymer composite materials (PCM) based on polytetrafluoroethylene (PTFE) due to its unique operational properties - the lowest coefficient of friction among polymers, high chemical inertia, thermal and cold resistance. However, low wear and thermal conductivity, high coefficient of thermal expansion and creep limit the possibilities of its application in its pure form. The technical progress leads to the complication of the use of PCM, in which they no longer meet the necessary requirements. This causes the need for new macromolecular substances or the modification of al-ready existing polymers. First, it requires large material costs (for the synthesis of new polymers and the creation of new technological productions). The second is more economical and promising. Technically, it can be implemented by modifying polymers. In the case of PTFE it is advisable to modify the polymer by mechanical activation, which is related to the low energy and metal capacity of the equipment, the simplicity and safety of the process, as well as the possibility of introducing the corresponding functional fillers. The influence of modes of mechanoactivation processes in the technology of preparation of ingredients on the structure and properties of composites is insufficient. The problem of increasing the efficiency of composite sealing elements of friction units and increasing the life of their operation remains un-resolved. Therefore, the study of the specific features of the activation and modification of the matrix and fillers, the development of the principles of obtaining tribotechnical composites based on PTFE is an actual task of the technology of polymer and composite materials, which is an important scientific and technical problem. The information provided may also be useful to engineers and technical staff in technical practice organizations that are producers of ensuring series production and production of spare parts in the automotive and other demanding industries. Monograph is also based on its own experience and discussions with various companies and organizations.

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LIST OF USED SYMBOLS AND ABBREVIATIONS

CM – composite materials,
PMC – polymer matrix composites;
MMC – metal matrix composites;
CMC – ceramic matrix composites;
CAMCs – composite matrix composition of carbon;
PTFE – polytetrafluoroethylene;
ACN – artificial crystalline nuclei;
CF – carbon fibers;
I – intensity of wearing, $10^{-6} \text{ mm}^3/\text{N}\cdot\text{m}$;
V – material volume, m^3 ;
 ρ - density, kg / m^3
 c_n – concentration of the inclusions oriented in the n-direction, %;
 σ_{pp} – tensile strength, MPa;
 δ – elongation at fracture, %;
 l – average fiber length;
 d – diameter;
 σ_{ij} - tensions;
 e_{ij} - deformations;
 ε_{ij} – deformation rate;
 χ_n – indicator function;
 u_i - shifts;
W – the functionality of the elastic energy of deformation;
 μ, λ - Lamé parameters;
E – modul of elasticity;
 c_s – volume content of dispersed particles;
 c_f – volume content of fibers;
Q – the function of the geometrical fiber parameters;
 Q_1 – the function of elastic properties;
 W^* - the functionality of the elastic deformation energy dissipation;
k – the limit of the material plasticity;
 η - the material viscosity;
H – the hardness of material;
 τ – the criterion of coherence of macro-properties.
cc – cubic centimeter

INTRODUCTION

The automotive industry is a large and critical sector within the global economy. Modern development of the automobile industry is not possible without improving the tribological properties of materials of units of friction. Increasing the reliability of the units of friction of the car mechanisms is important for reducing the cost of maintenance and repair. The study of friction, wear, and lubrication is the main task of increasing the durability of automotive mechanisms [1, 2, 3]. Friction is a complex process of the interaction of coupled solids. This process is accompanied by the following phenomena:

- oxidation due to the interaction of the surface of the friction with the environment;
- selective mass transfer;
- structural and phase transformations;
- absorption decrease in the strength of the surface layer;
- stress distribution in conjugated surfaces and depreciation of the latter.

At the same time, under the influence of the accompanying friction of physical, chemical, electrochemical and mechanical influences of the properties of the material, its composition and structure in the surface layers of contact interaction are subjected to continuous changes. As a result, products of deterioration and secondary structures on the working surfaces may be formed, the chemical composition and structure of which differ in composition and structure of the starting materials of the friction pairs, which affects the wear resistance of the units of friction.

Units of friction of the car are exposed to adverse factors: high humidity, dustiness and others. The resistance of the material of the surface layer, the adhesion forces and the wear and tear mechanism are continuously changed under the influence of external factors.

Particularly active wear is subjected to plain bearings [4, 5]. Mostly wear parts of the car chassis.

Promising materials for the manufacture of sliding bearings are polymer composites. The use of polymers can significantly reduce the cost of expensive materials and reduce energy consumption. The polymer matrix-based composites have high antifriction properties and are suitable for use at medium loads and slip rates. An urgent issue is the use of self-lubricating polymer-composite materials in units of friction, where undesirable or impossible external lubrication [6, 7].

Composites are one of the most widely used materials because of their adaptability to different situations and the relative ease of combination with other materials used to serve specific purposes and to exhibit desirable properties. Contemporary tribotechnical industry requires production of new polymer-composite materials (PCM) with high level of operational characteristics [6, 8].

In particular, the inclusion of polytetrafluoroethylene (PTFE) into oxide layers on aluminium can considerably improve practically all their properties, such as hydrophobic, anti-friction and anticorrosion ones that enables the use of them in components working in friction junctions and production of anti-icing coatings [9, 10, 11].

The optimization of technological regimes of producing and converting PTFE-composites and coatings on their basis allows to provide optimal combination of deformation-durable and tribotechnical characteristics of the product as well as technical-and-economical and techno

Introduction

logical parameters, to start the production of materials adapted to concrete industrial conditions and practical application.

The intensity of PCM wear depends greatly on mechanical properties, nature, structure and sizes of particles of matrix and fillers, composite material structure, its hardness, toughness, elasticity, level of the external force effect on the contact "composite – counterbody". The abrasive composite wear depends on the fact how effectively the composite material mi

crostructure can resist different processes of the material separation during the deformation. The main contribution into the amount of wear is made by the chain of plastic deformations and break in the thin surface layer. The distribution of the energy absorbed by the active layer determines the kinetics of accumulating damages and breaks and change of friction processes.

The perspective direction to improve the mechanical properties and increase the life service of such materials is a modification of the structure using the external physical fields. Thus an important aspect is the development of the technology of formation and improvement of technological properties of the components that determine the technical and economic efficiency of application of the developed composite materials and provides forecasting of PCM operational characteristics. The wide use of composite materials based on polymeric matrixes in tribotechnical engineering is conditioned by savings of high-value composites based on nonferrous metals, low-density products and comparatively low energy expenses connected with parts production.

The experience of many theoretical and practical works concerning the technology of formation of polymer composites has been analyzed and systematized.

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. 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. Replacement of traditional tribomaterials in friction units of industrial equipment 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 [11, 12].

Identifying the influence regularities of fillers, chemical and technological factors on the formation processes of composites with deepening the scientific ideas about the formation

Introduction

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. The implementation of matrix and fillers modification methods and application of composites formation technology 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.

PTFE-based (polytetrafluoroethylene) plain bearings are a cost-effective alternative for many industrial and automotive applications [12, 13].

Design and creation of new structures of three-component antifriction composite materials are based on the researches modeling their behavior in the conditions of tension. In the presented models the uniform approach based on the variation principles of mechanics of a solid body and allowing formulating boundary value problems in the form of a condition of minimality of functionality is used. The multifactoriality of the dependence of abrasive wear of a composite on its elasticity, viscoplasticity and durability is considered. Macroscopic characteristics of composite material are directly connected with its structure which is characterized by spatial distribution of components and their properties.

CHAPTER I

SOME OF THE KEY FEATURES OF COMPOSITE MATERIALS

1.1 General information about composite materials

Composite materials are solid product consisting of two or more distinct phases, including a binding material (matrix) and a particulate or fibrous material [8, 9, 10, 14].

Composite materials (CM) have a specific set of characteristics [10, 11, 15]:

- consist of two or more components that have different chemical composition and have a clear limit distribution [16];
- have properties that are different from the properties of the source components [17, 18];
- heterogeneous in micro and homogeneous in macro volume [19, 20];
- properties are determined by each of the components if it is in the matrix in sufficient quantity [21, 22].

The component that is continuous throughout the volume, called the matrix. The inhomogeneous solid phases are reinforcing elements (reinforcement fibrous material (such as yarn, fabric or mat) added to a resin matrix in order essentially to improve its mechanical properties [7, 13, 14, 16]).

The requirements for matrices can be divided into 3 groups: the first group can be attributed to strength, rigidity, heat resistance of the polymer matrix, to the other - plasticity, crack resistance, impact strength; to the third - processability, manufacturability of the binder. The task of the researcher who designs the composite material is to find a compromise, to optimize the choice of the binder, taking into account environmental, economic, market and other considerations [18, 19, 23].

In composite material, each component performs its specific function. The matrix creates the properties of composite material (provides plasticity). The reinforcing components are uniformly distributed in the matrix. They have high strength, hardness and modulus of elasticity [4, 15, 17, 24, 25].

In order to systematize CM by various criteria, to correctly implement the procedure for selecting CM for the manufacture of various parts, to streamline terminology in the field of materials science of composites, a reasonable classification of these materials is necessary [26, 27, 28]. There is no single generally accepted classification of composite materials. This results from the fact that CM represent the widest class of materials uniting metals, polymers and ceramics. The most commonly used classification of composite materials based on their division by material science characteristic can be found in [29].

CM are classified according to the following features (fig. 1.1) [4, 6, 13, 14, 26, 27, 30]:

- on matrix material and reinforcing elements [31];
- the geometry of the elements [32];
- by structure and arrangement of elements [33];
- on methods and technologies for obtaining [34];
- by appointment [35].

Classification of CM on the matrix material (material science principle)

Matrix composite materials are metals, alloys, polymers, organic and inorganic, ceramic, carbon and other materials. Different combinations of the components determine the physical, chemical, biological and performance properties of composite materials. The common name of composite materials usually comes from the matrix. The four main categories of composites - polymer matrix composites (PMC), metal matrix composites (MMC), ceramic matrix composites (CMC) and composite matrix composition of carbon (CAMCs). Composite material containing two or more different composition and nature of matrix components is called poly matrix [12, 14, 17, 28, 36].

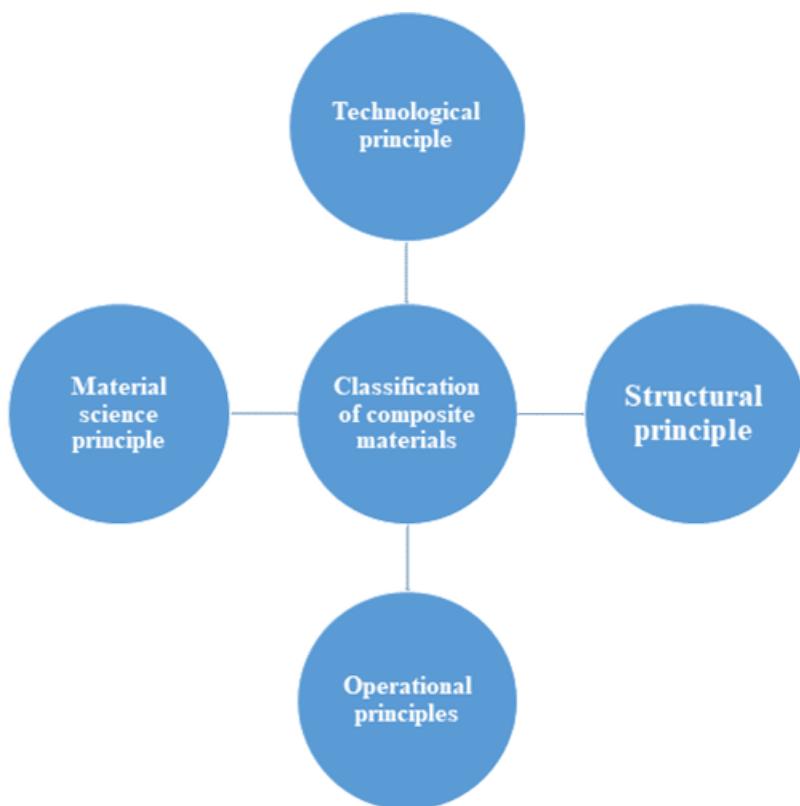


Fig. 1.1 Principles of classification of composite materials

Classification of CM on the reinforcing elements

There are several types of reinforcing elements particle size [15, 16, 29, 37]:

- macro filler – 10...100 MKM;
- mini filler – 1...10 MKM;
- micro filler – 0.1...1 MKM;
- nano filler – 0.01...0.1 MKM

Composite materials containing two or more different types of nature or composition of reinforcing elements called poliarmovanymy.

Classification of CM on the geometry of reinforcing elements

According to the geometry of reinforcing elements, composite materials are divided into [18, 20, 23, 31, 38]:

- powdered (composite materials of the type of pseudoalloys, composites obtained from a mixture of different powders, fine and nano-dispersed composite materials);
- fibrous (composite materials, which are reinforced with continuous and discrete fibers);
- lamellar (composite materials, which are reinforced with continuous and discrete plates).

Classification of CM on the structure and location of components

In accordance with this classification, CM are divided into groups with a matrix, layered, frame and combined structure. The matrix structure is dispersed-strengthened and reinforced with CM. Materials with a layered structure include compositions obtained from a set of alternating foil layers or sheets of materials of various nature and composition. Composite materials with a frame structure include materials obtained by the method of impregnation. Combined structure have materials containing combinations of the first three groups [6, 19, 20, 21, 39, 40].

Classification of matrix KM according to the scheme of reinforcement (structural principle)

According to the orientation and type of reinforcement, all CM can be divided into two groups - isotropic and anisotropic. Isotropic materials are called, which have the same properties in all directions. The properties of anisotropic materials depend on the direction in the object under study. CM with a matrix structure are divided into chaotic-reinforced and orderly-reinforced. Chaically reinforced CM contain reinforcing elements in the form of dispersed inclusions, discrete or continuous fibers. These materials are isotropic or quasi-isotropic. The term “quasi-isotropic” means that CM is anisotropic in the microvolume, but isotropic in the volume of the entire product. Orderly reinforced CM are subdivided into unidirectional, i.e., uniaxially reinforced, biaxially reinforced (with flat arrangement of reinforcement) and triaxially reinforced (with volume arrangement of reinforcement) [5, 20, 21, 22, 41, 42].

Classification of CM by methods of production (technological principle)

In accordance with this classification, CMs are divided into materials obtained by liquid-phase and solid-phase methods, as well as methods of deposition - sputtering, by combined methods [21, 32, 43].

Liquid-phase methods include impregnation (impregnation of reinforcement with polymers or molten metals) and directional crystallization of alloys. Solid-phase methods for producing CM include rolling, extrusion, forging, stamping, explosion sealing, diffusion welding, drawing, etc. Composite materials produced by solid-phase methods are used in the form of powder or thin sheets. Upon receipt of CM by deposition methods - sputtering, the matrix is applied to the fibers from salt solutions or other compounds, from the vapor-gas

phase, from plasma, etc. The combined methods consist in the sequential or parallel application of several methods.

Classification of KM by appointment (operational principle)

The classification of CM by purpose is rather relative, since often composites are multifunctional materials. However, among the many CMs, there are general engineering materials (bearing structures of ships, airplanes, automobiles, etc.), heat-resistant materials (blades of aircraft turbines, combustion chambers), heat-resistant materials (products operating under frequent thermal cycles), friction materials materials (brake pads), anti-friction materials (plain bearings), impact-resistant materials (armor of aircraft, tanks), heat-shielding materials, materials with special properties (magnetic, electrically), etc. [18, 21, 24, 25, 38, 44].

1.2 Composite polymeric materials for functional purposes

Polymeric matrix for composite materials is chosen, taking into account the operating conditions of products. The properties of the composite significantly depend on the matrix material: strength, heat and moisture resistance, resistance to aggressive media, the method of obtaining the product. Polymers as a matrix are used either in pure form (powders, granules, sheets, films), or in the form of binders. The binder is a two- or multicomponent system of synthetic polymer and hardeners, initiators or catalysts, and accelerators of hardening. Solvents, dyes, plasticizers, stabilizers and other components can be added to the binder in order to impart the necessary technological and operational properties. In the production of reinforced plastics, thermosetting binders are most often used, when heated, irreversible structural and chemical transformations occur; The use of thermoplastic polymers and elastomers is continuously expanding. Below is a brief description of the main types (Fig. 1.2) of polymers that have found application in the manufacture of PCM [3, 11, 24, 26, 28, 33].

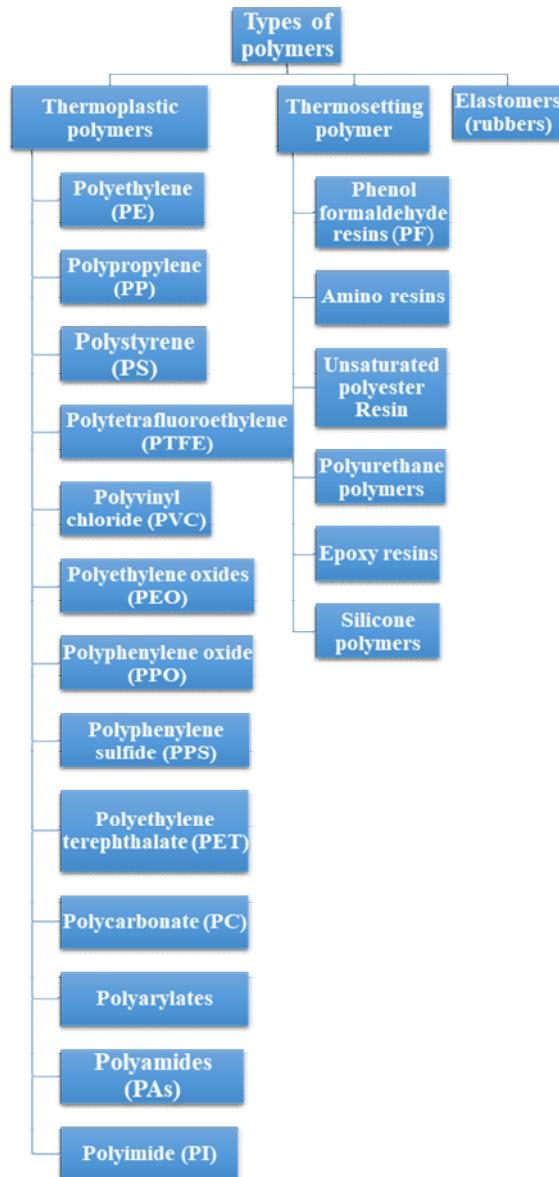


Fig. 1.1 The main types of polymers that are used in polymer composite materials

1.2.1 Thermosetting polymers

Thermosetting polymers under the action of heat and chemically active additives can acquire a spatial structure, which is accompanied by loss of fluidity. Thermosetting polymers are relatively rarely used in pure form when they contain only structuring additives. Usually, compatible and incompatible additives are introduced into them, such as fillers, diluents, thickeners, stabilizers, dyes, lubricants, and due to this, complex multicomponent materials are obtained - thermosets. The polymer base of thermoset - thermosetting polymer - is called here "resin" or "binder" [7, 42, 43]. Reactive oligomers with a molecular weight of up to 1500 are used as binders, in the molecule of which there are more than two functional groups. At the initial stage of obtaining materials and products, thermosetting binders have a low viscosity, which facilitates the process of molding products. The difference in the chemical structure of thermosetting binders, a wide range of hardeners, initiators of curing, modifying additives,

the use of various fillers allow to obtain structural materials with a very large range of strength, electrical, tribological and other operational characteristics. Depending on the type of binder, thermo-plastics are divided into phenoplasts, aminos, polyester, epoxy, polyurethane, silicone and other plastics.

Phenol formaldehyde resins (PF) or phenolic resins

Phenolic resins are products of the interaction of phenols and aldehydes, most often phenol and formaldehyde (Fig. 1.2). Depending on the conditions of production, the final products differ in chemical structure, molecular weight and ability to cure. There are two types of phenol-formaldehyde resins (CFF) - rezol (thermosetting resins, obtained with an excess of formaldehyde) and novolac (thermoplastic resins, obtained with an excess of phenol) [44, 45].

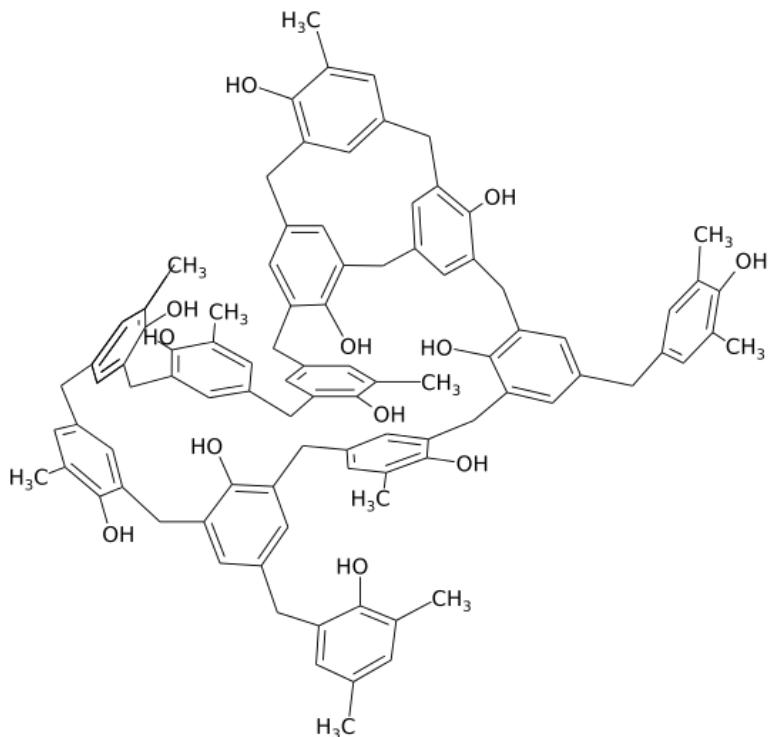


Fig. 1.2 Formation and structure

In the uncured state, phenol-formaldehyde resins are fragile transparent amorphous mass, passing into a liquid state at 60 ... 120 °C. The properties of resole resins change over time, and novolac resins, in the absence of moisture, are stable during storage. The maximum curing temperature of the resin lies in the range of 140-200 ° C. Resins curing products - resitic - brittle materials with non-crystalline structure, possessing high strength, electrical insulating, anti-corrosion properties. Resites are resistant to most acids. The degradation temperature of phenol-formaldehyde resins is above 300 ° C [46, 47].

Recycling of phenol-formaldehyde resins in the production of polymer composite materials includes the impregnation of woven and non-woven fiber fillers, paper and other materials [48, 49]. After curing, composite materials are processed by direct and injection molding, injection molding, extrusion, and vacuum molding [48, 50].

Amino resins - binders obtained by condensation of urea (melamine, aniline) with formaldehyde.

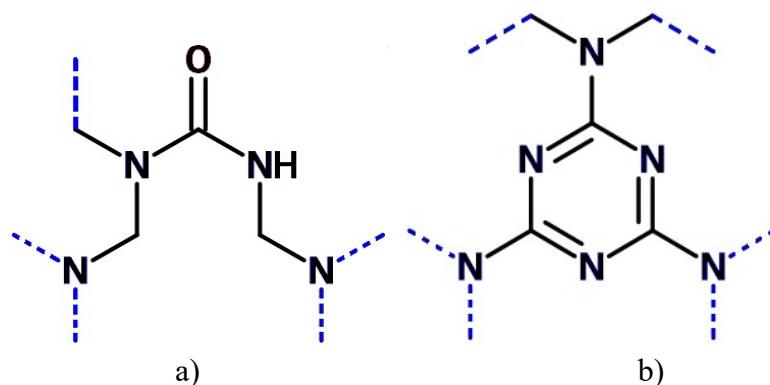


Fig. 1.3 The structure:

- a) of the molecule urea-formaldehyde, also known as urea-methanal,
- b) of the molecule melamine.

Urea-formaldehyde (or urea-formaldehyde) resins are obtained by heating aqueous solutions of a mixture of mono- and dimethylolurea with formaldehyde in a weakly acidic medium (pH 5-6) at a temperature of 60-100 ° C with a ratio of methylolurea and formaldehyde 1 to 1.5-2.

The resin molecule contains reactive methylol groups, which, while reducing the pH of the medium, are capable of further polycondensation with the formation of high molecular weight products and the release of water and formaldehyde.

The transition from low molecular weight products of a linear structure to a three-dimensional high-molecular polymer occurs gradually with loss of solubility and melting ability. But due to the small number of cross-links, the resin swells in water, alcohol, formalin and glycerin, and has low resistance to hot water and aqueous solutions of acids. Urea-formaldehyde resins are transparent and are used for the manufacture of products using the casting method.

Unsaturated polyester resins are hetero-chain thermo-reactive oligomers and polymers containing ester groups and multiple carbon-carbon bonds [47].

Raw materials for the production of unsaturated polyesters are unsaturated dicarboxylic acids, their mixtures with saturated dicarboxylic acids and polyhydric alcohols [48].

Solutions of unsaturated polyesters (60-75%) in monomers (for example, styrene) are called unsaturated polyester resins. Since monomers can react with polyesters dissolved in them, they are called active solvents. In copolymerization of polyesters with active solvents, non-meltable and insoluble compounds of spatial structure are formed [49].

Polymaleinates and polyfumarates are oligomeric polycondensation products of maleic and fumaric acids (or their derivatives) with aliphatic, less frequently with aryl aliphatic and alicyclic glycols (Fig. 1.4) [51].

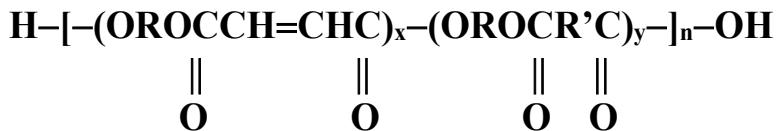


Fig. 1.4 General formula polymaleinates and polyfumarates

where R and R' are radicals that are part of glycols and unsaturated acids, usually x is 1-5, y is 1-5, n is 1-20.

Maleic acid is easily converted when heated to maleic anhydride, which is used in the synthesis of polyesters. The reaction of formation of polyester is as follows (Fig. 1.5):

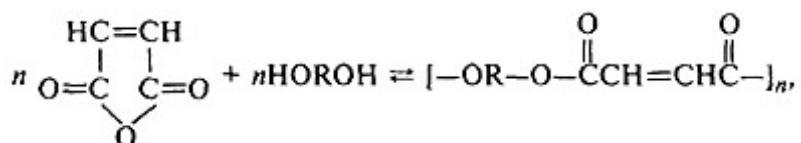


Fig. 1.5 Polyester formation reaction scheme

where R is C_2H_2 , C_4H_8 , C_6H_{12} , C_4H_6 groups.

Polyurethane polymers (PU) contain urethane groups (Fig. 1.6) in the main chain of macromolecules

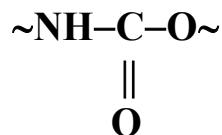


Fig. 1.6 Urethane group

They can have both linear and spatial structure (cross-linked polyurethanes). Cross-linked PUs are obtained by reacting di- and trifunctional compounds containing hydroxyl and isocyanate groups (Fig. 1.7) [52, 53].

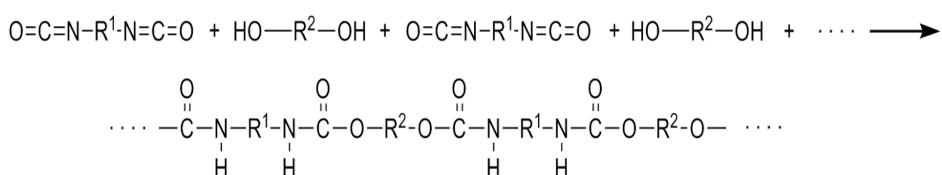


Fig. 1.7 Getting a polyurethane polymer through a reaction between diisocyanate and polyol

In industry, for the one step synthesis using crosslinked PU diisocyanates and oligomers containing three hydroxyl groups per molecule (polyoxytetramethylene glycol, polyoxyeth-

ylene and polyoxypropylene glycols, ethylene oxide copolymers, polycondensates of adipic or phthalic acid or mixtures thereof with ethylene, propylene or diethylene glycol) [54].

Crosslinked PUs can have both amorphous and crystalline structure. Their ability to crystallization is determined by the structure and molecular weight of the oligomeric unit. Unlike other thermosets, physical bonds (van der Waals and hydrogen) in PU make up 50 ... 90% of the total number of cross-links in the polymer volume. Therefore, the structure of PU has, even in the crosslinked state, the ability to collapse and rebuild when heated or mechanically loaded, i.e. it is capable of “self-healing” defects arising during deformation. The predominance of physical bonds in the network of crosslinked PU leads to the fact that the glass transition temperature is determined not by the number of cross-links, but by the nature of the oligomeric block and the number of urethane groups in it. With an increase in the number of urethane groups, the glass transition temperature increases [55].

By changing the nature and molecular weight of the oligomeric block and the density of the mesh, it is possible to obtain highly elastic or solid, rigid crosslinked PU. The physicomechanical properties of PU are determined by the structure of the diisocyanate, oligoether and hardener used in their preparation.

Cross-linked PUs are used as elastomers, lacquer bases, enamels, adhesives, sealants, fibers and artificial leathers, as well as in the form of elastic and rigid foams

Epoxy resins are monomeric, oligomeric or polymeric soluble compounds whose molecules contain at least two epoxy or glycidyl groups (Fig. 1.8) [52]:

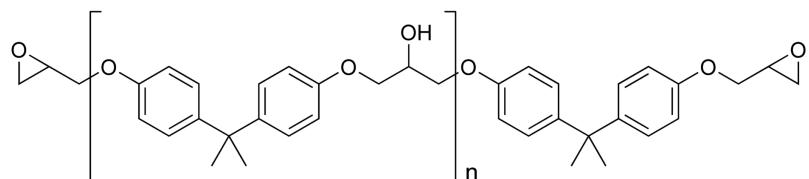


Fig. 1.8 Structure of epoxy resin - a product of condensation of epichlorohydrin with bisphenol A, n = 0–25

The preparation of epoxy is carried out by condensation in an alkaline environment of epichlorohydrin or glycerol dichlorohydrin with compounds containing mobile hydrogen atoms (phenols, amines, glycols, acids), as well as by direct epoxidation of unsaturated compounds with organic peroxy acids or hydrogen peroxide.

The reaction between epichlorohydrin and diphenylolpropane results in dianova epoxy:

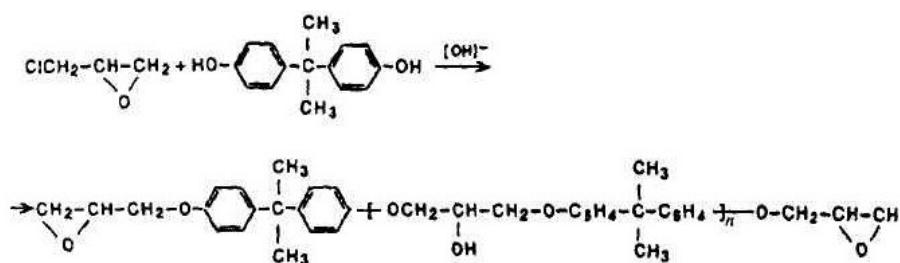


Fig. 1.9 Scheme of the reaction between epichlorohydrin and diphenylolpropane

Uncured resins are thermoplastic viscous liquids or brittle solids [48, 49].

There are two types of functional groups in the molecules of Dianov resin - epoxy and hydroxyl. Therefore, the hardeners of these resins can be compounds of various classes, and the modes of curing vary in a wide range: as without the supply of heat, when heated, in water.

Dianova epoxy resins with a molecular weight below 600-1000 are liquid products, above 1000 - glassy products. Resins are soluble in ketones, ethers, aromatic hydrocarbons. They are highly resistant to alkalis, salts, oxidizing agents, organic solvents. Polymeric composite materials made on the basis of epoxy resins have high mechanical properties.

The technology for producing materials based on epoxy resins is impregnated with fibers, fabrics, paper; curing and processing by the methods of direct pressing, contact molding, vacuum molding, etc. The processing temperature is 20 ... 180 °C [42, 44, 46].

Organosilicon compounds are organometallic compounds containing carbon–silicon bonds are heat-resistant high molecular weight organometallic compounds containing silicon and carbon atoms in the elementary unit of the macromolecule (Fig. 1.10). The polymers are resistant to most acids and alkalis. Resins are processed into polymer composite materials by impregnation of fillers, followed by curing. Products are made by direct pressing, contact molding, etc [57].

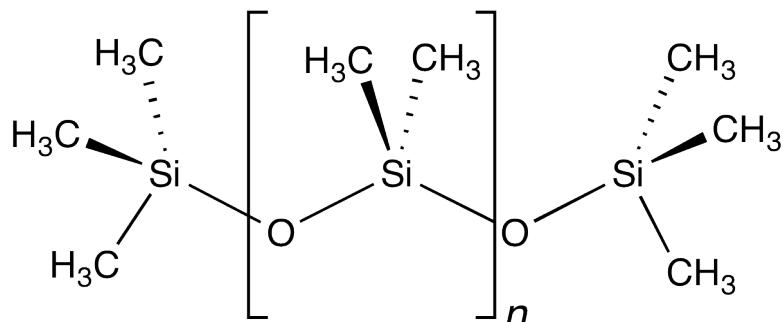


Fig. 1.10 Polydimethylsiloxane (PDMS) is a major component of silicones

Thus, thermosetting binders are relatively low-viscosity liquids (at processing temperature), which, after impregnation of the reinforcing material (fibers, yarns, tapes, fabrics) due to chemical reactions, turn into a non-meltable solid polymer matrix [8, 13, 23, 43 47].

Thermosetting binders have good technological properties (low viscosity and curing temperature). Well moisten and impregnate the reinforcing material; have good adhesion to most fibers, increased heat resistance, resistance in various environments. Their properties can be adjusted over a wide range by varying components, adding modifiers, catalysts, and changing curing conditions.

The disadvantages of these binders are brittleness, low fracture toughness and impact strength, the impossibility of recycling, the limited lifetime of the prepreg, significant chemical shrinkage in most cases.

1.2.2 Thermoplastic polymers

Thermoplastic polymers (thermoplastics) are polymers that soften when heated and harden when cooled [59, 60].

At normal temperatures, thermoplastics are in a solid (glassy or crystalline) state. When the temperature rises, they become highly elastic and then into a viscous state, which allows them to be molded by various methods. These transitions are reversible and can be repeated many times, which makes possible, in particular, the processing of household and industrial waste into products.

The choice of thermoplastic is determined by very many factors: the operating conditions of the product, the technological properties of the polymer, the cost of the plastic, its availability, the ability to be painted.

Polyethylene or polythene (abbreviated PE; IUPAC name **polyethene** or **poly(methylene)**) is one of the most widely used polymers. The industry produces low-pressure polyethylene (HDPE) and high-pressure polyethylene (LDPE). Durability, heat resistance and chemical resistance of HDPE are higher than LDPE. Gas permeability, on the contrary, is higher in LDPE. The destruction of polyethylene occurs at temperatures above 290 ° C, and solar radiation leads to thermal aging. At room temperature, polyethylene is resistant to diluted sulfuric and nitric acids, concentrated hydrochloric, phosphoric and hydrofluoric acids, has low water absorption [41, 43].

PE is processed by injection molding, extrusion, extrusion, well welded and mechanically processed.

Polypropylene (PP) has a high wear resistance and withstands bending. In the absence of air, thermal destruction occurs at 300 ° C. Polypropylene is resistant to many acids and alkalis. Concentrated sulfuric acid weakly destroys poly-propylene at room temperature and catastrophically at minus 60 ° C. Polypropylene is unstable to the action of strong oxidizing agents. Polypropylene is processed by injection molding, extrusion, vacuum molding, pneumatic molding, blowing, welding, pressing, spraying, it is processed by cutting [41, 44].

Polystyrene (PS) is a brittle polymer with high radiation resistance, easily aging. Thermal destruction starts at temperatures above 266 ° C. Polystyrene is resistant to some mineral and organic acids, alkalis, transformer oil, is destroyed by concentrated nitric and acetic acids [45, 46].

Polystyrene processing technologies: injection molding, extrusion, vacuum molding, pneumatic molding.

Polytetrafluoroethylene (PTFE) is a linear polymer having the chemical formula $[-CF_2 - CF_2 -]_n$. The degree of crystallinity of the polymer is 95%, the melting point (T_m) is 310–315 °C, the density is 2100–2300 g/cc (the highest among the known polymers). The polymer is opaque. Decomposes with the release of fluorine compounds at a temperature (T_{test}) above 415 °C.

Polytetrafluoroethylene has the properties of self-lubricating, has a low coefficient of friction. It is the most chemically resistant to the action of highly concentrated and dilute ac-

ids and alkalis, strong oxidizing agents, a polymer that is not affected by fungi. Excellent dielectric [61, 62].

Polytetrafluoroethylene is processed by sintering pre-pressed tablets. After special pre-treatment, the polymer is machined, welded and glued. Some modifications of polytetrafluoroethylene are processed by powder metallurgy, pressing, extrusion, injection molding, and sputtering.

Polyvinyl chloride (PVC) is an amorphous polymer with good electrical insulation properties, resistant to chemical reagents, does not support combustion. Atmospheric-resistant, at temperatures above 150-170 °C, decomposes with release of hydrogen chloride, heat and the formation of double bonds. It has low frost resistance (down to minus 10 °C) and heat resistance [43, 46, 48].

Polymethylene oxide (PEO) is a linear polymer having the chemical formula $[-\text{CH}_2 - \text{O}-]_n$. Polymethylene oxide is known abroad under the name "acetal or polyacetal resins". The polymer is well resistant to fatigue and dynamic alternating loads, has low creep and high wear resistance, has a low coefficient of friction on steel (0.2-0.35). In the processing of polymethylene oxide using the method of injection molding, extrusion. The material is well processed by cutting.

Polyphenylene oxide is a simple aromatic polyester of a linear structure. Receive dehydropolycondensation of 2,6-dimethylphenol. Polyphenylene oxide can be processed several times without changing the properties on injection molding machines, it is distinguished by high processability. The polymer is non-toxic, resistant to aggressive media, fungal mold. Processed by injection molding, extrusion. From polyphenylene oxide can be obtained thin-walled products of complex shape [3, 6, 47].

Polyphenylene sulfide (PPS) is a simple aromatic polyester. It is obtained by polycondensation of salts of diphenylopropane with 4,4'-dichloro-diphenylsulfone. It is characterized by high heat resistance, resistance to oxidation, radiation resistance. By chemical resistance is second only to polytetrafluoroethylene. Products made from polyphenylene-sulfide can be used for a long time at 260 °C, the mechanical and physical properties of the polymer remain unchanged for 200 hours at 260 °C, and complete decomposition occurs at 720 °C. Polyphenylene sulfide is processed by injection molding, pressing, plasma spraying, used for impregnation of fabrics [4, 23, 35, 43].

Polyethylene terephthalate (PET) is a complex linear aromatic polyester of terephthalic acid. The polymer has a low friction coefficient and hygroscopicity. For products made from it, is characterized by the stability of the form. Polyethylene terephthalate is resistant to the action of weak acids, mineral salts, esters, fats. In the polymer product is processed by injection molding [45, 47].

Polycarbonates (PC) is a complex polyester of carbonic acid chloride (phosgene) and diphenylopropane. The polymer is optically transparent, resistant to ultraviolet radiation, has

low hygroscopicity and resistance to microorganisms. For products made from it, characterized by high dimensional stability. Polycarbonates are recycled by all methods used to process thermoplastic polymers. The processing temperature is 240 ... 300 °C. Products obtained from polycarbonates are welded, glued, machined, joined with rivets and nails [45].

Polyarylates (the general formula [- (O) CRC (O) OArO-] n, where R is the residue of a dicarboxylic acid and Ar is the residue of a dihydric phenol) are complex aromatic polyesters of diatomic phenols. Obtained by polycondensation of terephthalic acid chloride with salts of diphenylolpropane. They have high strength and heat resistance. In some cases, successfully compete with structural metal materials. The temperature of thermal decomposition of polyarylates is 420 °C. The polymers are resistant to ultraviolet and ionizing radiation, to the long-term effects of diluted mineral and organic acids, gasoline, kerosene. Depending on the brand, polyarylates are processed into products by injection molding, injection molding and compression pressing, extrusion, and blow molding [5, 8, 46].

Polyamides are plastics based on linear synthetic high-molecular compounds containing amide groups –CONH– in the main chain. Polyamides are used in mechanical engineering, automotive, aviation, textile industries, as well as in medicine and other fields. The main distinctive properties of polyamides among most other plastics are: high strength, wear resistance, high resistance to environmental influences. It is obtained by ionic polymerization of caprolactam (–NH–CO–(CH₂)₅–). Polymers are characterized by high fatigue strength, wear resistance, impact toughness, low hygroscopicity, stability of properties at elevated temperatures, a pronounced melting point. Polyamides are resistant to organic solvents. The main methods of obtaining products from aliphatic polyamides are injection molding and extrusion. Aromatic polyamides are processed by direct compression with preheating. In the automotive industry in the form of cases of various electronic components, protective parts, fuel and hydraulic tubes, pens and other products [44].

Polyimides (sometimes abbreviated PI) is a class of polymers containing imide cycles in the main chain [45], as a rule, condensed with aromatic or other cycles. Heat-resistant aromatic polyimides, derivatives of tetracarboxylic acids with five-membered imide cycles in the main chain, have found the greatest use. Polyimides (PI) are obtained by polycondensation of pyromellitic acid and dianodiphenyloxide. The physicomechanical properties of polyimides are stable over a wide temperature range (from minus 200 to plus 300 °C). For products made from polyimides, they are characterized by high dimensional stability, low creep at high temperatures, high heat resistance and resistance to radiation, fast electrons and neutrons. Diluted acids have almost no effect on polyimides. They have a low coefficient of friction for steel (0.05 ... 0.17). Polyimide press powders are processed by the methods of direct and compression pressing, injection molding, and hot pressing [45, 48, 50].

Thus, most thermoplastics are characterized by higher productivity and more intensive processing methods; molding parts less energy-intensive; possible formation of large, complex configuration of parts; recycling is possible; characteristic is almost infinite viability of prepgs (time between manufacturing and processing into a product); reduced flammability, smoke emission during combustion and toxicity of combustion products; high resistance to

radiation; a combination of high strength and heat resistance (polyethersulfone, polyetherimide, polyphenylene sulfide) with high impact strength and crack resistance.

1.2.3 Elastomers

Elastomers are used in the plastics processing industry, most often as high molecular weight plasticizers to reduce the fragility of glassy or crystalline polymers. The use of elastomers in the composition of polymer composite materials is made difficult by reduced resistance to heat aging and thermal-oxidative degradation. In addition, the increased stickiness and deformability of elastomers usually do not allow them to be released in granular form (only a few elastomers are available today in the form of granules), which also complicates their use [48, 50].

However, the use of elastomers as components of composite composite materials (including structural materials) is continuously expanding.

1.3 Features modification of polymers

Modification of polymers is a directed change in the physicochemical, mechanical or chemical properties of polymers [25, 26]:

– structural - the modification of physical and mechanical properties without changing the chemical composition of the polymer and its molecular weight. The structural modification of PTFE includes mechanical activation [61], shock-wave processing [67], radiation exposure [66], the use of magnetic [78] and electromagnetic fields [77], etc.

– carried out by the introduction into the polymer of substances capable of interacting with it, including high molecular weight (plasticization, stabilization, filling). The latter is the introduction of various solid components in PTFE [52, 53]; matrix modification with activating additives of various sizes, forms and properties [54, 55]; the creation of nano-phase matrices with essentially different characteristics [66].

– chemical - the influence on the polymer of chemical or physical factors, which is accompanied by a change in the chemical composition of the polymer and (or) its molecular weight, as well as the introduction of a small amount of substance in the synthesis stage which enters the main monomer in copolymerization or copolycondensation. This, in particular, the synthesis of polymer matrices of various composition and structure [87, 88]; formation of mixtures by a combination of polymers and oligomers [99], etc.

It is expedient in the case of PCM based on PTFE that the polymer is modified by mechanical activation, which is associated with low energy and metal capacity of the equipment, the simplicity and safety of the process [68-70], and the introduction of appropriate fillers [40].

Depending on the time of impact and the momentum in the mixing process, due to the energy of elastic deformation in the surface layers of the material, there are active non-equilibrium excited states due to atomic oscillations, electron excitation and ionization, deformation of bonds and valence angles, as well as processes of migration of structural elements and mass transfer [51]. This process is called mechanical activation of the material.

There are two cases of mechanical activation: in the first, the time of mechanical action and the formation of the field of stress and its relaxation, the longer the chemical reaction

time (these processes are called mechanochemical); in the second, on the contrary, the time of mechanical influence and the formation of the field of stress is less than the time of the chemical reaction, or in general, these processes are separated in time. In the latter case, it is a question of mechanical activation [28, 42].

Mechanical activation is used to change the reactivity of solids, which means accelerating or increasing the effectiveness of chemical or physical processes, and is the most important stage of mechanochemical processes [29].

It is believed that when mechanical activation, in contrast to mechanical degradation and mechanosynthesis, mechanical forces do not initiate chemical reactions, but only reduce the activation energy in accordance with the costs of mechanical energy [56, 76].

The process of mechanical activation of substances is accompanied by a variety of phenomena. The following basic physical and chemical processes are registered: radiation of electromagnetic waves, heat release, emission of electrons, implementation of elastic and plastic deformations, slow relaxation of deformations and excess stresses in solids. This leads to the preservation of the substance composite excess energy, changes in the thermodynamic characteristics of the substance, increasing its reactivity [29].

The grinding of substances is carried out in order to obtain the maximum surface of the powder at minimum energy consumption, and activation - in order to accumulate energy in the form of defects or other changes in solids, which allow lowering the activation energy of its subsequent chemical transformation or improve the steric conditions for the process [41].

Fillers are introduced into polymers in order to create new polymer materials with a complex of valuable operational properties; improvement of technological properties and processability of filled polymers; cheaper materials; utilization of waste and environmental problems; getting decorative effects. The main types of fillers are dispersed (chalk, asbestos, aluminum hydroxide, talc, etc.), fibrous (metallic, glass, carbon, boron, organic, ceramic, filamentous crystals - mustaches), sheet (fabrics, paper, wood veneer, tapes, canvas, grids, non-woven materials), volumetric (volumetric fabrics, frame systems) and filled polymeric materials.

When developing a given structure of dispersion-filled material it is necessary to have data on the main characteristics of the filler: the form of particles; the size and distribution of particles in size; specific surface; porosity of particles; bulk density and true density; maximum volume fraction; pH of the surface of the particles.

Almost all fillers are polyfractive with a wide or narrow particle size distribution. Differences in granulometric composition of fillers are manifested in the packaging of particles, in rheological physico-mechanical and other properties of materials.

CHAPTER II

MATERIALS AND METHODS OF RESEARCH

2.1 Materials

2.1.1 Polymer composites based on polytetrafluoroethylene

Polytetrafluoroethylene is a high-molecular composition, molecules of which consist of a large number of identical atomic groups (-CF₂-) with: (-CF₂-CF₂-)_n chemical bonds. Tetrafluoroethylene is a primary monomer for PTFE [63, 64]. The resulting polymer is a loose, fibrous and cloggy white powder [61, 65, 66]. Its molecular weight is 140 – 10 000 t.

Tetrafluoroethylene is produced by heating chlorodifluoromethane (Freon-22). At the first stage, chloroform is fluorinated by reaction with dry hydrogen fluoride in an autoclave at 100°C

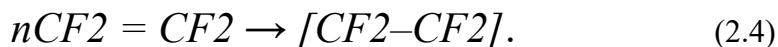


At the second stage, the pyrolysis of difluorochloro methane is carried out in a silver or platinum tubular reactor at 600–800°C.



As it is seen from the scheme of the process (2.2 – 2.3), difluorocarbene is the intermediate product.

Tetrafluoroethylene is easily polymerized by a radical mechanism with a high heat release (197 kJ / mol), which requires effective heat removal. Along with the high molecular weight polymer, oligomers are formed



Peroxides and azo compounds are the initiators of polymerization of tetrafluoroethylene, as well as various redox systems. The process is carried out in the absence of oxygen, which is not only an inhibitor but can cause an explosion of the monomer with its decomposition to carbon and CF₄. Suspension and emulsion polymerization methods at temperatures below 70°C are most commonly used methods [67, 68].

Materials and Methods of Research

On the basis of experiments, it was found out that PTFE used for these studies is the most relevant for the requested requirements (Table. 2.1).

Table 2.1
Characteristics of PTFE – unfilled [69, 70]

Characteristic	Value of the index for the material
Mechanical Properties	
Density, g/cc	2.13 – 2.19
Tensile strength (Moulding direction), MPa	15 – 35
Elongation at break (Moulding Direction), %	150 – 350
Hardness (Shore D)	57 – 64
Deformation under load, %	
1 hr, 23° C, 14.2 MPa	11.8
24 hrs, 23°C, 14.2 MPa	14.3
permanent deformation	7.9
1 hr, 150°C, 5 MPa	10.0
Compressive modulus at 0.2% off-set, 23°C, MPa	600 – 700
Flexural modulus at 0.2% off-set, 23°C, MPa	690
Electrical properties	
Volume resistivity, Ohm-cm	10 ¹⁸
Surface resistivity, Ohm	
Dielectric constant	
60 Hz	2.1
10 ⁶ Hz	2.1
Dissipation factor	
60 Hz	<0.0003
10 ¹⁸ Hz	<0.0003
Dielectric strength, Kv/mm	
– in air (tape)	60 – 80
– in oil (extruded or moulded)	35 – 24
Thermal properties	
Melting temperature (DSC point of fusion), °C	327
Coefficient of thermal expansion (TMA method) (23 – 200 °C)	
– in moulding direction (MD), 10 ⁻⁶ /°C	142
Thermal conductivity, W/(m K)	0.24
– in moulding direction	
Max. working temperature, °C	260

Max. working temperature – short term, °C	300
Min. working temperature, °C	-200
Flash point, °C	530
Limiting oxygen index, %	>95
Friction Properties	
Coefficient of friction, dry sliding	
– static	0,08
– dynamic	0,06

Polytetrafluoroethylene is a crystalline polymer. The degree of powder crystallinity obtained by polymerization in the aquatic environment can reach 97%. At temperatures as low as 327 ° C, monolithic PTFE consists of crystalline and amorphous regions in high-plastic state. Its melting temperature is about 327 ° C. In this case, there is no melting in the usual sense of the word, and the polymer goes into an amorphous state; it softens, becomes semi translucent and gel-shaped. The temperature of the amorphous phase is about 120 ° C. The degree of crystallinity of monolithic PTFE depends on the cooling rate below the melting point. It is possible to obtain the degree of crystallinity of PTFE up to 85% during the slow cooling of low-molecular PTFE, and the degree of crystallinity of the highest molecular PTFE may be no more than 65%. At high cooling rates (quenching), the degree of crystallinity of PTFE is about 50%. The density of PTFE depends on its molecular mass and the degree of crystallinity [71, 72, 73].

PTFE of five grades is obtained in the form of bulk, fibrous powder (density 2.19 – 2.21 g/cc) with the bulk density of 0.40 – 0.50 g/cc.

Monolithic (compact) PTFE is obtained by pressing the powder with subsequent heat treatment (sintering) in a free state or under pressure at temperature 370 – 390 °C.

The elasticity coefficient of PTFE depends on the degree of crystallinity and temperature. The polymer does not become brittle at the temperature below the glass transition temperature and even at the temperature of liquid helium (-269.3 ° C)

According to ISO 13000-1, depending on the purpose and methods of processing, there are such grades as [74, 75]:

C – for production of special products;

P – for insulation and condenser films;

PN – for electro technical and other products of increased reliability;

O – for common items and compositions;

T – heavy section and pipe arrangement.

The PTFE is characterized by the phenomenon of shear thinning or pseudo plasticity, which is the limiting value of deformation during the action of external loading. PTFE is plastically deformed, when high loads are applied. The residual deformation without violation of integrity can be very large (with bending, PTFE can be squeezed by 3.5 times). It should be borne in mind that PTFE has a perfect “plastic memory”. The restoration of its former form starts while heating above the temperature at which the deformation of PTFE occurred, and it finishes at 327 ° C [76, 77, 78].

The main properties of the different grades of PTFE are given in table 2.2 [62, 79].

Materials and Methods of Research

PTFE is the most stable of all known plastics. Neither acids and oxidizing agents, nor alkalis and solvents influence it at all. It is not wetted by water for short-term immersion (wetting angle 126 °), but it is wetted in case of prolonged periods in distilled water (within 15 – 20 days). In salt water (for example, seawater) a film of salts is deposited on the surface of PTFE after 15 – 20 days, and it can be washed off with distilled water. It almost does not absorb water [62, 80].

Table 2.2
Properties of polytetrafluoroethylene of different grades

Indicator	Grade of PTFE-4				
	C	P	PN	O	T
Density, g/cc	2.19	2.19	2.19	2.2	2.21
Failure resistance, N/mm ²	25.5	24.5	24.5	22.5	14.7
Breaking elongation, %	350	350	350	350	350
Thermal stability, g	100	100	100	100	15
Volume resistivity, Om·m	1019	1019	1019	–	–
Tangent corner of dielectric losses at frequency of 108 Hz	0.00025	0.00025	0.00025	–	–
Dielectric constant at frequency of 108 Hz	2	2	2	–	–
Electrical strength at constant voltage (thickness of sample 0,098±0,004mm) kV/mm	50	60	50	–	–

Mass moisture permeability of PTFE at 20°C is $(3 - 6) \cdot 10^{-8}$ g/(sm·g·kPa), vapor transmission at this temperature is $(0.6 - 1.2) \cdot 10^{-8}$ g/(sm·g·kPa).

PTFE is resistant to tropical conditions and has funginertness.

PTFE is transparent for visible light in case of the small film thickness.

PTFE is not resistant to ionizing radiation. A marked deterioration in mechanical properties is observed at integral dose of 104 rad.

Even at temperatures above the decomposition temperature (415 °C), PTFE does not pass into the viscous flow state (its melting viscosity is equal to 10⁹ Pa·s at 370 °C, that is, one million times bigger than the viscosity required for casting under pressure). Therefore its processing is possible only by the method of sintering (free or under pressure) of pre-pressed pre-forms (rods, plates, parts). Depending on the cooling rate (to the temperature below 250 °C), after sintering, it is possible to get products with a crystallinity degree of 50% and a density of 2.15 g/cc or with a degree of crystallinity more than 65% and a density above 2.20 g/cc [81, 82].

In this research, PTFE grades PN, which is industrially manufactured at the Ural Chemical Plant (PA “Halogen”, Perm, Russian Federation) according to ISO 13000-1 is used for the production of the compositions. The main indicators of the material are given in Table 2.3 [83, 84].

Table 2.3
Main indicators of PTFE grades “PN”

Average particle size of powder, μm	50 – 500	Conductivity factor, $\text{W}/(\text{m} \cdot \text{K})$	0.25
Molecular weight, ths.	100 – 150	Compression strength, MPa	18.0
Degree of crystallinity before sintering, %	95 – 98	Compressive modulus, MPa	686.5
Degree of crystallinity after sintering, %	50 – 70	Tensile Modulus, MPa	410.0
Density, g/cc	2.15 – 2.26	Longitudinal strength, MPa	25.0
Melting point of crystallites, K	600 ± 10	Tensile elongation, %	50.0
Glass transition temperatures of the amorphous sections, K	150 ± 10	Water sorption per 24hours, %	0.0

The material has an abnormally low coefficient of friction (0.01–0.04), but it is prone to cold flow, which can be reduced by the introduction of fillers.

2.1.2 Antifrictional properties of PTFE composites

The positive effect of PTFE filling for the improvement of tribotechnical characteristics is due to the weakening of intermolecular bonds in the polymer, the formation of the optimal structure of the material. The participation of fillers in friction as inhibitors increases the performance of the surface film for frictional transfer [15, 40, 85].

In the practice of tribotechnical materials for PTFE, many potential fillers are used. Additives of inorganic and organic nature are used, having different shapes, sizes, concentrations, surface conditions, the nature of their distribution in the matrix [86, 87]. Applied as dispersed and fibrous fillers to improve the performance properties.

The influence of fillers on the properties of amorphous-crystalline polymer materials is determined predominantly by two factors: the influence on the structure-forming processes in the polymer matrix and, consequently, the change in its properties, as well as the mechanical, thermophysical and other properties of composites at the expense of the fillers themselves [59, 62, 88]. An important role in this is played by the content of the filler in the composite.

At low concentrations, its particles manifest themselves, mainly as artificial crystalline nuclei (ACN), and at large they impose a complex effect on the structure and properties of the polymer, resulting in amorphous polymer, with the formation of continuous structures of the filler particles, an increase in the number of defects in the form of emptiness and so on [60, 61, 89, 90].

Particulates of highly dispersed filler may be centers of spherulites, and also displaced during crystallization in intereron disordered regions and located, mainly, within the boundaries of the section of the spherulites, in the places of defects. Particles of low-disperse fillers, the size of which is large in comparison with the diameter of the core of the spherulites, can not be their centers - on the nucleation is influenced by the surface of these particles

When the filler particles have anisodiametric shape, depending on the ratio between their length and the size of the spherulites, several morphological types of spherulite structures can be formed - from spherical spheroidal processes to long spherulite chains. The highly-filled crystallized polymers have a loose spherulite structure and contain aggregates of filler particles.

The technology of PCM processing and the introduction of fillers actively influences the size and morphology of spherulites in the structure of PTFE. However, there is a certain limit of concentration of the latter, above which their effect on the size of the spherulites is negligible.

The degree of this effect depends not only on nature, but also on the size and shape of the particles. The density of packaging of spherulites in a filled polymer is greater if the filler contributes to structure formation [62, 95]. There is a dependence of properties on the size in the case of the identity of processes, namely, the larger size of the spherulites reduces the strength and deformability of polymers [24, 62, 66, 93]. The growth of crystalline formations with a large number of centers in the presence of ACNs and the deceleration of linear growth of crystalline structures appears to be effective for high crystalline polymers. It is established that the structure and its changes at all levels of the molecular and supramolecular organization are the determining factor in the mechanism of frictional interaction of polymers and materials on their basis. Changing the structure in the surface layers of the polymeric material with friction is accompanied by a reorientation, amorphization, destruction and recombination of individual molecules and structural formations. The conclusion is drawn on the promising use of friction sites for filled polymeric materials, in particular, based on PTFE [63, 94]. Research on the mechanisms of influence fillers Tribotechnical properties of thermoplastics, dedicated unreasonably little work. Among them, one can identify complex studies [5, 6, 8, 12, 20, 64, 78]. Structural-phase transformations in modified PTFE, depending on time, temperature and contact pressure in the friction pair, were investigated by X-ray diffraction analysis. The influence on tribotechnical properties of modified PTFE fillers, temperature, friction conditions was studied. The search for the optimal technology for combining the components of the filled system is determined by the design and purpose of the friction unit. The same fillers or their compounds in different volumes have a different effect on the antifriction properties of the friction pairs, depending on the operating conditions and the matrix. The development of a formulation suitable for use in a wide range of operating conditions is practically not feasible - a complex system approach is required.

Nevertheless, the research results show that in order to significantly improve the antifriction characteristics of polymer compositions as a whole, at least 20% of the filler is required.

The filling of more than (30-40) % leads to a decrease in the cohesive strength of the composition due to an increase in the specific surface of the fillers and a decrease in the thickness of the phase-layer in the filled system [69]. Established some features of friction and wear of composite materials based on PTFE [70, 74, 78, 95].

For the unfilled polymer together with the thermo-oxidation destruction there is a significant structural reconstruction associated with the melting of the surface layer, followed by its crystallization at the time of removal of the material from the friction zone. Due to the structural and kinematic features of the PTFE molecule, the torsional oscillations of its segments can occur in a coherent manner, accompanied by the promotion of chains or by changing the

direction of the spirals [12, 75, 96]. Such conformational rearrangements are associated with intense rotation around longitudinal axes, significant elongations and translational displacements of molecular chains.

A conformational-mobile model of PTFE friction surface and a turning-isomer mechanism of interlamellar sliding, which explain the low adhesion and antifriction properties, as well as their anisotropy in fluoropolymers, is proposed. Introduction to the PTFE matrix of the filler, as a rule, increases the generation of thermal energy in the friction zone. The process of wearing this polymer and its composites during friction on metallic adjacent surfaces is determined by the macrocycles "thermal expansion - wear" of the heat-loaded near-surface layer, which are periodically repeated [22, 76, 97]. In work [77, 98, 99] the influence of fillers of various chemical nature (bronze, glass fiber, explosives, carbon, graphite, polymer) on the tribotechnical properties of PTFE at ambient temperature and at high temperature was investigated. The results showed that the wear resistance of all composites was significantly higher than that of pure PTFE. Composites filled with graphite or polymer showed lower friction and moderate resistance to wear at ambient temperatures and at high temperatures.

The following can be noted:

- in the superficial layers of PCM, friction occurs at the same physical and chemical processes, regardless of the composition of fillers;
- the polymer matrix of the composite, when friction, is amorphous due to the destruction of crystalline regions, the breakdown of the molecular chain links in the amorphous phase;
- in the transfer film formed on the metal countertile, a texture of both crystalline and amorphous portions of the PTFE matrix is observed;
- at high content of the fiber filler, the PTFE matrix on the transfer film is almost in an amorphous state;
- the introduction of fillers in all cases leads to a deterioration of the antifriction properties of modified PTFE (the coefficient of friction increases in (1.5-2.0) times, at the same time significantly increases wear resistance (for some materials up to 2000 times).

The physical model of the friction and wearing mechanism and the thermodynamic model of the metal-polycrystalline tribosystem [3, 15, 99, 100] are proposed on the basis of joint structural and thermodynamic analysis of the mechanism of formation of the film of frictional transfer and of the physicochemical processes of the formation of dissipative tribonstructures as a result of the frictional interaction of a filled PTFE with a metal counterfilm.

The principles and regulations that underpin these models allowed to formulate the basic technical requirements for the composition, structure and properties of composite materials and technologies for their preparation. In particular, the introduction of fillers into the matrix of the polymer should contribute to:

- the highest strength and stiffness and minimum reduction of these parameters at higher temperatures;
- the highest possible thermal conductivity and heat capacity change maximum;
- minimum force (coefficient) friction;
- the ability polymer matrix to form a layered ordered (oriented) structure type ACN amorphous phase.

The strength of the adhesive polymer and filler connection, that the energy of interaction at the interface determines the strength characteristics of the composite. You need to strive for increased interaction at the interface of the polymer and filler limits [30, 78, 80, 101].

2.1.3 Carbon Fiber

High molecular weight carbon fibers are widely sought after in the production of composite materials due to the unique combination of physical, mechanical and chemical properties (Table 2.4) such as high modulus of elasticity and strength, low density, high electrical conductivity, low coefficient of friction and thermal expansion, high resistance to atmospheric influences and chemical reagents [102].

Table 2.4
Main characteristics of carbon-fibers [103, 104]

Parameter	Value
Carbon content, %	80.0 – 99.5
Diameter $d \cdot 10^{-6}$, m	4 – 30
Density, g/cc	1.40 – 2.00
Longitudinal strength, Pa	0.1 – 3.5
Tensile modulus, hPa	10 – 7000
Tensile elongation	0.5 – 1.3
Specific thermal capacity $\lambda \cdot 10^3$, J/(kg·K)	0.8 – 1.7
Conductivity factor, W/(m·K)	0.8 – 125.6
Electrical resistivity, Ohm·m	$1 \cdot 10^{-5}$ – $1 \cdot 10^4$
Thermal expansivity $\alpha \cdot 10^6$, K ⁻¹	2 – 20
BET surface area, m ² /g	0.3 – 1000.0
Burning duration, s	3 – 300
Resistance K to oxygen under an inert or reducing atmosphere	to 673 – 723, to 3273

CF (carbon fibers) are manufactured as strands of infinite length, cords, riCFons, staples, knitted fabric, yarn, felt, paper, cardboard, mattress, net, etc. Unlike other types of fibrous fillers, the textile shape of carbon fibers is determined by geometry of the source material. Note that CF are not made specifically for anti-frictional purposes.

In modern scientific and technical literature, the classification of CF is often based on the value of the final temperature of heat treatment in the production of CF by thermolysis of organic material and carbon content in the composition of the product.

By this CF is divided into three classes (Table 2.5):

- 1) partially carbonized (charcoal, pyrolysis), heat treatment temperature (HTT) to 773 K, carbon content up to 90% (mass);
- 2) carbonized, HTT 1 073–1 773 K, carbon content is 91 – 98% (mass);
- 3) graphitized, HTT more than 1 773 K, carbon content is above 99% (mass).

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CF has a relatively high chemical and corrosion resistance under normal conditions. However, under the influence of strong oxidants and halogens, their resistance is significantly reduced (especially at the elevated temperatures). It is used to the surface dressing of high-modulus fibers, which is carried out to increase the interlayer strength, the small value of which was a serious problem in the first years of the carboplastics production. Usually carbon and graphite are resistant to the influence of alkaline solutions at all concentrations and temperatures, as well as aqueous solutions of most inorganic salts up to their boiling point.

Table 2.5
Classification of physico-mechanical properties of CF

Class	Longitudinal strength, Pa	Tensile modulus, hPa	Density, g/cc	Elongation, %	Electrical resistance, 10^5 Om·m
HM	1.4 – 2.5	342 – 540	1600 – 2000	0.4 – 0.6	0.7 – 1.0
HT	2.3 – 3.4	196 – 314	1700 – 1800	0.5 – 1.1	1.0 – 3.0
MM	1.2 – 2.3	63 – 176	1400 – 1700	0.8 – 1.8	3.0 – 7.0
LM coal graphitized	0.5 – 1.2 0.4 – 0.9	37 – 40 41 – 42	1500 – 1600 1400 – 1500	2.0 – 2.5 1.5 – 2.0	12.0 – 18.0 5.0 – 6.0

Carbon fibers at 323 K do not significantly reduce the strength or modulus of elasticity under the influence of such reagents: 50% (v/v) of hydrochloric, sulfuric and nitric acids, sodium hydroxide solution, hydrophosphoric and orthophosphoric acids. At 293 K, the fibers are resistant to glacial acetic acid, 90% (v/v) formic acid, 32% benzene sulfate acid and 0.880 molar aqueous ammonia solution. Carbon fibers easily react with most metal melts.

The thermal coefficient of the linear expansion of the carbon fiber is approximately $1 \cdot 10^{-6}$ K⁻¹ in the direction of the axis of the fiber and $19 \cdot 10^{-6}$ K⁻¹ in the transverse direction. Low coefficients of the thermal expansion of CF make it possible to produce composites, in which there is practically no shrinkage during press molding. This allows more accurate production of the details of different wall thicknesses without distortion and formation of cracks.

Modern ideas about the structure of CF are presented in the works of W. Ruland, B. Wiks and M.K. Norr, as well as other authors [105, 106].

By the generalization of the proposed models, the structure of anisotropic CF can be represented by a scheme where the main element of the structure is the molecular (base) band of aromatic condensed carbon. Such intermediate band heteroaromatic polycondensed structure with a certain placement of carbon hexagons, called parquet components, is already formed at the initial stages of carbonization of the polymer. The molecular bands are predominantly oriented along the axis of the fiber. In the process of CF producing, neighboring macromolecules are oriented towards each other in such a way that the parquet planes are arranged in a parallel manner, forming a turbostratic structure of carbon [107]. This structure differs from the graphite structure by the fact that the basis planes are parallel and unfolded under different angles to each other. Turbostratic carbon is formed in the microfibrils that contain bundles of parallel turbostratic planes (crystallites). Measured parameters of crystallites CF with HTT

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1 173 – 2 773 K, where $L_a = 2 – 20$ nm, $L_c = 1 – 12$ nm, the distance between adjacent planes in the crystal is $d_{002} = 0,372 – 0,339$ nm. The average size of the microfibril is 5 – 10 nm.

The parameters L_a and L_c are being increased with increasing of HTT and the interplanar distance d_{002} and the orientation angle decrease (Table 2.6).

Table 2.6
Structural characteristics and properties of carbon fiber [108]

HTT, K	d_{002}	L_a	L_c	$\phi_0/2, {}^\circ$	σ	E
	nm				MPa	
CF on the basis of PAN						
3073	0.343	18.0	10.0	14.4	0.7	579
3073	3.420	9.0	4.1	–	–	9
CF on the basis of PAN borated						
3073 (0,8–1,0 % B)	0.336	80.0	40.0	5.7	0.80 – 0.93	632 – 820
3073 (0,3 % B)	3.360	28.0	11.0	–	–	902
CF on the basis of mesophase pitch						
1273	0.345 – 0.355	–	2.5 – 6.0	30 – 40	0.69	37
1773	0.340 – 0.343	–	8.0 – 10.0*	10 – 20*	1.0 – 1.5	170 – 240
2273	0.336 – 0.370	–	>100.0	5 – 10	1.72 – 2.51	520 – 834
Note. * at HTT = 2 223 K						

The study of the structure of the CF cross-section allows selecting a surface shell, in which the crystallites are oriented predominantly along the axis of the fiber and the core with a random orientation of the crystallites [45, 109].

CF has a variety of internal and superficial micro- and macrodefects that are found in the original organic fiber, and which arise in the process of heat treatment.

Vacancies and foreign inclusions belong to the bulk microdefects of CF. Imperfection of the CF structure lays the foundation of its hydrophilicity [20, 48, 110].

The superficial and internal layer of CF are similar and have a fibrillary structure. The surface of the explosives is characterized by microhardness, transverse and longitudinal cracks, open voids, external inclusions, deposits of carbon dioxide and other graphitization products.

The highly oriented surfaces of the fiber have base planes of the low-energy crystallites and sharp edges with high energy. The first ones chemosorb part of the oxygen to form non-persistent carbon-oxygen complexes, the latter form strong oxygen complexes. The less oriented part of the fiber is also involved in oxygen chemisorption. Other gases are sorbed physically or chemically on the CF surface.

A part of oxygen forms either acidic or neutral groups, and the presence of oxygen-containing groups leads to the chemisorption of the CF water. It increases the hydrophilicity of the PTFE-composite from CF and the growth of its water sorption.

Structural defects distort the surface of the CF, thus affect their interaction with the matrix, and combined frictional surface. Heterogeneity of the CF structure leads to the microanisotropy of the mechanical, thermophysical and frictional properties, and complementing the anisotropy of these properties, caused by macroanisotropy of the composite structure. Under the influence of alternating loads and frictional forces, the flaw of CF and the ability of their surface to chemisorption of carbon are increased. All these phenomena reduce the durability of PTFE-composite from CF as a filler and increase its moisture absorption.

Natural and chemical organic fibers are the primary raw material for the production of CF. Organic fibers turn into carbon fibers because of the heat treatment in the inert atmosphere [21, 43, 67, 111]. This complex transition is accompanied by the simultaneous flow of a large number of sequential and parallel heterotic and homolithic reactions. There is a change in the structure while preserving the elements of the original polymeric skeleton. The type of raw material and the processing conditions determine the strength and physic mechanical properties of CF.

PAN-B (poliacrylonitrile fiber) and HC-B (hydrated cellulosic fiber) are the main types of raw materials for obtaining CF as well as fibers based on poliacrylonitrile, lignin and oil pitch (NP) [22].

Carbonized carbon fibers, which are less destructive in the process of obtaining and recycling of filled PTFE [23, 28, 62], were under research in this study. The fibers were obtained from hydrath cellulose tissue using a mixture of antipyraines $\text{Na}_2\text{B}_4\text{O}_7 = 10\text{H}_2\text{O} + (\text{NH}_4)_2\text{HPO}_4$. Hydrath cellulose fabric processed by the antipirane is thermally treated in natural gas CH_4 at 723 ± 20 K by pulling through a continuous furnace at the speed of 10 m / h. Partially carbonized UT-4 fabric is the result of the process. Carbonized fabric UTF-8 was obtained after further annealing of UT-4 tissue in the atmosphere of CH_4 at 1123 ± 50 K [18 – 20].

2.1.4 Epoxy Polymers

Epoxy resin is high-viscosity transparent liquid, which is structured at normal and elevated temperatures without external pressure [10, 34, 43]. Hardener polyethylenepolyamine – PEPA was applied for structuring epoxy compositions. 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 increase the hardness, loading capacity and wear resistance.

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 $-100\dots+200$ °C, in water, gas and in other environments. Nowadays polymer self-lubricating materials – tribopolymers are designed and used [8, 9, 46].

In the work complex of ingredients was used as a 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 [5, 9, 42]. Hardness on

a Moths scale of graphite is 1, density – 2.09…2.23 g/cc. Introduction of graphite in epoxy composite materials increases the stability of dimensions, antifriction characteristics, thermal and electrical conductivity [11, 24, 34]. 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 1.25…1.9 g/cc. Hardness on a Moths scale – 2.5-3. The powder of copper is chemically little active. The dimensions of copper particles copper are 30…100 mkm.

The powder of oxide copper (CuO) was used in the work. The density of CuO is 6,31 g/cm³, 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 microns.

2.2 Research method

The methodology of studying the composite properties included determining the density ρ (g/cc), breaking strength σ_b (MPa), relative elongation δ (%), and wear intensity $I \cdot 10^{-7}$ (mm³/N·m) (volume lost per unit normal load per distance of sliding) in accordance with the regulations.

Test samples were obtained by cold molding technology (molding pressure $P_{mold} = 50.0 - 70.0$ MPa), followed by the free sintering of tablet blanks in air at 365 ± 5 °C at a speed of heating-cooling of 40 °C/h.

The tests of strength and relative elongation at break were performed on ring samples of 50×40 mm in diameter and 10 mm in height using rigid half-discs (ISO 527-1:2012 [115] and standard ASTM D638-14 [112]) on an R-1 disruptive installation (ASTM D695-15 [113]) at the motion speed of sliding member of 0.25 cm/min.

The density ρ (g/cc) of the samples was determined by hydrostatic weighing (ASTM D1505-10 [114]).

The study of the wear rate was carried out on an SMT-1 serial friction machine according to the “partial insertion-shaft” scheme.

The set of samples was tested in the friction mode without external lubrication at the sliding speed of $v = 1$ m/s and pressure of $P = 1$ MPa. The counterbody was a roller having a diameter of 48 mm made of steel 45 (Rockwell hardness number HRC 25, Ra = 0.38 micron). The partial insertion was manufactured using PTFE and was a sector with the width of 16 mm from the ring—diameter of 80 on a diameter of 60 mm—and the height of 9 mm.

The rate of mass wear was assessed by the mass loss of samples per unit time. The magnitude of wear of the samples was determined gravimetrically on an analytical balance within the accuracy of 10^{-5} grams and transferred to the intensity of wear. The moment of friction was recorded using a Termodat 17E3 (Sistemy kontroly, Perm, Russia) device.

In the assessment of the intensity of wear, the mean square error was regulated by measurement errors of the mass of a sample and the speed and duration of friction, and did not exceed 5%.

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The “insert – shaft” scheme without external lubrication was used. The manufactured samples for determining the intensity of wear were the sector insert (with diameter (50 – 0.5) mm, width (16– 0.5) mm and length (9 – 0.5) mm), the steel shaft was the counterbody of steel 40X with hardness of 48 – 50 HRC and roughness $R_a = 0.16 – 0.32 \mu\text{m}$.

The wear rate of the samples was determined gravimetrically on the analytical scales with the accuracy of 0.0001 g, which was recalculated on the intensity of the wear according to the known techniques [32].

The relative linear velocity and specific load of the friction pair were selected according to the real friction pairs of the “piston rings–cylinder” in the compressor 4GM 2.5 V–2 / 3–250 (pressure $P = 10.4 \text{ MPa}$, linear velocity 2.0 m/s)

During the estimating of the wear rate of the PCM, the mean-square error was regulated by errors in measuring of the sample mass, velocity and duration of friction and it did not exceed 5%.

The study of the composite structure before and after the friction, and the study of the supramolecular structure of the activated PTFE powder was performed on a high-scanning electron microscope of TESCAN MIRA 3 LMU.

The surface morphology of CF was carried out using a raster electron microscope (REM-200) (Selmi, Sumy, Ukraine)

The processing of experimental data was performed using the mathematical design of experiments and mathematical statistics.

The degree of crystallinity and the parameters of the crystalline lattice were determined by an X-ray method (diffractometer DRON-4-07), using filtered CuK α radiation (wave length 0.154 nm) and focusing on the Bragg–Brentano θ – 2θ (2θ is Bragg angle). The current and voltage values of the X-ray tube were 20 mA and 40 kV respectively. Sampling was done in the step-by-step mode (exposure – 3 s), range of angles 2θ from 16 ° to 20 °.

Infrared spectra of PTFE surfaces and wear products were recorded by the FT–IR Nicolet5700 spectrometer in display mode. Wear products were pre-pounded at the room temperature under pressure of 50 MPa. The band of absorption of CF₂ of the PTFE groups at 1 206 cm⁻¹ was used as the comparison band. The relative error in determining the optical density in a series of the three measurements is ~ 20%.

The thermographic studies of the activated PTFE were carried out by the derivatograph Q–1500 in terms of the temperature from room to the temperature 60–70 K (approximately 700 K) higher than the melting point of the crystallites. The mode of linear heating in the air at a rate of 5 to 10 K / min or cooling samples with a furnace at a speed of about 5 K / min was used for the studies.

Planning and processing of experimental data were carried out by methods of mathematical planning of the experiment and mathematical statistics [33].

CHAPTER III

CURRENT STATE, PROBLEMS OF PRODUCTION AND MODIFICATION OF PTFE COMPOSITES

3.1 Technological process of PCM production on the PTFE basis and its peculiarities

The structure of powdered PTFE before and after intensive mechanical activation was studied by a set of modern physical methods of research: electronic microscopy, differential-thermal (DTA) and thermogravimetric (TGA) analysis, X-ray diffractometry and IR spectroscopy.

As the analysis of the compressor equipment efficiency shows, the friction units are most exposed to frequent failures [66, 115, 116]. The costs of repair and reconstruction works, the losses of production shortfall, the need for the retention of backup equipment and the availability of large quantities of spare parts lead to significant detriments.

Analysis of causes of poor reliability and durability of parts of friction units showed that two problems need to be solved in the first place – increasing the operational characteristics of the used materials and their rational application.

An urgent task of modern science of polymeric composite materials is the development of the theory of PCM formations with the aim of solving the problem of optimization of modes of this process and prediction of properties of finished products.

At the current stage of PCM developments based on PTFE, special attention is paid to research of connection of composite production technology with technological and operational properties of a finished product [3, 50, 61, 66, 67]. This is due to a comprehensive clarification of a number of processes that occur during PCM production, and thus to the possibility of its affecting the operational capability of the finished product.

Application of different technology modes of manufacturing composite materials based on PTFE can change the parameters of their mechanical properties and wear resistance several times. [68, 117] At that of great value are the brand and the properties of the original PTFE powder, stage of polymer crystallinity and dispersion, shape and orientation of the filler particles. In some cases it may overlap the changes obtained by varying the composition of composite material [5, 118].

Literary review of the sources indicates that the close attention of the researchers is basically paid to the properties of fluoroplastic composites [34, 47, 55, 78] and only a small number of publications links the characteristics of the filler and the composition with the type and the operating modes of supporting technological equipment [4, 119]. Scientific substantiation of such connection will ensure producing the filler with the needed distribution by lengths (fractions), particle size and in the composition volume and, as a result, the composite with the necessary functional performance.

At this time the industrial process of fluoroplastic composite production mainly consists of the following technological chain links of operations [120] (fig. 3.1):

- I Acceptance, culling, warehousing of raw materials.
II Preparation of PTFE and fillers to mixing (combining).
This link requires the following operations:
1. Drying the components of composition.
2. Preliminary processing of matrix and fillers: chemical, thermal, chemical-thermal, mechanical, radiation, combined and other types of processing.

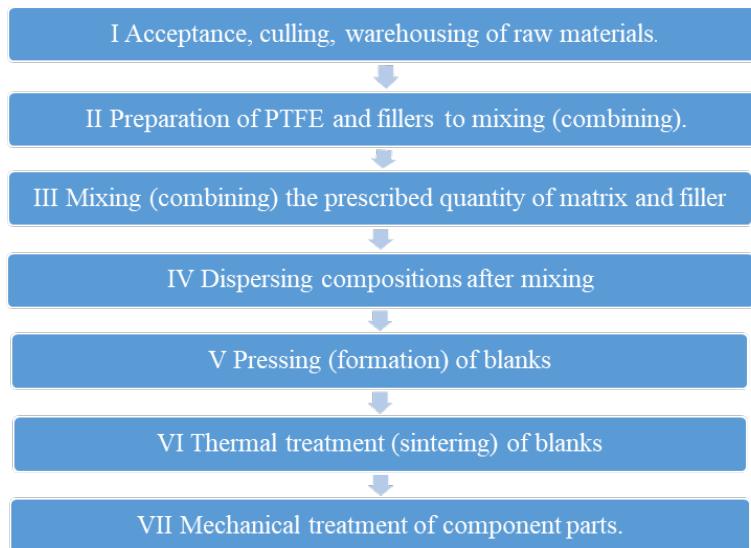


Fig. 3.1 Scheme of the industrial process of composite production based on PTFE

Each of these types of treatment is defined with some clearly in the relevant literature [17, 45, 66, 121] and has practical application.

3. Grinding and dispersing of matrix (PTFE) and fillers.

The process is very important and especially its importance becomes significant, if you consider that to these processes not only to the components of the compositions in their preparation for the combination are exposed, but also the composition of the material after mixing the prescribed quantity of composition components before processing to products.

4. The final (closing) treatment of matrix and fillers.

It can repeat the technological operations of point 2, be their combination or have its own specifics.

III. Mixing (combining) the prescribed quantity of matrix (PTFE) and filler to produce the composition of a given content.

There are many types and varieties of mixing devices, but if you receive compositions based on PTFE then the most justified was the technological process of dry mixing of fillers with matrix on the appropriate mixing equipment.

IV Dispersing compositions after mixing

This technological process can be carried out on the same technological equipment as in point 3, but it has its own specifics, because during the process, as a rule, the final grinding of

fillers is performed (in particular to sizes smaller than those in the project of the composition), which ultimately leads to change of the expected physical and mechanical properties of the composite material [59, 121, 122].

V Molding (formation) of blanks of composite material based on PTFE.

Compression molding is one of the first and most common methods of producing composite blanks from composition powder.

VI Thermal treatment of blanks of composite material based on PTFE.

In the process of molded material sintering on the stage of alloyage of particles of PTFE and fillers the chemical, physical and mechanical and operational properties of future product are designed, therefore sintering and subsequent heat treatment is an important point in the technological process of manufacturing products from composite.

VII Mechanical treatment of blanks of composite material based on PTFE

These operations of technological process are carried out on the equipment and using the technology of metal treatment. The treatment specific of polymer composites is widely enough described in the specialized literature [123].

Thus, the entire technological process of obtaining a product from fluoroplastic composite consists of the whole technological chain (I-VII), given above. Note that the structural links of this chain can be supplemented by new elements (processes) [16, 89, 124] or vice versa, some components of the links can be removed from the technological process as unnecessary.

The literature and patent sources review [9, 23, 125] allows to state low potential of traditional technological approaches in PCM production on the PTFE basis.

Obviously, the only systematic approach [62, 126] to the technology of producing polymer composite materials based on PTFE will provide the creation of effective technological processes, instrumented with the appropriate equipment, as required by the development of modern industry [56, 61, 127].

3.2 Technological methods of PTFE-matrix modification

Despite the uniqueness of PTFE characteristics, it has a number of properties, which limits its use as tribological material. They include [11, 12, 25, 26, 61, 128]:

- high creepage of the material that appears when stretched under load of only 3 MPa under normal temperatures;
- high coefficient of thermal expansion under normal temperatures that abnormally varies with the temperature in the area of structural phase transitions (in the temperature range from about 280 to 310 k);
- low thermal conductivity (10-50 times smaller than that of metals);
- low wear resistance at dry friction, especially for high speed slip.

The heat released in the friction area due to the low thermal conductivity encourages significant rising of the temperature on the surface of friction. As a result the physical and chemical processes are accelerated that reduce the strength and rigidity of the polymer, which significantly increases the linear dimensions and can eventually lead to the destruction of the frictional unit [27, 58, 63, 71, 126].

In this connection there is a necessity of the application of physical and chemical methods of PTFE modification. These are, in particular, the synthesis of polymeric matrices of different composition and structure [29, 30, 67, 129]; the formation of mixtures by means of combination of polymers and oligomers with different level of interaction [31, 32, 64, 130]; the modification of matrices of different origin by means of directed change of the structure and structural interaction under energy influence [32, 34, 67, 71, 131]; matrix modification by means of activated dopants of different size, shape and properties [35, 37, 65, 132]; the creation of the nanophased matrices with significantly different characteristics [38-40]. Basic methods of modification are shown in Fig. 3.2. It should be noted that the industrial implementation of the enumerated technologies is associated with significant energy, material and labor costs and requires managerial treatment in the light of the "price-quality" trend.

The most appropriate in the case of PCM with PTFE-matrix seems to be the technology of energy influence on its structure and properties by means of conducting the mechanical activation (mechanical influence) [33], with good reason named "mechanical alloying".

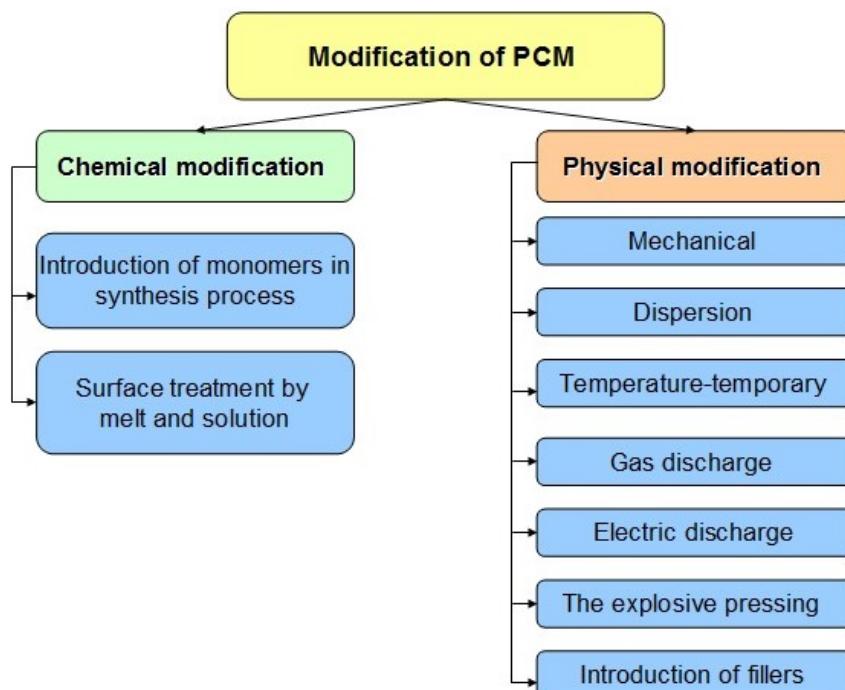


Fig. 3.2 Scheme of the basic methods of PCM modification based on PTFE

There are two cases of mechanical activation: in the first one – the time of the mechanical impact and the formation of the field of stresses and its relaxation is more than the time of the chemical reaction (such processes are referred to as mechanochemical); in the second one, – on the contrary, the time of the mechanical impact and the formation of the field of stresses is

less than time of the chemical reaction or these processes are even separated in time. In the latter case, it is the question of mechanical activation [41, 62, 65, 133].

3.3 Peculiarities of production of the fibrous filler with the necessary distribution by fractions and properties

Numerous studies in the field of PCM creation based on PTFE convincingly proved the legitimacy of the use of the fillers of carbon fibers of different nature with a wide range of special properties [42, 62, 67, 134].

Practice of composite polymer materials science shows that composite material, reinforced by fibers of equal length, has the greatest rigidity (and other performance characteristics) [43, 65, 71, 135].

To achieve this result in the actual conditions of CF preparation for the composite material is very difficult. Modern crushing equipment and techniques of shredding the fibers lead usually to production of the filler of different lengths.

Thus that filler is actually used, which has parametric distribution of fibers by lengths by a particular law with the fixed values of the distribution parameters [42, 61, 64, 71, 136]. Here it is appropriate to note that the characteristic ratio of fiber length L to its diameter d – L/d is a defining characteristic in the theoretical design of the composite with specific properties and the description of change of its elasticity modules within the variational "range" of Hashin–Shtrikman with the increase of the volumetric content of filler [43, 137].

Note also that the technological methods of obtaining carbon reinforced fibers for PTFE-composite significantly change the size, structure, and properties of carbon fibers, the adhesion of filler to matrix and allow creating composites with projected operational properties [44, 62, 67].

Therefore, an urgent task at this stage of the research is the creation of CF preparation technologies that would ensure the achievement of a complex of required composite properties and the provision of its efficiency during the required period of service. It should have a scientifically justified connection between the stay time of CF in the crusher chamber and the rotation speed of the crusher cutting element, which will ensure the required distribution of elements of fibers and composite properties.

The peculiarity of formation of CF fractional and granulometric composition is that the choice of structural features is influenced not only by the deformation-elastic properties of fibers and the thermodynamic parameters of work of equipment [20, 45, 67, 78], but also by the possibility of obtaining the required distribution of the crushed fibers by lengths in it. Numerous studies [12, 20, 43, 45, 65, 67] have shown that exactly this distribution can ensure the compliance of the project [45] and obtained properties of PTFE-composite [46, 47, 73].

It is known [13] that to produce a close-packed structural framework of a polymer composite based on PTFE the average length of fibers should be within 80-150 microns at their defined distribution by lengths as a whole [44, 132].

While receiving CF of the necessary length for creating PCM based on PTFE the hammer crusher KSU-2.0 was used with the modernization of its operational units and the technological process of crushing [46, 131].

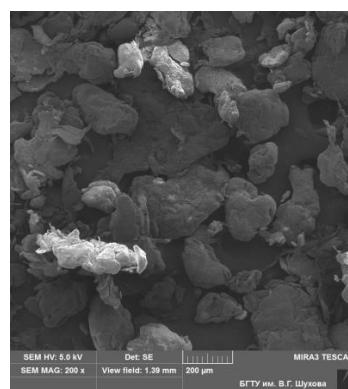
The original CF was the fleece-shaped clods of fibers bound together.

For the fine and superfine crushing of CF the crusher with the fast-rotating 7 000 min⁻¹ bottom working bodies is applied [12, 24, 45, 72, 89]. Study of the dependencies of influence of the technological factors of CF production on their distribution by length and volume [24, 130] showed that there are critical correlations between the speed of rotation of the crusher working body and the crushing time, which determines the degree of dispersing and fractional composition of carbon fiber.

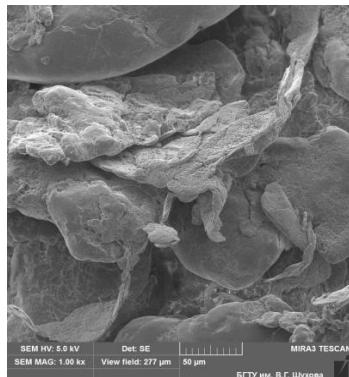
Limitation in the choice of the number of crusher rotations ($n = 7\,000\text{ min}^{-1} = \text{const}$), which was used in the previously conducted studies [12, 42, 44, 47], leaves the possibility to obtain the distribution of the crushed fibers, close to theoretical one, only by variation of time during which the crushed volume of fiber is in the crusher chamber. At this it fails to reach the distribution of fibers by fractions [11, 12, 24, 67, 134], close to project one, because the time increase of the technological process of dispersing the fiber (its time in the crusher chamber) leads to the emergence of a considerable number of small fibers [46, 48, 89, 123]. Therefore, to create an effective technology of CF production with the necessary distribution, close to theoretical one [47, 124], it is important to consider and explore the common effect of the number of the crusher rotations and the time of crushed CF stay in the crusher chamber on the distribution of CF by lengths and fractions, as well as the properties of fluoroplastic composite with such a CF division and to offer the effective technology of CF preparation as PTFE filler [48, 56, 78].

The structure of powdered PTFE before and after intensive mechanical activation was studied by a set of modern physical methods of research: electron microscopy, differential-thermal (DTA) and thermogravimetric (TGA) analysis, X-ray diffraction and IR spectroscopy.

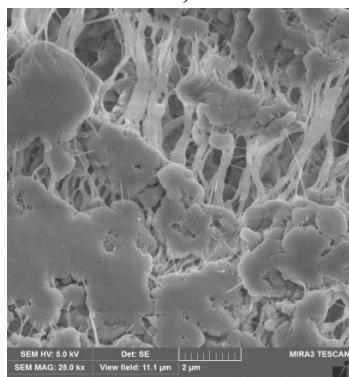
The presence of particles of arbitrary shape with dimensions differing in several orders of magnitude is typical for industrial PTFE (Fig. 3.3, a).



a)



b)



c)

Fig. 3.3 – Microstructure of industrial PTFE

Large particles of irregular shape are formed mainly due to the agglomeration of smaller fractions and form cluster structures with a statically undetermined shape and size (Fig. 3.3, b). The PTFE particle is formed by fragments of arbitrary shape with pronounced structural differences. This leads to the formation of units having a fibrillar structure with a diameter from a few nanometers to (300-500) nm (Fig. 3.3, c). Such aggregates are capable of growth with the subsequent formation of irregular structures, connected by fibrillar elements.

The indicated features of the initial structure of PTFE under the influence of technological factors (intensive mixing) make it possible to obtain a high molecular weight product, which is a polydisperse mixture with different molecular weights, gabiosis of individual particles and arbitrary mass, size and morphology of cluster structures (Fig. 3.4). As a result, the industrial PTFE determines the technologies of the formation of semi-finished products and products with given parameters of deformation-strength, tribotechnical, and others. characteristics.

In the structure of PTFE, after the mechanical activation, lignosite formations are observed in the form of granules with micron size in area and thickness (Figs 3.4, a, b), filamentous strands of fibers in the length from 10 to 50 μm and in diameter from 10 to 100 nm (Figure 3.4 , c) other forms ("web", "frost patterns", "lace" and "branch" structures, etc.) (Fig. 3.4, d, f, g), which are absent in the structure of inactivated PTFE (Fig. 3.3).

From the analysis of the data of electron microscopy it follows that the NMS PTFE undergoes a significant change in mechanical activation - from a lamellar disorder it goes to the highest orderly up to the spherulite. The difference in morphology of fraction particles is due to the fact that products obtained with different energy influences have mixed proportions of

molecular components, and each of them is due to the construction of certain morphological formations.

The presented research results show that the division into nano- and micro-sized objects in the case of fluoropolymers is conditional. Basically, the first are parts that form microobjects.

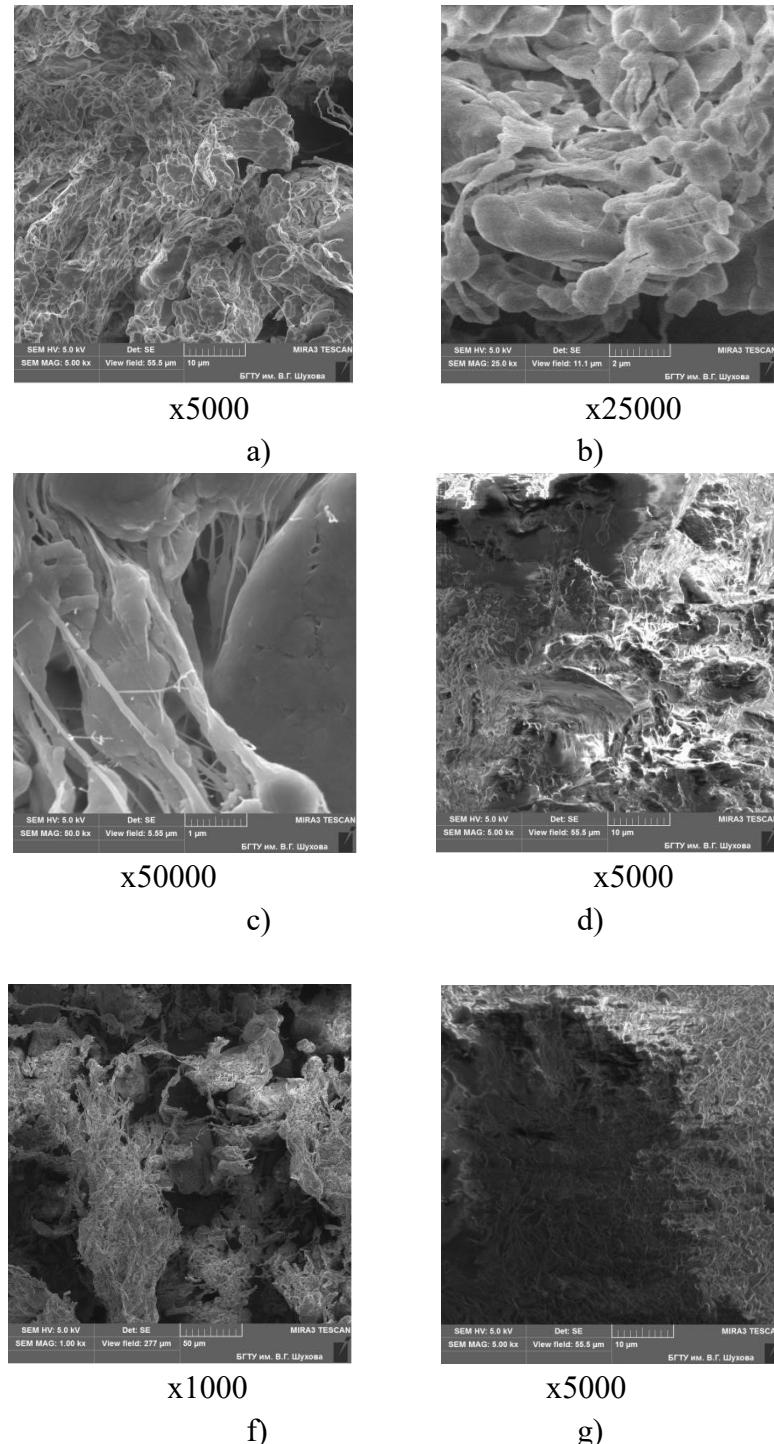


Fig. 3.4 – Microstructure of PTFE after mechanical activation

3.4 Priority trends of CF modification

Peculiarities of CF structure and the properties of its surface caused the mismatch between the high values of the module, strength during the stretch and the low indexes of resistance to stratification (shear strength) of carbon fiber polymer composite materials. Therefore, the issue of improving the adhesion strength of connection carbon fiber-polymer matrix is of paramount importance when creating composites [17, 49, 67, 132].

Surface modification of carbon fiber is designed to: increase its stability to oxygen of air, strength, elasticity and, most importantly, increase the adhesion of the binders to it (the matrix).

Modification is conducted in various stages of obtaining the carbon fiber processing initial organic fibers, intermediates in the process of heat treatment or final fiber materials.

So, the increase of carbon fiber stability to oxygen in air is reached by means of addition of various organic mixtures of metals into solution [50, 65]; soaking of the initial partly carbonized or carbonized carbon fibrous material by aqueous solutions of salts of such metals as Ti, Zr, Mo, Th [51, 74]; addition of reagents into solution, which at further heating to 1 273 K creates cover like boron nitride [52, 67]; treatment by mixtures that decompose at carbonation with the formation of such oxides as ZrO₂, MgO, MnO, SiO₂, BaO, MoO, which are fixed on the fiber in the amount of 25-50% [53, 124]; application of pyrogafite and carbides to the fiber from the gas phase [54, 55, 134].

The problems of surface modification of carbon fibrous materials for the purpose of researching the ways to improve the adhesion of PTFE to the carbon fibers are covered in the literature widely enough. It's possible to hold the classification of modification methods both by the techniques and by the used chemical reagents.

The most common ways are surface oxidation of fibers; treatment at high temperatures (1 473 k) in the neutral-air environments; surface deposition of boron carbides, silicon, whiskerizing (growing single crystals of metal on the surface of carbon fiber); inoculation of monomers and polymers; dressing. Often, in order to increase the effectiveness, several ways of processing are combined or produced consistently.

In the common case the modification of the surface, associated with the increasing specific surface area of the fiber, leads to the improvement of wettability and adsorption. It is shown by the gas chromatography method [56, 67, 72] that the oxidation treatment of the surface of graphitized fibers leads to the growth of specific surface area. Effective treatment of the carbon fiber surface is in the atmosphere of argon or hydrogen at a temperature of 1 473 k [56, 130].

It is ascertained [57, 135] that the thermal vacuum treatment leads to an increase of specific surface area: with the temperature increasing from 293 to 1 273 k the specific surface of carbon fiber (based on polyacrylonitrile) increases from 0.24 to 1.0 m²/g. As far as the mechanical properties of fibers do not change at that, such an increase of the surface is connected with the gas desorption from the cracks in the fiber structure.

The specific surface area increase does not always correspond to the improvement of shear characteristics of polymer composite material. Found by the authors [58, 68] the dependency between the shear strength and specific surface area is connected, obviously, with a short range of investigated specific surface areas (from 4 to 11 m²/g). During the study of the

influence of specific surface area of carbon fibrous material of brand UUT-2 in the range from 0.4 to 69 m²/g on the mechanical characteristics of the polymer composite material it is found [59,] that the shear strength is maximum when the value of the specific surface area is 2-3 m²/g, and further is slightly reduced.

Matching the literary data one can assume that the increase of the resistance to stratification is associated not with the increase of CF specific surface area, but with the increasing content of the polar oxygen groups able to enter into the chemical interaction with the active groups of the polymer binder. However, it is considered [60, 61], that the role of the mechanical component of adhesion in the formation of solid mixture carbon fiber-polymer matrix is large enough.

The study of wettability [62] found that the processing of the high-modular fiber by 60% HNO₃ weighing 1 gram at 373 K leads to the reduction of wetting angle from 72 °C to 66-57 °C and the destructive shear resistance of CFRP (carbon-fiber-reinforced polymer) increases 2.6 times. The authors think that at the nitric acid treatment the structure of the surface changes and, most importantly, the carbon fiber polarity increases. Some researchers [63, 64] consider that the magnitude and the speed of wettability can be the comparative characteristics of carbon fiber properties that are well correlated with the magnitude of interlayer shear strength in the finished products.

The surface modification of carbon fibrous materials with oxidation is widely practiced. The proposed methods of modification differ not only by the type of the used oxidizers, but also by the environment in which the process is carried out (liquid or gas), the temperature of treatment, the concentration of reagents and some other technological features [58].

Thus the carbon fiber reactivity is a complex property that depends on the chemical element composition, the crystallographic structure, the morphological features of the surface, and the presence of weakly bound layers and oxygen complexes in it [65].

All the considered factors significantly affect the strength of the adhesion connection carbon fiber – polymer matrix, but at the present level of research it is difficult to highlight the most significant ones and set the quantitative connection between them and the indicators of functional performance.

The disadvantage of the thermal-oxidative treatment of carbon fibrous material is that it is accompanied by the surface corrosion – a decrease in physical and mechanical characteristics.

Analytical review of the literature and patents [66-77] did not find any close relationship between the type and the parameters of the technological process of CF modification and properties of PTFE-based composites with the carbon fibrous filler, so it's necessary to carry out the additional research of the influence of CF modification on the properties of fluoroplastic composites with them and to identify the most effective of them.

Analysis of information sources showed the relevance of the proposed research theme and identified the promising trends for its solution.

3.5 The influence of mixing technology on the properties of PTFE-composites

Mixing is complex physical, chemical and physical-mechanical processes associated with the impact of force fields, the movement of the original components of the mixture in the vol-

ume of the mixing apparatus along the complex trajectories, with the formation of the system, which is characterized by the statistically random distribution of the components [11, 20].

In the process of the production of plastic masses the fillers, stabilizers, plasticizers, lubricants, dyes, pigments and other modifiers and impurities are added into polymers. The composition of the mixture can include two or more source components. The mixing process for the multicomponent mixtures can be seen as blending of each following component with the previously obtained mixture.

The process of mixing may be periodic or continuous.

The periodic process of mixing is downloading of all the components at once, or in a specific sequence in a mixer, mixing them within a specified time to obtain the required quality of the material, then it is removed from the mixer. This process is most common in the industry of plastic processing. On the basis of this principle various types of mixers work: drum mixers, vortex mixers, turbo-mixers, roll mixers, closed type Benberi mixers as well as various types of stirring machines. These mixers are user-friendly, allow you to easily change the sequence of addition of components and adjust the temperature.

The continuous process of mixing is the most progressive and consists in performing the mixing of the original components in the device volume under the influence of working bodies, getting the finished material of the set mixing quality and its continuous unloading.

There are two main mechanisms of mixing: simple and dispersed.

The simple mixing is understood as a process, which results in statistically random distribution of the particles of the source components in the mixture volume without change in their original sizes.

The dispersed mixing is a process of mixing, accompanied by the change (reduction) of the initial size of the component particles associated with their fragmentation, destruction of aggregations, deformation and collapse of the disperse phase.

The main task of the dispersed mixing is destruction of the aggregations of solid particles and their distribution in the liquid polymer volume.

The elementary act of aggregation destruction is overcoming the forces of adhesion between the solid particles as a result of the influence of the inhomogeneous field of mechanical stresses at the deformation of the medium. Calculations show that the irreversible disintegration of aggregations and their spraying in the liquid disperse phase occurs when the ratio is:

$$6\pi R\tau/F \geq 4, \quad (3.1)$$

where R is a particle radius; τ is shear stress; F is the force of adhesion of particles in the aggregation.

This means that the higher the viscosity of the medium, the more efficient the dispersing. Lowering of the temperature, increasing of the rotation frequency of the mixer working bodies, reduction of the gap, where the disperse system is in progress, facilitate the dispersing.

Reduction of the adhesion forces of the particles (F) in the aggregation also leads to its destruction and enhances the dispersing. The addition of surfactants (SAA), low molecular weight liquids and other substances that adsorb on the surface and weaken the interaction of the particles also enhances the dispersing.

In the production technology of PTFE-based composite materials there are two main ways of obtaining the composition (a mixture of polymer with fillers): "wet" and "dry".

The "Wet" way of production by means of original material, as a rule, is a suspension of PTFE in the water with the size of the particles of 0.05 – 0.5 microns, to which SAA are added to ensure the aggregation stability of the particles. Mixing of the suspension of PTFE and the filler occurs in the globular mixer or vibromixer, and also in the colloidal mill type mixers in ethyl alcohol medium. The best results were obtained as a result of mixing at low temperatures. Solid phase is separated from the alcohol in the vacuum filter. Drying is carried out at 100-120 ° C for 24 hours, then the product is ground into fine-dispersed powder, from which with a pressure of 30-35 MPa the blanks are pressed and sintered [78]. However, the most simple, productive and least energy intensive is the "dry" way of mixing the components of PTFE-based composition.

Realization of the "dry" mixing way has become possible after the development of the equipment for the reception of finely powdered PTFE [79].

One of the key issues in defining the dependence structure-properties of PCM is the influence of spatial distribution of particles on the composite mechanical and tribo-engineering characteristics [80]. As it has been noted [11, 81], the initial structure of the filled PTFE-material is laid on the stage of mixing composition components. At that it is necessary to take into account that the mixing process not only affects the distribution of the composition components in the volume, but also leads to a change in the polymer matrix structure, the filler structure and the interaction level between them [82].

The main factors affecting the process of formation of the material structure and its properties at dry mixing of PTFE and CF are [83-86]:

- 1) mechanical-physical properties and mass ratio of the mixture original components;
- 2) type and technical descriptions of mixer equipment (rotation speed of mixer working bodies, form of working bodies, degree of mixing chamber loading, power of drive etc.);
- 3) time of composition mixing;
- 4) technology of addition of the mixture components into the mixer;
- 5) influence of the temperature, pressure or dilution into the components of composition in the process of mixing [80, 85, 87].

The process of dry mixing of PTFE and CF results from the action of external forces (tension of shear as a result of existence of the relative motion of polymer particles).

As a result of the mixing process, there are structural changes of the components of composition and mixture on the whole at the macro- (particles of the mixture components) and micro- (molecular structure of the components) levels.

In the process of mixing at the macro level in view of the fact that the contact between the filler and the polymer is made on the surface of the particles, there are two limiting cases [11]:

- 1) the surface of the filler particles exceeds in many times the surface of the polymer particles;
- 2) the polymer surface is significantly larger than the filler surface.

In the first case the filler covers the polymer particles to create a shell that prevents them from alloying into monolith on the subsequent stages of the heat treatment, which significantly reduces the strength and frictional properties of such material or leads to cracking the

blanks. This phenomenon was observed when using fine-dispersed fillers with dispersion less than 7 microns and serial powders PTFE with the size of the particles of about 100 microns.

In addition, the same situation can be observed, if the powder of PTFE is in heavily agglomerated condition, and the used equipment does not provide the complete destruction of lumps while mixing.

The second case occurs when the polymer particles are much larger and its volume content is not high. In this case, although the entire surface of the filler is completely used, a polymer particle, however, involved into the sphere of the filler action, is small, and therefore, the effect of composite material strengthening after addition of this filler is negligible.

In this regard, during the development of the technology of mixing and compounding of the composite material based on PTFE and CF, one should consider, in addition to the filler dispersion, also the size of the polymer particles that previously was not taken into account by the developers of the PTFE - based composite materials.

At the macro level under the influence of centrifugal forces in the process of mixing there is the mechanochemical destruction process of the material of the matrix and the filler.

In the matrix material as a result of the loosening of the tight molecular packing of the polymer the split of chains occurs along the intermolecular interaction line and the creation of "free" functional groups, uncompensated by the interaction with neighbouring groups of chains. The presence of such groups leads to the growth of the polymer chemical activity and its reactivity [11, 88].

The dispersing effect of fillers, including CF, on the properties of PCM strength in the mixing process on the different equipment is noted in the works [11, 82]. In the paper [12] there are given data on the influence of the mixing time on the distribution of the fibers by lengths when mixing PTFE powder with CF in the grinder MRP-1. In the paper it is noted that the mass fraction of long and short fibers increases during the mixing time depending on the dispersion of source fibers. Addition of short fibers to the source polymer, which have a Weibull distribution and gamma-distribution by lengths at the brief mixing time, does not change the law of distribution. When adding the long fibers the law of distribution by lengths changes from normal to gamma-distribution and Weibull distribution. The author [12] analysed the volumetric (mass) gamma-distribution of fibers by lengths when mixing the fluoroplastic compositions with 20% of pre shredded within 3 – 30 min. low-modular CF ($T_{TO} = 120$ K; $\sigma_B = 0.55$ hPa), the mixing time is 5 min. The whole cycle of the carried out investigations is at one and the same rotation frequency of the mixer working bodies, which significantly limits the information value of the research.

It was concluded that the procedure of adding the fibers into polymer significantly affects the parameters of the distribution of fibers and, therefore, the dependence of the physical-mechanical properties on the parameters of the mass (volumetric) distribution of fibers.

When adding the short fibers (having a gamma-distribution) into PTFE in the process of mixing the tensile strength and the resilience are largely dependent on the dimensional parameter of distribution, and the elongation at a rupture – only on one dimensional parameter. As the value of tensile strength grows the dependence on two parameters of distribution increases.

When adding the long fibers that have a normal distribution and transition to the gamma distribution in the process of mixing with PTFE, all indices depend on two parameters of the distribution.

In his investigations [12] the author restricted himself to only one brand of CF filler, which significantly reduces the amount of information and the community of conclusions.

Addition of PTFE fibers of other brands into the matrix will, most likely, lead to other laws of CF distribution by lengths and to other PCM properties.

Analysis of the literature sources [80, 83-87] allows assessing the impact of technological and physical-chemical factors in the process of mixing on the structure and the properties of the received composition.

In order to improve the performance of the mixing process at producing the PTFE compositions with CF the optimal time of mixing the ingredients acquires a special value, it is necessary to take into account that the technological process of mixing takes place in conjunction with the dispersing of both components, to which is given insufficient attention in the analyzed literature sources.

In the works [89, 90] it is stated that in any case the joint effect of a temperature and shear stresses leads to uneven distribution of internal stresses and breaking a part of the covalent bonds in CF and the matrix. This effect, known as the mechanical effect, is responsible for the progress of various secondary reactions in the matrix. Most often they lead to the reduction of the mid-numerical molecular weight of the polymer, the expansion or, vice versa, the narrowing of molecular mass distribution, the formation of branches and sewn inclusions. The direction of the progress of the secondary reactions is difficult to predict because it depends on the output characteristics of the polymer and the treatment conditions, however, it is significant that the changes in the molecular structure occur always and they need to be controlled.

Systematization of the literary and patent sources shows the lack of the data about vacuum impact on the technological process of PTFE and CF mixing. There is information about the results achieved by stirring the components of metal powders in vacuum in drum mixers [91]. The authors mentioned [91] that at the mixing in vacuum the behavior of the components does not practically depend on their density and the particles inside the mixer move with almost identical speeds that provides a high dimensional uniformity of volume distribution of the components in the received mixture. This is an essential prerequisite for conducting the research on the vacuum influence on the technology of composition producing based on PTFE with CF.

Thus, it is shown that in the process of the dry mixing of PCM components not only redistribution in volume and dispersing the mixture components, but also different physical-chemical processes take place directly in the mixed materials.

So there arose a grounded necessity for research of the influence of different technological methods of mixing the composition on the basis of PTFE with CF, which is important for the modeling of its properties and the development of the producing technology.

3.6 Formation of PCM properties by means of technological methods of pressing

The technology of pressing is pressing of discrete materials compacted in the pressing form under the influence of pressure to obtain a billet or a product of a specific size, shape and density, which ensures the efficiency of obtaining composites with the necessary operational properties [92].

Compacted material is a body consisting of discrete structure forming elements (phases), to a certain extent mutually oriented and packed in their entirety with creation of mechanical, adhesive other ties in the areas of mutual contact of PTFE particles and PTFE– carbon fiber [25]. The nature of the spatial placement of structure forming elements, consolidated in a coherent solid body, defines the structural composition of the material, which is a system of arbitrary channels (pores) [93].

The essence of the process of pressing the discrete material is similar to pressing a solid body, with the difference that the possibility of a solid body to deform in the transverse direction is replaced with the possibility of movement inside itself by means of reducing the porosity [94, 95]. The volume of a discrete body changes while pressing as a result of filling the cavities between the particles due to their displacement and plastic deformation [96-98].

To solve the deformation problems of discrete environments the phenomenological approach is commonly used [99], developed in the works of V. M. Antsyferov, A.K. Grigoryev, B.A. Druyanova, V.L. Kolmogorov, M.B. Shtern, et al. According to the mentioned approach the discrete material is supplied by means of compressed environment that satisfies the system of differential equations of the fluidity theory. It is shown [100, 101] that there are variation principles for solving the boundary value problems of deformation of porous bodies.

The main feature of sealing materials, based on the discrete nature of blanks, is the porosity [102], which value in PTFE sintered samples can reach 10-15% [103]. Any consolidation of porous materials involves the presence of residual porosity, if not to consider the possible ways of further treatment to ensure the material compaction. The consequence of porosity of sealing materials is often their permeability for liquids and gases (gas-and moisture absorption) [104] that can greatly reduce their longevity and eventually their physical-mechanical and operational properties [105].

The formation of products from composition is classified according to the degree of powder heating before the formation, the type of load, the kind of forms, the conditions of external friction, etc. [106, 107].

According to the degree of powder heating before pressing, i.e. to the highest pressing temperature, there are cold pressing, at the temperatures lower than indoor, warm pressing, as well as hot pressing in a fixed volume [108].

Literature and patent search revealed that for the formation of the PTFE-based composition cold pressing is used [11], as well as hot pressing in a fixed volume, but with a cold pre-pressing [109]. This is due to the structural changes in PTFE that occur at the temperatures, higher than indoor, and are accompanied by the further shrinkage [110].

Cold pressing of PTFE compositions is conducted in press-forms (stamping tool with stable working details of high strength and hardness) and elastic ruCFer membranes [111].

By the type of the applied load the pressing of PTFE-based compositions is conducted mainly using the static application of a load. In this mode, as the experience of earlier conducted studies shows [112], you can achieve the optimum extending of the applied load front in the PCM volume and, consequently, the absence of stratifications, the uniform density, the structural homogeneity, etc.

The selection of a pressing technology determines and limits the range of the obtained products.

Producing the blanks of a wide range of items, including the sealing elements for compressors (piston and sealing rings), is performed by the compressive pressing. This method allows obtaining the simple shaped blanks in the form of sleeves, plates, rods, from which after the heat treatment the products are manufactured mostly by mechanical treatment [11, 21].

Method of pressing determines the synthesis of phases, the structural homogeneity, the stability of properties by the blank volume and the level of a PTFE-composite moisture absorption [113]. They must be such that the designed composite structure was preserved, the phase adhesion of the developed composition was aided at most [82] and the indicators of the operational properties were qualitatively improved [114].

According to the modern views the pressing process consists of three stages [115].

At the first stage the PTFE-composition powder compaction occurs due to the redistribution of powder particles and their occupation of the pores, formed during the free filling of the material powder. Such compaction is not accompanied by the plastic deformation of the particles of a powder composition. As the pieces of research show [116], this stage is characterized by the considerable influence of the elastic unloading of some contacts, which occurs already at the very beginning of the compaction process of composition powder mass. Such local unloading of a part of contacts reduces the forces of adhesive connection between them, and also leads to reduction of the collision area of the appropriate contacts between the particles, and thus to the emerging of contact stresses.

The second stage of the process is characterized by the fact that the particles of composition powder that have dense packing show a certain resistance to compression, the pressure of compression is growing, and the powder body density is not increasing for some time. At this because of the elastic deformation of the particles the role of the local unloading of contacts is negligible, and the plastic deformation in the near-contact area has a limited local character.

When the pressure of compression exceeds the resistance of the powder particles, and their plastic deformation begins, the process of composition powder compaction transfers to the third stage. From this moment the plastic deformation covers the entire volume of each particle of PTFE-composition phases, the shift of contacts actually stops, and they are fixed or destroyed when the values of the contact stresses are higher than the limit of strength.

In practice, in the pressing process there is a mutual overlap of the mentioned stages, which take place simultaneously, and therefore, we can only speak about the prevailing character of each of the above stages [117, 118]. But in any case the described mechanism of the composition pressing process leads to an increase of composite density and reducing of its porosity. This causes the decline of composite moisture absorption, but the excessive pressing effort causes the increasing of tension in the carbon fiber filler, leading to its destruction. The morphology of CF filler phases shifts towards the smaller values, which is the cause of a sharp reduction of the composite operational properties [119, 120].

The powder in a mold during the sealing behaves to some extent similarly to fluid and tends to flow into the sides, which raises the pressure on the walls of the mold, which is called lateral [121].

However, unlike fluid that evenly transfers the applied efforts in all directions, in the composition a considerable unevenness of this distribution is observed. As a result, the composition compression degree in different sections is not the same, and on the lateral walls of the mold much less pressure is transmitted than in the pressing direction, mainly due to the friction between the particles, the jamming and other factors that complicate the moving of the particles into the sides. This reduces the adhesive activity of the phases of polymer-filler system, leads to a decrease in the values of the composite operational properties and increases the moisture absorption due to the presence of micropores in the blank volume. In this regard, an important quantity of the technological process of pressing is the so-called coefficient of lateral pressure ξ , which is the ratio of lateral (horizontal) pressure p_{ϑ} (powder pressure per unit of a mold wall surface) to the compressing pressure p

$$\xi = p_{\vartheta}/p \leq 1. \quad (1.2)$$

The quantity ξ accurately characterizes the plasticity of the compacted material.

Lateral pressure decreases by the height of the extruded pellets, since the friction forces arising between the composition particles, which are moving, and the walls of the mold reduce the quantity of the compressing axial pressure. This is necessary to be taken into account during the development of the technological pressing process of composite material and its mathematical model.

Thus, in the pressing process the applied pressure decreases due to the friction of the composition particles on the mold walls and the composition internal friction (interparticle), which causes the emergence of a density gradient by the height of a pressed blank, which is more, the greater the height of the filled powder of a press-composition is. This is especially noticeable because of the high altitude of a tablet. In the tablets, higher than 40 – 50 mm, and making a one-sided effort after sintering the difference in diameters can be often spotted; at this on the one side, to which the pressure was applied, the diameter is always greater, which attests to the smaller shrinkage as a result of a larger compacting during the pelletizing.

Uneven pressing density can directly affect the curvature of a shape and sizes of a blank during the sintering, as well cause unwanted changes of the properties of a sintered product, such as reducing the strength and the durability during compression [12, 122, 123].

Part of the pressing efforts to overcome the external friction is directly proportional to the height of a blank and inversely proportional to its diameter. For a certain volume of the composition pressed powder and the sizes of a mold the share of a vertical pressure wasted on friction is a constant, proportional to the applied pressure.

Interparticle (internal) friction in the composition volume, which coefficient may significantly differ from the external friction coefficient, during pressing plays a certain role, because the work of pressing is also wasted on its overcoming. In the general case the losses of the pressing efforts on external friction depends on the coefficient of friction in a pair pressed blank material– mold material, susceptibility to setting in this pair, the treatment quality of the

mold walls, the presence of greasing, the height of the pressed powder filling (weighed portion) and the diameter of the mold.

The last technological operation is removing the blank from the mold. The pushing operation should be performed in one continuous and smooth course of the pusher, which eliminates jerks and stop while moving. In the process of pressing the blank is subjected to radial stresses that do not pass after the compressing pressure removing. These stresses may cause a slight increase in a blank diameter (up to 1-3%), so any stop in the process of their pushing may lead to the premature expansion of the material, as a result of which the circular cracks are formed, that will be revealed during the blank sintering.

To avoid this, the compacted blank must be endured in a free state at the room temperature for some time, depending on the weight and dimensions of the blank.

From the above said it can be concluded that the pressing strength in the technological process of forming the PTFE-composite blanks is defined by both the mechanical adhesion and the interlacing of the surface asperities and imperfection of the composition particles, and the action of interatomic forces of adhesion (adhesion between the components of PTFE-composition), which degree of manifestation increases with the increasing of contact area of a matrix and a filler.

Since the strength is proportional to the contact surface between the PTFE-composition particles, it must be also proportional to the compressing pressure. At the first stage the speed of the strength growth increases due to a sharp increase of the blank density. At the third stage with the pressure increasing, the density and areas of contacts increase slightly, causing the speed decrease of the strength growth of PTFE-composite. According to the preliminary data during the second stage the PTFE-composite strength is approximately proportional to the first degree of the compressing pressure growth [124].

Under the other identical conditions the strength of blanks is significantly affected by the granulometric composition of the PTFE-based press-composition. In the process of obtaining the composition (PTFE + CF) it's necessary to maintain a constant temperature, pressure and humidity of the environment due to a high lumpiness of the material. This peculiarity requires the previous loosening before the stage of the composition compaction to a product. As the research shows [125], the optimum length of CF fibers of PTFE filler is within 80-150 microns at their natural distribution in the composition volume. Violation of the pressing modes of PTFE-composition leads to a reduction of the composite operational properties as a result of CF crushing and losing their reinforcing qualities.

The described mechanism of the composition pressing process leads to increasing the composite density and reducing its porosity. This causes the decline of the composite moisture absorption, but the limit-free pressing effort causes the increasing of tension in a CF-filler, which leads to its destruction.

The pressing scheme, unlike the mechanical scheme of deformation is defined by not only the kind of a deflected mode, the combination of normal and tangential stresses, but also the direction of the biggest pressure application [126, 127]. There are schemes of a one-sided, two-sided and hot pressing in the fixed volume [128].

The relative implementation simplicity of the schemes of a one-sided (uniaxial) pressing [129, 130] in the closed molds caused their wide distribution and active research. The application of an all-round pressing scheme is technologically feasible and economically justified to

produce special oversized, long products – mainly in the conditions of individual and small-scale productions. Any real compaction scheme is usually accompanied by the uneven distribution of density. Its consequence is heterogeneity of the area of the composite material characteristics inside a product. Among the reasons that lead to the formation of the inhomogeneous density field, the most important role belongs to friction of a composition on the matrix walls, which is always present, despite the use of different oils. It may stipulate a marked density gradient even when pressing the products of a simple shape, when the ratio of a height to a diameter is essential.

CHAPTER IV

INFLUENCE OF TECHNOLOGY OF OBTAINING PTFE COMPOSITES ON THEIR STRUCTURE AND PROPERTIES

4.1 Structural conformation of the matrix of PTFE composites under the influence of mechanical activation

PTFE has a number of unique properties and it is actively being studied by various methods. Work on the producing of some new forms of PTFE, free from deficiencies of the base polymer has been successfully promoted [1, 2]. The structure and properties of modified forms, and therefore, the possibilities and fields of their application in many respects depend on the technology of their usage [3, 4]. Therefore, there is a need for a thorough study of each product obtained by the new technology [5].

Mechanical activation of the PTFE powder was carried out in a high-speed mixer MRP–1M by rotation with varying frequency of the working bodies in the range $n = (5000 – 9000)$ min^{-1} and at the experimentally determined time interval $\tau = (3–8)$ min [6].

During mechanical activation, the mechanochemical destruction of the PTFE macromolecules with the formation of radical fragments takes place. On the one hand, existence of the active surface of the filler particle, and on the other hand, the free radical of the PTFE macromolecule, may initiate the grafting reaction of the polymer to the filler. Although such reactions with the formation of chemical bonds between the polymer and the surface of the filler are likely to occur only between active centers, their contribution to the strengthening of the composite material is very significant [7].

It also leads to the preservation of the polymer's excess energy, some changes in the thermodynamic characteristics, and increasing its reactivity [8].

In addition, mechanical loading as a result of the collision of particles leads to the appearance of metastable states of the surface layers of polymer particles. Such collision of particles occurs within a few seconds and local increase of temperature and pressure at the points of surface contacts accompanies it. All these phenomena lead to the formation of uncompensated valences on the surface of the particles, facilitate the interaction of the filler particles in the composite, initiate the polymerization reaction of the monomers or the formation of a chemical bond with polymeric radicals [7, 8].

The difference in the structure of the activated and inactivated PTFE leads to the difference in physical and mechanical properties (Table 4.1) [9, 10].

The morphology and fractional composition of PTFE at the process of mechanical activation with a number of revolutions less than 5.00 min^{-1} does not provide an equal distribution of the activated PTFE particles by volume. A number of revolutions more than 9.00 min^{-1} leads to the coagulation of the activated particles and the formation of a heterogeneous structure of the material.

Data analysis given in Table 4.1, shows that the mechanical activation of PTFE for 3 minutes at any frequency of rotation in a series of experiments practically does not lead to the

significant increase in the physical and mechanical properties of PTFE. That is why we did not use samples No. 2, 5, and 8 for further research.

Table 4.1

The influence of mechanical activation on the physicomechanical and tribotechnical properties of PTFE

No. of sample	Technology of obtaining	Density ρ , g/cc	Breaking strength σ_b , MPa	Relative elongation δ , %	Wear intensity $I \cdot 10^{-7}$, $\text{mm}^3/\text{N} \cdot \text{m}$
1	non-activated	2.269	9.5	96	113.3
2	$\tau=3 \text{ min.}, n=5000 \text{ min}^{-1}$	2.208	10.2	240	108.0
3	$\tau=5 \text{ min.}, n=5000 \text{ min}^{-1}$	2.211	21.6	416	93.0
4	$\tau=8 \text{ min.}, n=5000 \text{ min}^{-1}$	2.175	17.3	280	80.0
5	$\tau=3 \text{ min.}, n=7000 \text{ min}^{-1}$	2.199	10.7	270	97.0
6	$\tau=5 \text{ min.}, n=7000 \text{ min}^{-1}$	2.205	23.5	423	82.0
7	$\tau=8 \text{ min.}, n=7000 \text{ min}^{-1}$	2.211	18.2	358	71.7
8	$\tau=3 \text{ min.}, n=9000 \text{ min}^{-1}$	2.203	19.6	290	89.0
9	$\tau=5 \text{ min.}, n=9000 \text{ min}^{-1}$	2.214	24.8	415	61.0
10	$\tau=8 \text{ min.}, n=9000 \text{ min}^{-1}$	2.213	18.0	340	72.0

Derivatographic studies have shown that the loss of weight of the industrial model of PTFE of F-4 (ISO 13000-1) occurs at temperatures of 500 – 580 °C. The thermal behavior of the activated PTFE is different: the expansion interval of the polymer is 580 – 600 °C (Fig. 4.1).

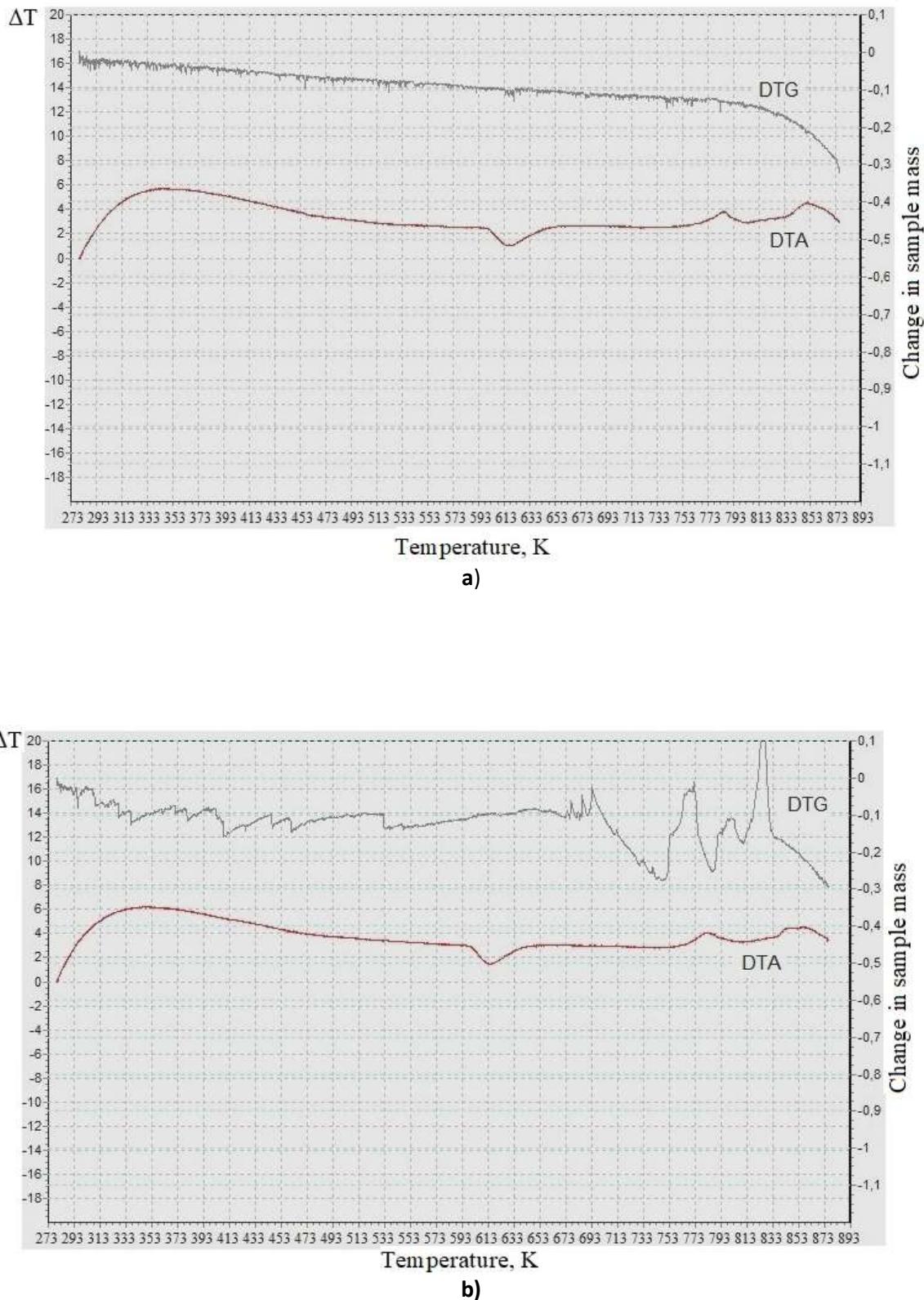


Fig. 4.1 - Derivatograms of the industrial sample of PTFE (a) and its activated form at activation mode $n = 9\,000\text{ min}^{-1}$, $\tau = 5\text{ min}$ (b)

The results of the thermographic analysis of the material samples indicate that the mechanical activation of PTFE increases the stiffness of macromolecules, which leads to the increase in the thermal stability of the modified polymer at 20 – 80 °C. This is due to the presence of phases with different thermal stability owing to their different molecular mass [11].

The difference is also found in X-ray diffraction patterns of the inactivated and activated polymer (Fig. 4.3).

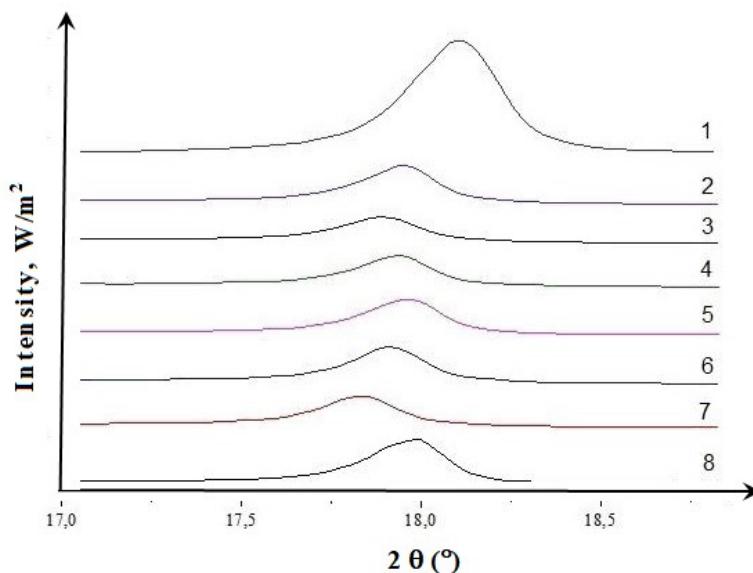


Fig. 4.3 – Diffraction curves of industrial PTFE (1) and its structural modifications (3 – 10)

From Fig. 4.3 (curve 1) we can see that the amorphous halo PTFE is at $2\theta = 18.10$ deg. Intensive mechanical activation shifts it to the region of the lower Wolf-Bragg angles ($2\theta = 17.82 - 17.98$ degrees), while reducing the intensity (Fig. 4.2, curves 3 – 10). Significant decrease in the intensity of diffracted radiation (3.1 times) is observed in specimens (sample 9) made after activation of PTFE at $n = 9\,000\text{ min}^{-1}$ for $\tau = 5$ min. In this case, cell parameters has been changed, as well as the size of the crystallites in the plane (100) (Table 4.2). It provides the optimal-reactive structure of PTFE with a maximum of physical and mechanical properties.

The physical and mechanical properties of PTFE are maximum at the tensile strength (σ_p) which is more than 2.6 times bigger than in non-activated PTFE, the relative elongation (δ) – 4.3 times, and the wear rate is less than 54%.

It is obviously connected with the formation of new reaction centers and the increase of surface energy of macromolecules individual fragments because of the action of elastic and plastic deformations.

Increase of the PTFE wear resistance during mechanical activation is associated with a decrease in the degree of crystallinity and an increase in the mean interlayer distance in the process of frictional interaction and structural adaptability of modified PTFE under conditions of friction and manifestation of the synergistic effects of self-organization tribont structures with increased wear resistance.

Table 4.2
X-ray structural analysis

Number of sample	The size of the crystallites in the plane (1 0 0), nm	Parameter of the lattice cell $a = b$, nm	Parameter of the lattice cell c , nm
1	29	0.566	0.972
3	28	0.570	0.949
4	26	0.572	0.949
6	29	0.570	0.921
7	29	0.571	0.959
9	27	0.574	0.965
10	31	0.570	0.965

Therefore, we may conclude that the intense energy effect in the form of mechanical activation significantly affects the formation of a special supramolecular structure PTFE, which, from the positions of polymer mechanics, positively affects the physical and mechanical characteristics of the polymer.

The study of the molecular and supramolecular structure of the activated polytetrafluoroethylene has been carried out by IR spectroscopy.

Fig. 4.4 shows the typical IR spectrum of the industrial polytetrafluoroethylene of fluoroplast grade [12].

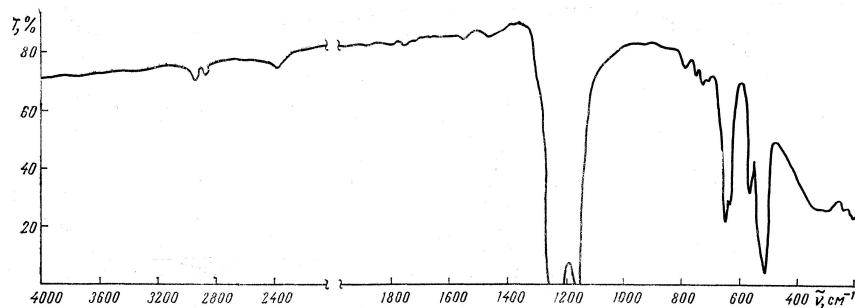


Fig. 4.4 – IR absorption spectrum of industrial polytetrafluoroethylene

As we see from Fig. 4.4, the most intensive bands refer to the valence fluctuations of the groups CF_2 ($1\ 211$ and $1\ 154\ \text{cm}^{-1}$) and the oscillation ν (SS), which manifests itself as a bend at $\sim 1\ 233\ \text{cm}^{-1}$. In the region below $650\ \text{cm}^{-1}$, the deformation and out-planar fluctuations of the CF_2 groups are located: the fan oscillations $\gamma\omega$ (CF_2) are detected at $639\ \text{cm}^{-1}$, the bands 555 and $516\ \text{cm}^{-1}$ characterize the deformation and oscillations of the CF_2 groups [12, 13].

During the modification of polytetrafluoroethylene with mechanoactivation treatment, the transition of the polymer into dispersed, ultradispersed and other states (filaments, granules, web, etc.) occurs (Fig. 4.2).

Usually, in IR spectra of such formations, the bands characterizing the valence fluctuations of C-F and C-C, the deformation fluctuations of CCC and CF_2 groups, the out-planar fluctuations of CF_2 -groups, individual fragments and the entire chain [12-16], even with in-

tense energy influence, are preserved. This confirms that the external influence does not lead to the complete destruction of the molecular chain of polytetrafluoroethylene. However, there is an assumption that certain changes occur at the molecular level, which lead to changes in the properties of the polymer.

Analysis of the research indicates changes in morphology and supramolecular structure PTFE after mechanical activation while maintaining the chemical structure of the polymer [16, 17]. IR spectra are sensitive to such changes and provide information about the structure of the polymer modified forms.

Fig. 4.5 shows the absorption spectrum of industrial brand PTFE after the energy impact by mechanical activation.

As should be expected, with PTFE mechanical activation observed change in the shape and intensity ratio of the bands most. Since the interpretation bands IR absorption spectra PTFE conducted by different authors, is not the same in some detail, we followed the interpretation of bands in the infrared spectrum PTFE made in the works [17].

Studies have shown which optical band density at 780 cm^{-1} , observed in IR spectra of PTFE, increases linearly with a decrease in the degree of crystallinity of the sample. This band is used to determine the degree of ordering in the structure of PTFE [12]. This and a number of other bands observed in the area of $700 - 800\text{ cm}^{-1}$, we refer to the fluctuations of the molecular chains in the amorphous phase.

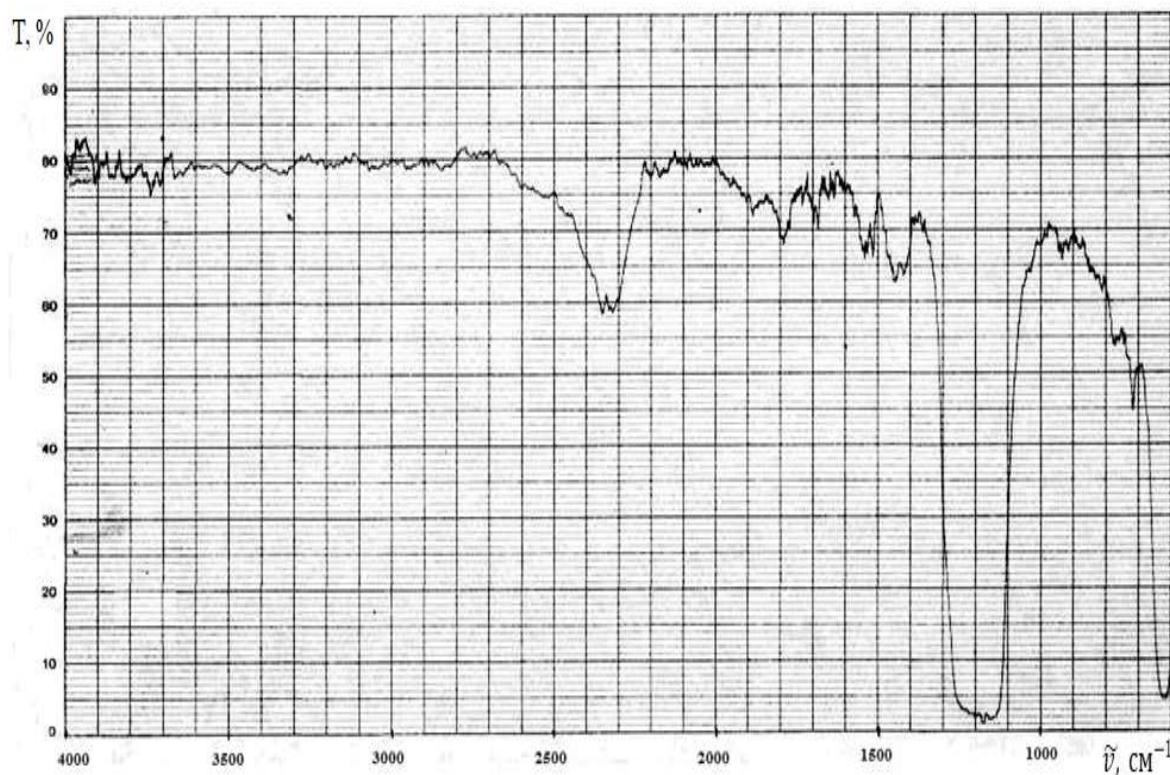


Fig. 4.5 – IR spectra industrial brand PTFE after mechanical activation in the mode $n = 9\,000 \text{ xB}^{-1}$, $\tau = 5 \text{ xB}$.

The bands at 640, 625 and 516 cm⁻¹ are considered as crystalline bands.

When comparing infrared spectra of non-activated and activated PTFE there are a number of differences. They consist in increasing the intensity of the bands in the areas of 700–800, 620, 575 and 490 cm⁻¹. In the IR spectrum of PTFE, the most intense bands 1 211 and 1 154 cm⁻¹, correspond to the valence fluctuations of CF₂ groups. In the activated PTFE there is a shift of these bands and an increase in their intensity (1 175 cm⁻¹).

Inflection vibrations ν (CC) at 1233 cm⁻¹ shifted to the high-frequency spectral area activated PTFE (1350 cm⁻¹). In the areas of 800–1100 and 1350–2230 cm⁻¹, there are a number of additional bands missing in the spectrum of non-activated PTFE. They can be attributed to fluctuations of finite groups and groups of lateral branches of structural fractions.

The band at 2 390 cm⁻¹ in the non-activated PTFE is shifted to the low-frequency region of the spectrum of activated PTFE (2 330 cm⁻¹), noticeably expanding and intensifying.

It should also be noted that oscillations in the spectrum of activated PTFE in the region of 2 900–4 000 cm⁻¹ in the non-activated polymer are absent at all.

In our opinion, the expansion of the band in the IR spectrum at the maximum absorption is due to the formation of a plurality of crushed crystallites in the structure of the polymer. This does not affect the degree of crystallinity dominant, but forms a structure that more effectively resists breaking the bonds and hence a wear and tear (up 54%) [11].

Thus, when modifying PTFE as a result of mechanical activation, the transition of the polymer into dispersed, nano-dispersive and other structural states occurs.

In the IR spectra of these structures are stored bands that characterize the fluctuations of individual pieces and the chain even under intense energy impact. Thus, the external mechanical influence does not lead to a significant fracture of the molecular chain of PTFE. In some cases, certain changes occur at the molecular level. This leads to increased physical and mechanical and operational properties of the polymer.

Mechanically activated PTFE more actively adheres to the surface of the CF (Fig. 4.6 a – c) than unactivated (Fig. 4.6 d) when obtaining PCM. As a result, modification of the surface layer of CF with activated PTFE occurs. Fragments of PTFE are distributed on the surface of the CF with a higher homogeneity. This enhances their activity during interaction with the PTFE matrix during the formation of the composite.

A homogeneous structure of a composite with a reduced number of voids and a more evenly distributed distribution of filler fragments in a matrix polymer is formed.

The particles of CF in contact with activated PTFE particles form the primary adhesive bonds, which reduces the defect of the composition and the probability of occurrence of defects in the formation of the composite.

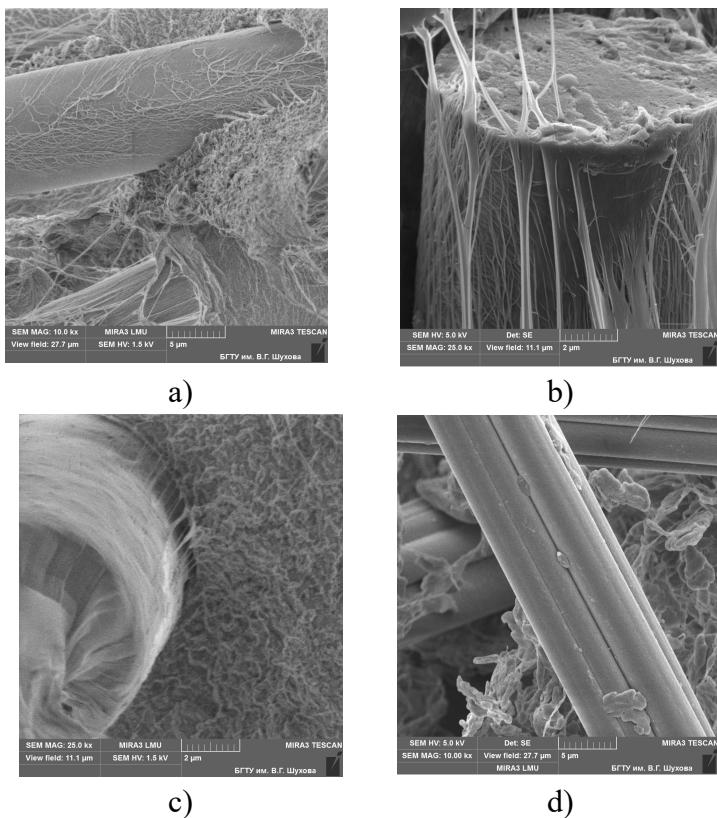


Fig. 4.6 - Microphotography of PTFE-composite structures with activated (a–c) and non-activated (d) matrices

Composites, based on this activated matrix and CF have much higher rates tribotechnical parameters than with an non-activated matrix [18 – 20].

Microphotographs of the friction surface of composites (Fig. 4.7) confirm that, as a result of an increase in the adhesion bond "activated PTFE filler matrix", the wear process is less active than that of a non-activated matrix composite.

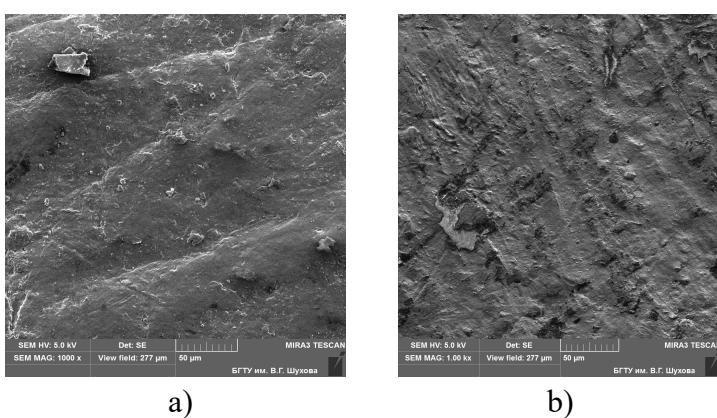


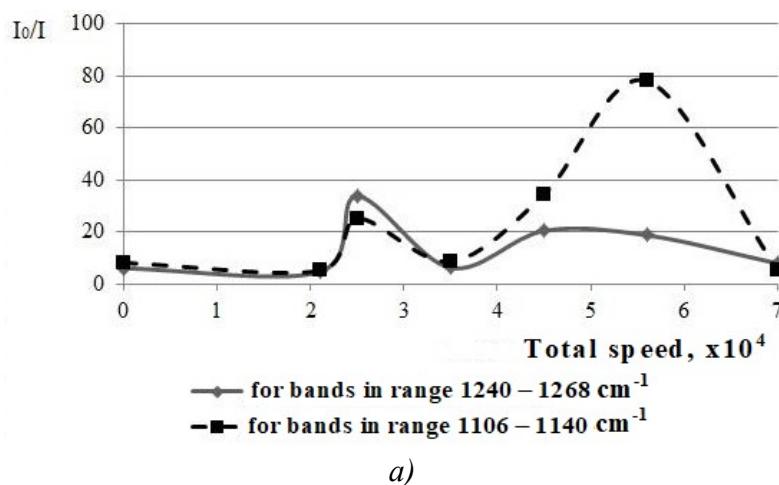
Fig. 4.7 - Microstructure of the friction surface of PTFE composites with non-activated (a)and activated (b) matrices

In microphotographs, we clearly see that in the case of wearing of a non-activated PTFE composite (Fig. 4.7a), the wearing patterns are deeper. Thus there are grooves softening material, etc. This was not observed in the composite wear activated PTFE (Fig. 4.7 b), which contributes to the durability of up to 50%.

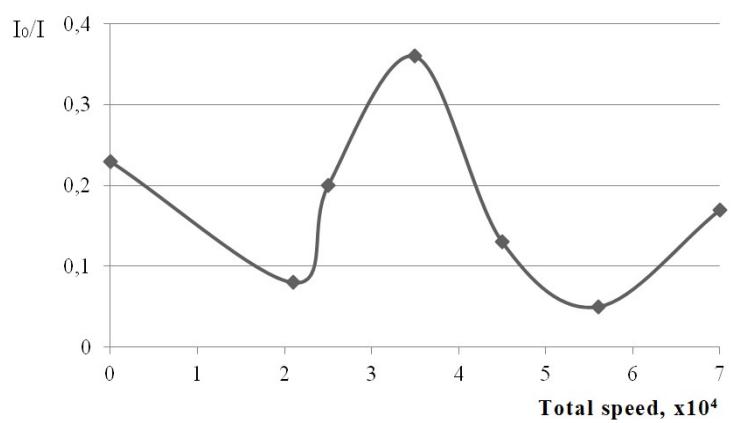
Using this composite for friction units (stuffing seals and piston rings), contributed to a general increase in their capacity for work 2.3 - 3.0 times.

Thus, mechanically activated PTFE and compositions based, due to the high physical, mechanical parameters and wear-resistant characteristics can be used in the manufacture of anti-friction parts in automotive and other equipment.

It has been established that with the increase in the total number of revolutions during mechanical activation, the concentration of CF_2 groups corresponding to their valence fluctuations in the absorption ranges ($1240-1268$) and ($1106-1140$) cm^{-1} (Fig. 4.8, a) increases.



a)

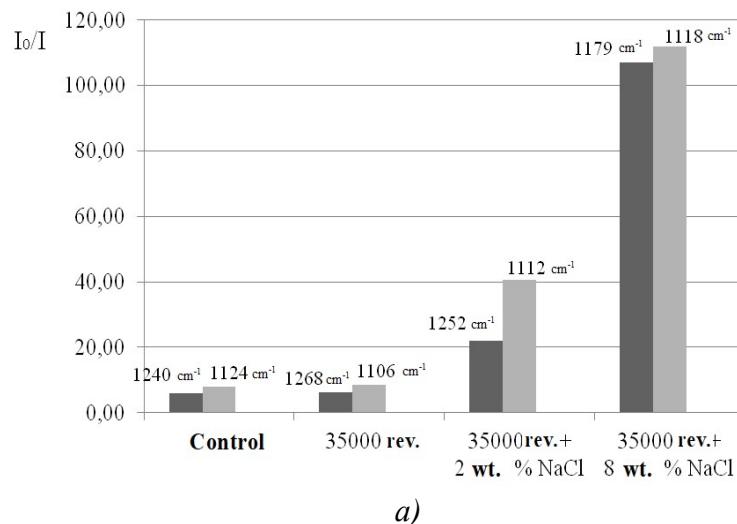


b)

Fig. 4.8 – Dependence of the indicator I_0/I on the number of revolutions in the absorption ranges: a) ($1240-1268$) and ($1106-1140$) cm^{-1} ; b) ($1778-1794$) cm^{-1}

In parallel, the concentration of the end-groups $-CF = CF_2$, whose fluctuations are reflected in the absorption range $(1778-1794) \text{ cm}^{-1}$ (Fig. 4.8, b), increases, which indicates an increase in the defect of the structure of the activated polymer.

Adding sodium chloride (NaCl) to PTFE leads to an increase in the concentration of CF_2 groups corresponding to their valence fluctuation at 5 and 14 times at 2 and 8 wt. % filling, respectively, in relation to the initial polymer (Fig. 4.9, a).



a)

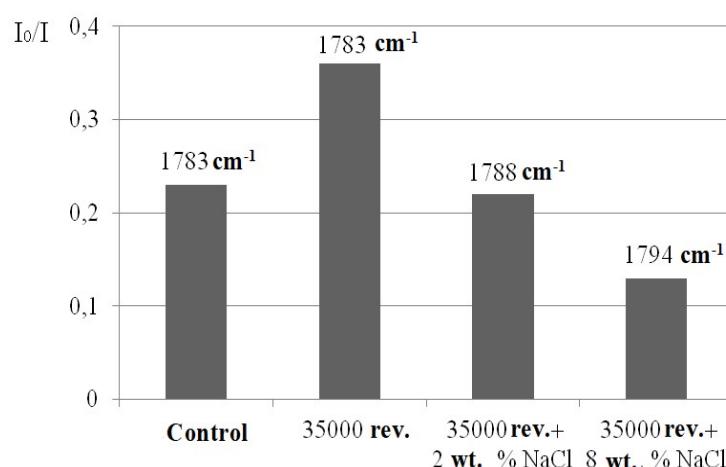


Fig. 4.9 – Influence of sodium chloride on the index I_0 / I in the absorption range: a) $(1106-1268) \text{ cm}^{-1}$; b) $(1783 - 1794) \text{ cm}^{-1}$

At the same time, the increase in the content of the filler contributes to an increase in the number of such groups in (2.8-4.8) times, as well as a decrease in the concentration of the final groups ($-CF = CF_2$) recorded in the absorption range $(1783-1794) \text{ cm}^{-1}$, in 1.7 and 2.8 times in comparison with the initial and activated polymer, respectively (Fig. 4.9, b).

That is, in the process of mechanical activation of PTFE, changes in the supramolecular structure of the polymer are possible, which consist in the formation of intramolecular double bonds, lateral branches, finite groups of different composition, while preserving the bands

characterizing the fluctuations of individual fragments and the whole chain. This suggests that mechanical activation does not lead to a marked destruction of the PTFE molecular chain, but conformational changes occur, which are to increase the concentration of valence and finite groups of CF_2 , which can lead to an increase in the physico-mechanical and tribotechnical properties of the polymer.

4.2 Technological methods of preparation and modification of fiber filler

The surface of CF under normal conditions inert [21].

The PTFE composition with CF is a complex heterogeneous system with numerous phase distribution surfaces.

In such compositions a significant contribution to the process of structure formation, and hence the fundamental performance properties make physical and chemical processes taking place in the boundary layer when forming composition [22].

Formation of reactive-active surfaces of the PTFE-matrix and CF is an important scientific and practical task, and its solution guarantees the achievement and reproduction of the design properties of the composite.

To ensure the technological combination of carbon fiber with the polymer matrix in anti-friction composite materials based on PTFE proposed to modify the surface of carbon fiber in various ways [23 – 25].

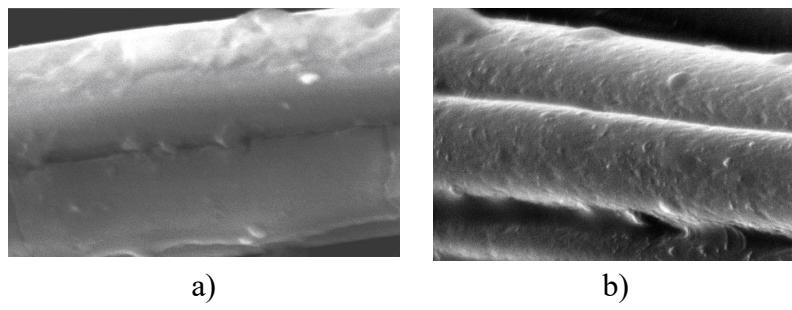
Such processing of the filler allows to enhance the characteristics of the composite material, which are largely dependent on the adhesion bond of carbon fiber and PTFE matrix [26].

The conducted studies have shown that the most common way of modifying the surface of the CF to improve the adhesion of PTFE to CF is the thermal oxidation of the surface of the fibers. Thermo-oxidation treatment of the surface of the CF leads to an increase in the specific surface area and an increase in the degree of adsorption [27]. The results of experiments studied the thermal features (before crush) and thermomechanical (during crush) surface modification of fibers.

Presented in table 4.3 the results of the study of wear resistance of carbon fiber plastics containing thermally treated fiber demonstrate the effectiveness of thermal (there is an increase in wear resistance up to 100%) and thermomechanical modification (an increase of almost 130%) of CF.

The greatest effect of thermal and thermomechanical modifications implemented at a temperature of 400 ° C (PTFE crystallites melting point 325 - 350 ° C). This is due to changes in supramolecular structures - due to increase flexibility of macromolecules PTFE. There is an increase in the strength of 50%, and wear resistance - more than double for carbon fiber plastics containing CF after thermomechanical modification.

Data of electron microscopy (Fig 4.9, b) indicate a significant change in the nature of the surface of the explosive after thermal modification.



a)

b)

Fig. 4.9 – Microphotography of scanning electron microscope of carbon fiber surface:
a - before thermal treatment ($\times 7\ 500$); b - after thermal treatment ($400\ ^\circ C, 15\ min$)
($\times 9\ 500$)

In order to enhance exposure to energy of carbon fiber chopping, mechanical modification was carried out under vacuum ($p = 550 \pm 10\ mm\ Hg$). Found that when crushing carbon fibers under vacuum conditions, the strength of carbon fibers increases by almost 50%. For carbon fiber, which contain modified fiber, wear resistance increases to 100% (Table 4.4).

Table 4.3

Intensity of wear of carbon fiber ($I \cdot 10^{-7},\ mm^3/H \cdot m$) when CF is introduced after thermal and thermomechanical modification

Modification	Monitoring	<u>Temperature, °C</u>					
		100	200	300	400	500	600
		12.0	10.0	8.0	6.0	12.5	13.0
		12,5	11.0	9.0	7.0	5.5	11.5
							-

Table 4.4

Physico-mechanical and tribotechnical properties of carbon fiber depending on the conditions of milling of the fiber (the term of crushing is 15 minutes, vacuum $p = 550 \pm 10\ mm\ Hg$)

The characteristics	Monitoring	Rotational speed of the shafts of actuating mechanisms, minutes ^l			
		7000		9000	
		environment			
		air	vacuum	air	vacuum
Tensile strength, MPa	15.0	20.0	22.0	21.0	22.5
Intensity of wear of carbon fiber ($I \cdot 10^{-7},\ mm^3/H \cdot m$)	12.5	7.0	6.0	7.1	6.5

Table 4.5

Properties of carbon fiber in the thermomechanical modification of crushed carbon fibers under vacuum ($p = 550 \pm 10$ mm Hg).

The characteristics	<i>Monitoring</i>	Treatment temperature, °C				
		100	200	300	400	500
Tensile strength, MPa	15.0	24.8	24.9	25.2	26.0	24.4
Intensity of wear of carbon fiber ($I \cdot 10^{-7}$, $\text{mm}^3/\text{H} \cdot \text{m}$)	12.5	4.4	4.4	4.2	4.0	4.5

Modern materials technology widely uses synergistic approach to solve the problem of increasing the strength of composites. The study of the joint effect of thermomechanical treatment and vacuuming of carbon fibers on the level of physico-mechanical and tribotechnical properties of carbon fiber was carried out (Table 4.5). The results of studies (Table 4.5) show that during thermomechanical modification of the fiber at a temperature of 400 °C for 15 minutes under vacuuming ($p = 550 \pm 10$ mm Hg), the strength of carbon fiber increases by more than 75%. Under these conditions, the wear resistance level is more than 3 times compared to the unmodified sample.

Thus, the analysis of a series of experiments to identify the effectiveness of the impact of various technological methods on the properties of the composite. It was established that the thermovacuum technology of CF modification was the most effective. This technology allows to increase the strength of PTFE composite by 18 - 22% and improve its wear resistance by 20-25%. This result has practical importance for industrial implementation.

4.3 Substantiation and choice of technological modes of mixing composition components

At this stage of experimental studies, the effect of changing the rate and mixing time on the properties of the composition and the samples of PCM made from it has been studied.

The research was carried out on an experimental installation with the standard mixing chamber of the MRP-2 mill. Preparation of the ingredients of the composition (for all experiments) conducted on such technology.

The carbon fiber filler was prepared for mixing. Preliminary, before mixing CF, the filler - a carbon fabric in the form of a cloth was cut into pieces in the size of 1×1 cm and crushed the weight (100 g) on the MRP-2 mill (grinding time $\tau = 15$ min, the number of revolutions of the working bodies of the mill is $7,000 \text{ min}^{-1}$.).

Such a mode of preparation of the CF of the filler was stored in all experiments carried out. Its chemical composition and properties are shown in Tables 4.6

Table 4.6
Elemental composition (wt.%) of carbonate UTM-8-1s

C	H	O	B	P	Ash
60–65	1.1–4.5	3.5–4.5	3.0–3.6	3.0–3.6	21–26

The value of bulk density and particle size characteristics of different CF filler after grinding are shown in Table 4.7.

The obtained characteristics of discrete CF particles are best combined with PTFE matrix, providing the necessary physical and mechanical properties of PTFE PCM [28].

The effect of mixing the composition of the composition on the properties of the composite material was established. The change in properties was determined depending on the change in the mixing time ($\tau \approx \text{var}$) and the number of revolutions of the working parts of the mill ($n \approx \text{var}$).

After receiving the compositions in different modes and time of mixing were determined:

- index of mixing;
- apparent density and particle size;
- granulometric characteristics of the selected compositions of the CF filler.

Microphotographs (Fig. 4.10) were processed using the computer program "Image Pro Plus". For each sample were analyzed at least 300 particles of CF filler.

The results of the research show (microphotographs shown in Fig. 4.10) that the most effective is the technological mode of mixing: the number of turns of the working members of the mill is $n = 500 \text{ min}^{-1}$ and the mixing time $\tau = 30 \text{ minutes}$.

The obtained results of the bulk density of the composition, the mixing index and the granulometric characteristics of the filler CF, depending on the technological mixing regimes, are given in Table. 4.8. The values of properties and test results of the developed composites are shown in the Table. 4.9.



Fig. 4.10 – Microphotographs ($\times 120$) of allocated fragments of CF with UTM-8, made for different mixing modes of the composition ($n = 500 \text{ min}^{-1}$): a) $\tau = 10 \text{ min}$; b) $\tau = 20 \text{ min}$; c) $\tau = 30 \text{ min}$

The best indicators of physico-mechanical and tribotechnical properties are the composition obtained during the process of mixing the ingredients: the number of revolutions of the mixing device operating $n = 500 \text{ min}^{-1}$, mixing time $\tau = 30 \text{ min}$.

These regimes are used in the manufacture of samples for further testing.

The study of the surface structure of samples obtained by the methods of optical microscopy, revealed a number of features in different technological modes of mixing.

In the first mixing mode (speed of rotation of the bottom mixing blade $v < 5 \text{ m/s}$) PTFE and CF in the samples revealed areas of accumulation, agglomeration of unbranched carbon fiber filler composite matrix (Fig. 4.11).

Characteristic is the presence of such macro regions in the length of 3 - 4 mm and a width of about 1 mm when used as a filler of explosives. In this case, the change in the time of mixing the composition ($\tau = 10, 20, 30$ min) does not lead to the destruction of agglomerates CF.

Table 4.7

Bulk density and granulometric characteristics of the CF of the filler after shredding

Carbon fibre	Bulk density, ρ , g/cc	Granulometric characteristics of filler CF			
		Diameter of a fiber, d, μm	Minimum length, L_{min} , μm	Mean length, L_{mean} , μm	Maximum length, L_{max} , μm
UTM-8	0.16	10	90	120	150

Tab. 4.8

Influence of composition mixing regimes (PTFE + CF) on bulk density and granulometric characteristics of fiber in composition

Carbon fibre	Speed , n, min^{-1}	Mixing period, τ , min	Den- sity, ρ , g/cc	Mixing index, G	Granulometric characteristics of fill- er CF		
					Min- imum length, L_{min} , μm	Mean length, L_{mean} , μm	Maximum length, L_{max} , μm
UTM-8	250	10	0.237	0.56	85	115	145
		20	0.240	0.66	92	117	142
		30	0.242	0.74	86	112	138
	500	10	0.244	0.72	90	112	134
		20	0.244	0.86	93	110	127
		30	0.247	0.92	95	107	119
	1000	10	0.250	0.78	65	89	113
		20	0.251	0.89	50	76	102
		30	0.259	0.95	14	44	74

Tab. 4.9
Physical and mechanical characteristics of composites

<i>Carbon fibre</i>	<i>Speed, n, min⁻¹</i>	<i>Mixing period, τ, min</i>	<i>Density, ρ, g/cc</i>	<i>Tensile strength, σ_P, MPa</i>	<i>Elongation, δ, %</i>	<i>Intensity of wear of carbon fiber (l·10⁻⁷, mm³/H·m)</i>
UTM-8	250	10	1.91	11.6	9.8	56.8
		20	1.93	13.6	13.1	54.7
		30	1.90	13.1	12.8	45.9
	500	10	1.93	15.9	12.1	20.8
		20	1.91	18.0	14.9	7.6
		30	1.92	22.9	13.7	2.8
	1000	10	1.93	11.1	9.8	52.9
		20	1.93	8.9	9.5	54.8
		30	1.92	9.9	12.9	46.4

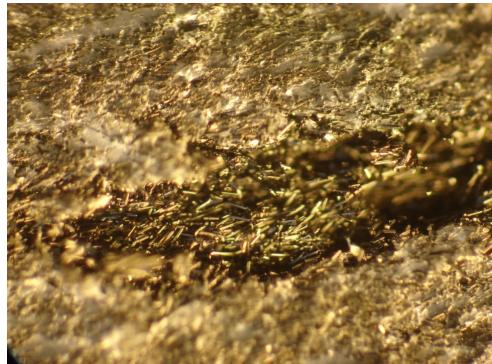


Fig. 4.11 – Zone agglomerate particles in composite CF ($\times 200$)

The presence of agglomerates of the CF of the filler (Fig. 4.11) in the carbon fiber composition for such a technological mixing regime may be due to the insufficient shear stress required for the destruction of the agglomerates of the CF when mixed with PTFE and CF. The presence of such stress-agglomerate concentrations in this material leads to a decrease in the strength of the material as a whole, as evidenced by the low values of the strength of the samples at stretching ($\sigma_r = 10-12$ MPa). The agglomerations of the fragments of CF in the PCM, in terms of the strength of the material, are defects in the structure of the composite, and in the case of strain of the sample under the action of the load, lead to the formation of trunk cracks and fragile fracture of the sample.

Undoubtedly, the presence of agglomerates CF leads to a decrease and tribotechnical properties of PCM. In the process of friction, during the load on the material, the removal of the unmixed with the matrix material CF of the filler will take place, and consequently, the area of friction will decrease, which will increase the load on the material and increase its wear, which is confirmed by the results of tests (wear decreases by 12 - 15%) compared to control samples.

In PCM samples obtained at higher velocities of the rotation of the bladder blade, the macromolecules of the agglomeration of the bulk carrier of the filler are no longer observed (Fig. 4.12).

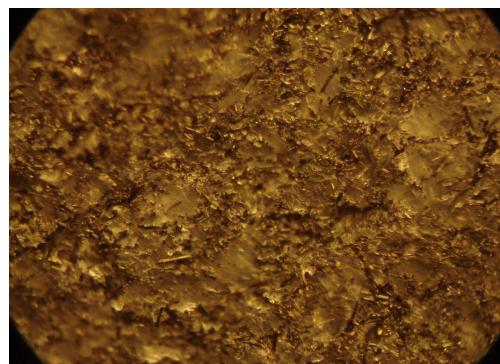


Fig. 4.12 Macrostructure of the surface of the samples obtained for the technological modes of mixing $v > 5$ m/c ($\times 200$)

The results of the experimental studies show that the change in the properties of PCM samples obtained at higher speed modes and at different mixing times is associated with the

effect on the microstructural characteristics of the material (the quality of the composition of the composition, the average fiber length in the composition after mixing and its physical and mechanical properties properties).

4.4 Two-stage mixing mode of PTFE composites

The strong connection between PTFE-matrix and CF is difficult to obtain by traditional methods of preparation of the filler. The surface of CF has insufficient effect of surface wetting with polytetrafluoroethylene, in addition, its surface is hydrophilic, which prevents the physical and chemical sorption of macromolecules PTFE-matrix.

Surface treatment of carbon fibers contributes to their interaction with the matrix of the composite [23, 27, 29].

According to the traditional method of obtaining a carbon-fiber filler [30] with a length distribution for certain dependencies, the carbon fabric is ground in a hammer crusher, and separated by a sieve the fibers from the fabric are subjected to further milling in a crusher with sub-knives.

Shredding process parameters guarantee obtaining of a ensemble of fibers with a certain length distribution.

But CF obtained fraction is less than "critical" length practically do not mix with the PTFE. In this case, dust-containing agglomerates are formed in the volume of the composition. They "sputter" longer, reactive-active fibers and reduce their compatibility with PTFE-matrix.

This leads to the production of polymer composites with insufficient high strength and wear resistance due to the considerable heterogeneity of the composite structure.

Improving the method for producing carbon filler is possible by further fragmentation CF. In the presence of PTFE powder, this allows the fibers with a length less than "critical" to be bound in carbon-fiber-based agglomerates to be bonded and to prevent them "sticking" to longer fibers. This qualitative and vuhetsevovoloknystyy reactive filler provides increased strength and wear resistance of PTFE composites [31].

With the help of raster electron microscopy, the structure of CF, prepared by the method in situ, was studied. As we see from the microphotography, a layer with high content of PTFE is formed on the surface of the CF (Fig. 4.13).

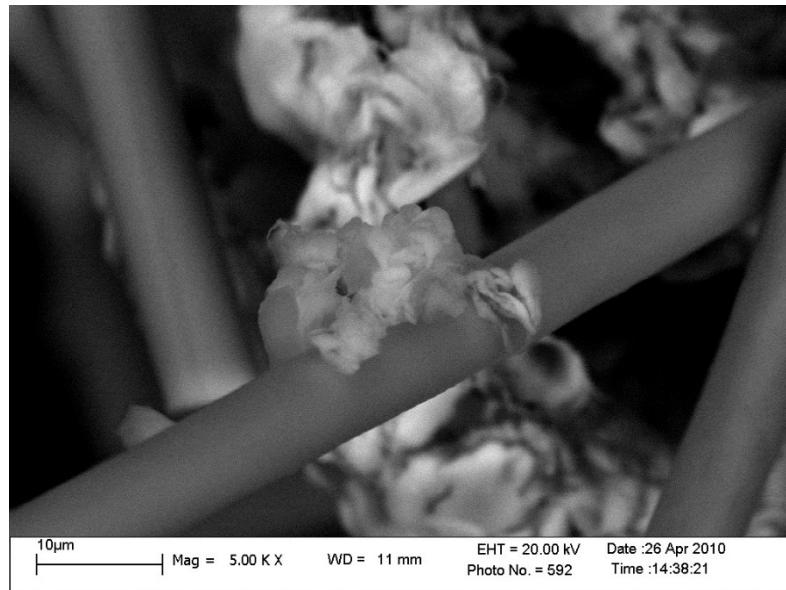


Fig. 4.13 – A layer with an increased content of PTFE on the surface of CF.

The analysis of the test results of the composition with CF, prepared by such a scientific and technical decision [31] and the known technological process [30], shows that the resulting PTFE-based composition with this filler exceeds the known for strength at breaking the 10 – 20%, wear resistance for 17 – 40%.

The effect of increasing the performance of composites due to the developed scientific and technological reception is that the mechanical combination of small (dusty) CF with PTFE powder results in the formation of a dispersed composite product before the composition as a whole is created.

At the end of the process of forming the skeleton of the composition ob'yemnostrukturovanoho it will consist of three fractals. The first – PTFE powder particles are flour particles of CF, the second - longer particles of CF, covered with PTFE layer (Fig. 4.13), and the third - unbound mass of matrix PTFE.

Such a structure of a polymer composite in accordance with the theory of percolation [32] is a prerequisite for the creation of an infinite filler cluster (FC) in a polymer matrix (PTFE).

Thus, the thermodynamic coupling of small particles of fiber with PTFE powder in necessary and sufficient volumes leads to the obtaining of a more reactive active filler. It has a higher thermodynamic compatibility compared to a mechanical mixture of components in similar proportions. This is confirmed by the data given in Table. 4.10. Introduction to the PTFE composition of the prepared CF substantially strengthens it and increases wear resistance [33].

Table 4.10

Physico-mechanical and tribotechnical properties of PTFE-composite from CF obtained by traditional and authored technologies

Characteristics	Conventional technology [30]	Copyright technology [31]
Intensity of the wear 10^{-7} , $\text{mm}^3/\text{H}\cdot\text{m}$	8.2	4.9
Tensile strength, MPa	18.0	24.0
The ratio of CF and PTFE powder (volumetric) in the preparation of the filler	-	1:1

To increase the efficiency of the mixing process of PTFE with crushed carbon fiber, the influence of the stage of the mixing mode of carbon fiber components was studied (Table 4.11).

According to the results of the research, a two-stage process is recommended: in the first stage, *in situ*, CF shredding is performed at a ratio of components (by weight) of 1: 1, and in the second stage additionally enter the required amount of PTFE (optimal ratio 1:4)

Table 4.11

Composition and powerliness in one-sided plastic for one-and-a-two-sided regime

Parameter	Control	Mode		
		One-stage mixing	Two-stage mixing	
			I-stage*	II- stage
Composition (mass. %)				
PTFE	100.0	80.0	20.0	60.0
CF	-	20.0	20.0	-
Mixture after I stage	-	-	-	40.0
Properties of CFRP				
Tensile strength, MPa	15.0	20.0	-	22.0
Strength under compression, MPa	28.0	31.0	-	35.0
Relative elongation, %	20.0	20.0	-	45.0
Wear intensity $I \cdot 10^{-7}$, $\text{mm}^3/\text{N}\cdot\text{m}$	12.5	9.0	-	7.0

As can be seen from the tables in the table 4.11 data, when making a composition in a two-stage mode, compared with the control, the strength of carbon fiber properties increases by 45%, and wear resistance – by 80%.

Positive effect is provided by "binding" of PTFE of dust particles (2 - 60 μm) CF and the formation of discrete energetically active centers of such composition at its high physical and chemical activity as a result of mechanical activation, which is proved by methods of electron microscopy (Fig. 4.14).



Fig. 4.14 REM-microphotography of carbon fiber plastics made in two-stage mode (x200)

Due to high strength and wear resistance, the polymer composition can be used to make parts of friction units for power, chemical and special equipment.

4.5 Features of compression technology

One of the main drawbacks of PCM on the basis of PTFE and CF remains moisture absorption in the operation of chemical and oil equipment with liquid and gaseous media [43].

The details material, operating under such conditions, shows an intermittent growth of wear, sometimes even critical over time. The positive results as the reducing of moisture absorption can be reached due to the optimization of the composition molding technology.

The provision of stable bond between fillers and PTFE-matrix in a composite is reached due to the optimal structuring of PCM during molding. This index reflects the provision of necessary thermodynamic, kinetic, and mechanical compatibility of system ingredients, gaining maximal physical and mechanical interactions in the polymer-filler interface and the homogeneity in the macrovolume of composites, the minimization of structure defects and moisture absorption of composites while operating in the conditions of high humidity [23].

The operation characteristics and operation life are reduced significantly (3-4 times) and the wear rate rapidly increases (4-8 times) with the increase of moisture exposure on the compressor sealing composite material. It requires shutdown and unscheduled repair, which finally results in additional expenses (replacement components, equipment stoppage expenses etc.).

As a control sample, the F4CF20 composite with such composition % (mas.) was used: PTFE – 80 %, CF – 20 %, which was obtained according to the known technology [25]. The industrial process of molding is realized under the following molding conditions – 40-45 MPa, molding speed – $0.5 \cdot 10^{-2}$ m/s, and time of molding at max pressure – 300 sec.

The research of mechanism and the nature of moisture absorption by CFRP and the evaluation of property loss of the composition were carried out.

The research results showed (Fig. 4.15) that surface microdefects (Fig. 4.15, a) could appear in CFRP during the product manufacturing, which can develop into destroying cracks (Fig. 4.15, b).

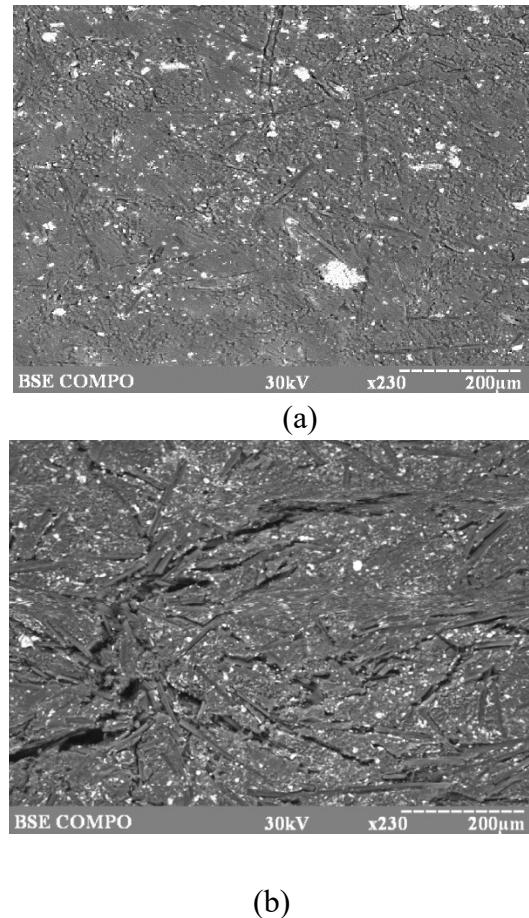


Fig. 4.15 Electron photomicrographs of CFRP F4CF20 before (a) and after (b) exposition to water (x230)

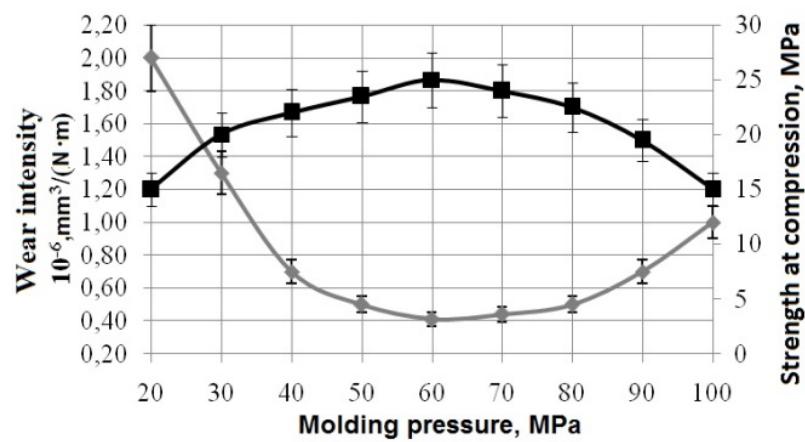
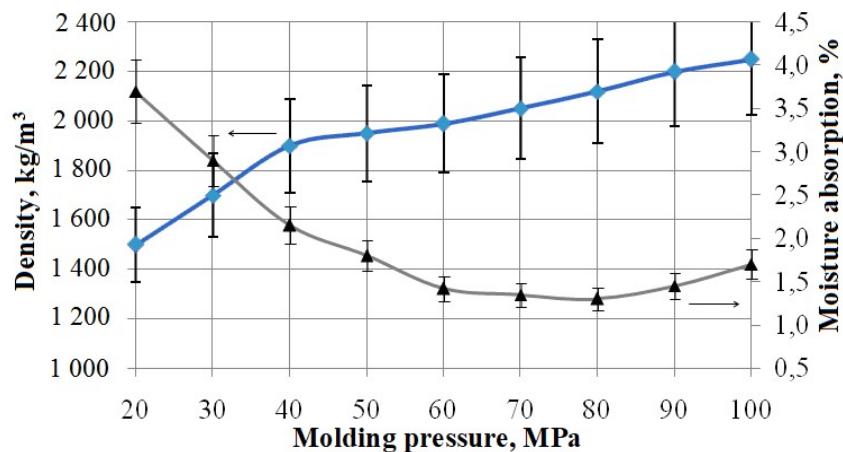
According to the analysis of research data, it was found out that the moisture absorption of the composite with CF must be adjusted by the molding technology, which defines the structure, properties and the durability of composite material.

The main ways of the composite moisture absorption and the preservation of its operation properties with the use of the obtaining technology were grounded. These are the choosing of optimal molding conditions; the previous processing of CF with PTFE particles; the introduction of processing aids into CFRP.

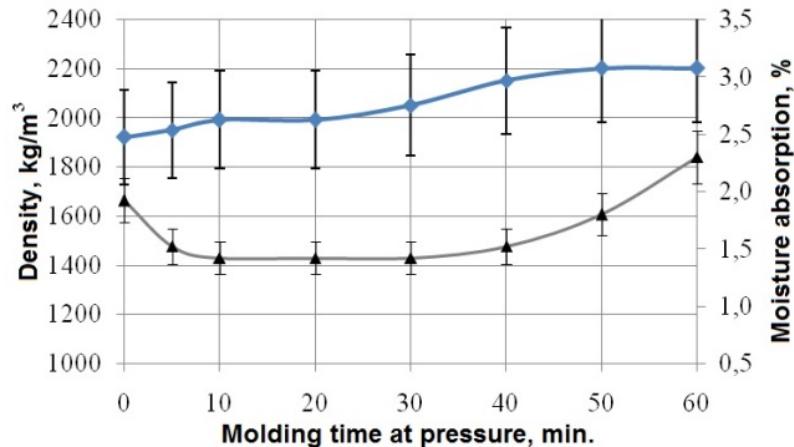
It was estimated that the main technological characteristics which influence the components compatibility, structure and properties of composite during its molding are: pressure, molding speed, time of molding under the pressure. These factors were taken as the main ones for experiment planning and the development of mathematical model of molding.

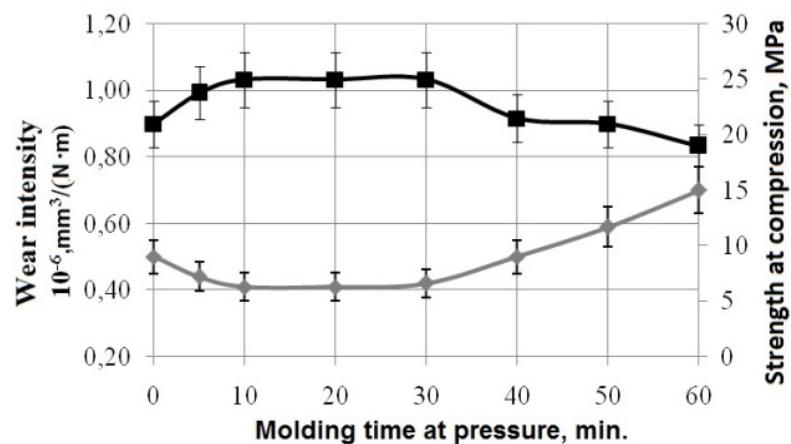
To gain optimal functional characteristics of PTFE composite, the crucial and main operation properties are wear rate and strength boundary at pressure, which regulate the operating capacity of frictional units in compression machines.

The research results of changes in physicomechanical and operation properties of composites depending on the technological characteristics of molding are shown in Fig. 4.16.

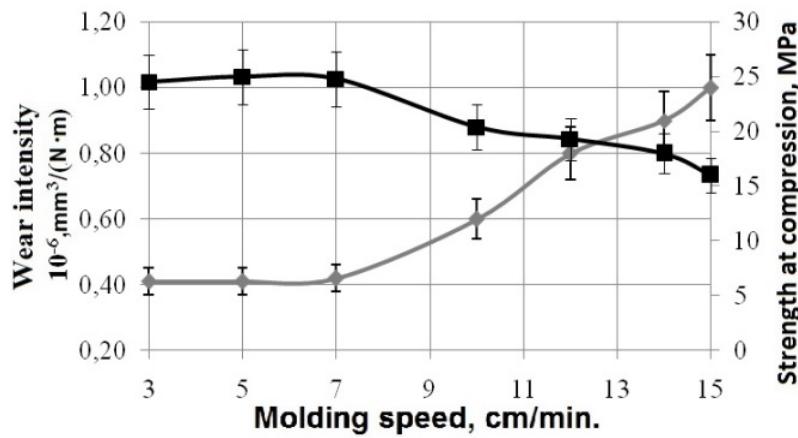
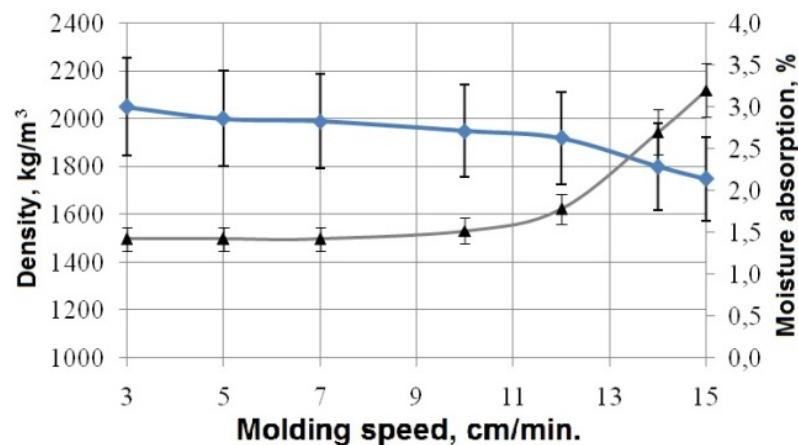


a)





b)



c)

Fig. 4.16 Dependences of CFRP properties on molding pressure (a), time of molding under maximum pressure (b) and molding speed (c).

It was found out and proved by the research results shown in Fig. 4.17 that the crucial factor which sufficiently influences the moisture absorption is the composite density. In this case, the molding pressure and molding speed are the crucial technological factors.

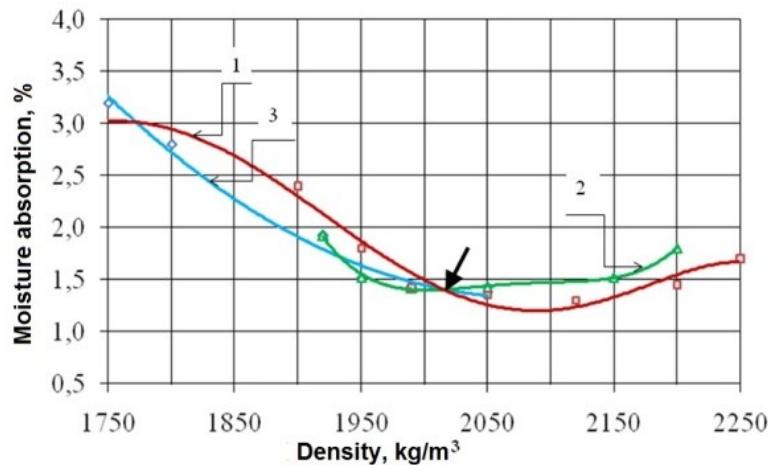
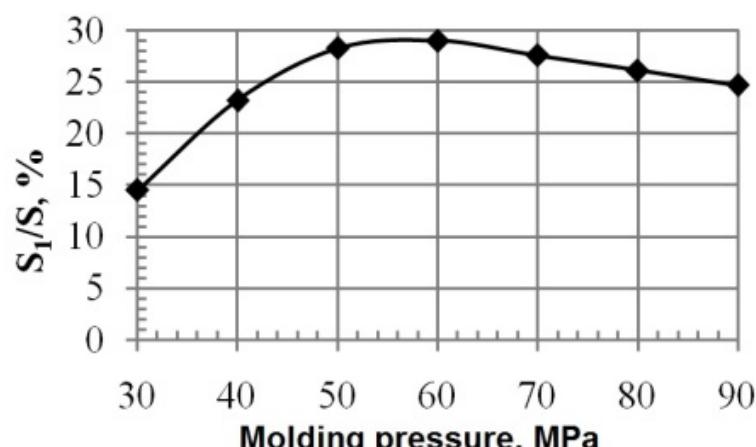


Fig. 4.17 Dependence of moisture absorption on density for a variation of parameters of pressing a composite: 1 – molding pressure; 2 – time of molding under the pressure; 3 – molding speed; 4 – optimum parameters.

It was theoretically grounded and experimentally proved (Fig. 4.18) that the optimization of parameters of the PCM molding technology contributes to an increase in adhesive activity of PTFE-matrix with CF.



(a)

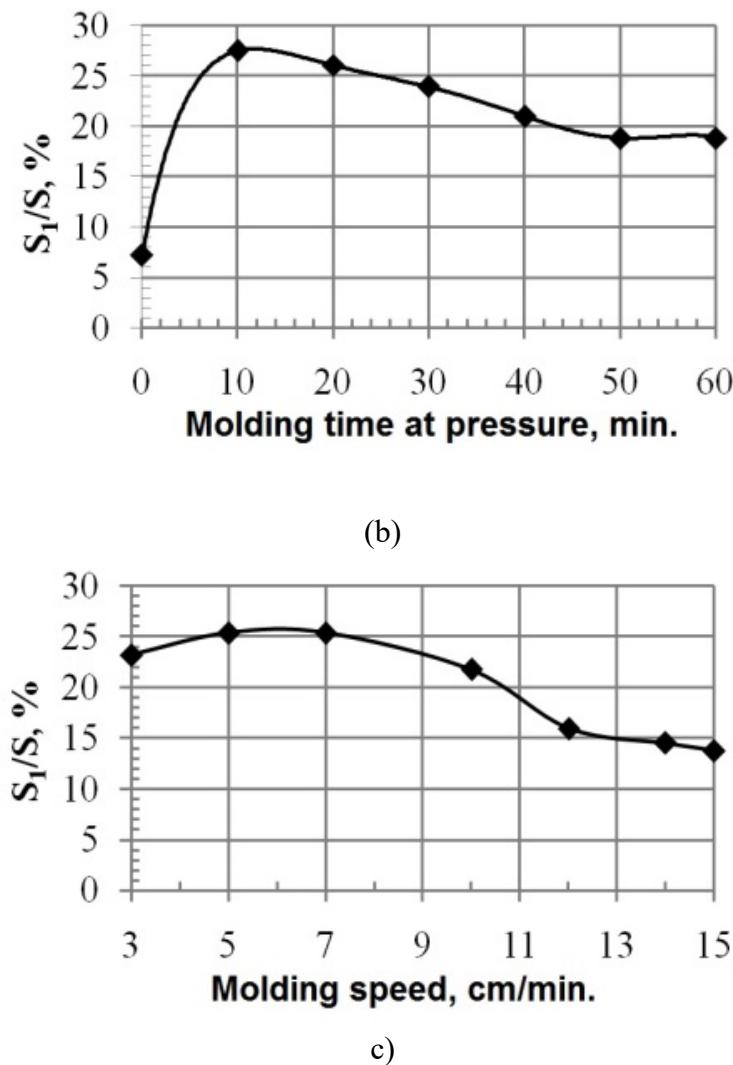


Fig. 4.18 Adhesive durability of CFRP depending on technological modes of pressing process (S_1 – surface area of ruptures; S – nominal area of sample): (a) molding pressure; (b) molding time at pressure; (c) molding speed

It is conditioned by the interaction activation of radicals on interphase and, as a result, the moisture absorption is decreased and the physicomechanical, tribotechnical properties of PCM are increased.

Thus, the carried out research revealed and scientifically proved that the optimal conditions, providing stable phases interactions between PTFE-matrix and CF during molding as to physicomechanical and tribotechnical properties are the following:

- molding pressure – 60 MPa;
- molding speed – 0.83 m/s;
- molding time at pressure – 600 s.

Such conditions provide CFRP with minimal moisture absorption (less than 15–20 % in comparison with the analog) and a high index of operation properties (compression strength is 15–25 % higher, wear resistance is 40–45 % higher than that of the analog) due to the optimal structuring of CFRP during molding.

4.6 Methods of modification of polymer matrixes. Technological operations for preparation and modification of polymer matrixes at the preparatory stage

Despite the unique characteristics of PTFE, it has a number of properties, which limits its use as a tribotechnical material. These include [7, 9, 12, 67]:

- high tensile creep loading PTFE that appears under 3 MPa of tensile loading at normal temperatures;
- high thermal-expansion coefficient PTFE at normal temperatures that changes abnormally at a temperature in the range of structural phase transitions (temperature ranges from 280 to 310 K);
- low resistance of epoxy polymers to dynamic loads;
- low thermal conductivity (10-50 times less than in metals);
- low thermal conductivity of polymer (10-50 times less than in metals);
- low wear resistance of polymer under dry friction conditions, especially at high sliding velocity.

The heat released in the friction zone due to low thermal conductivity facilitates a significant rise in temperature on the friction surface. 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. Review of the literature and patents [13, 67] reveals the low potential of traditional technological approaches in obtaining PTFE-based PCM. However, various advanced technological methods that allow obtaining composite materials and products with the required performance properties may be implemented. They are the synthesis of polymer matrices of different composition and structure [11, 65]; composition of polymer and oligomer mixture with different levels of interaction [14, 15, 54, 67, 128]; modification of matrices of various origins by aimed restructuring and structural interaction energy impact [16, 17, 65]; matrix modifying by additions of activators of different size, shape and properties [18, 19, 45, 56]; formation of nanophase matrices with significantly different characteristics [5, 8, 78, 89, 100]. 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 [20].

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) (Fig. 4.19).

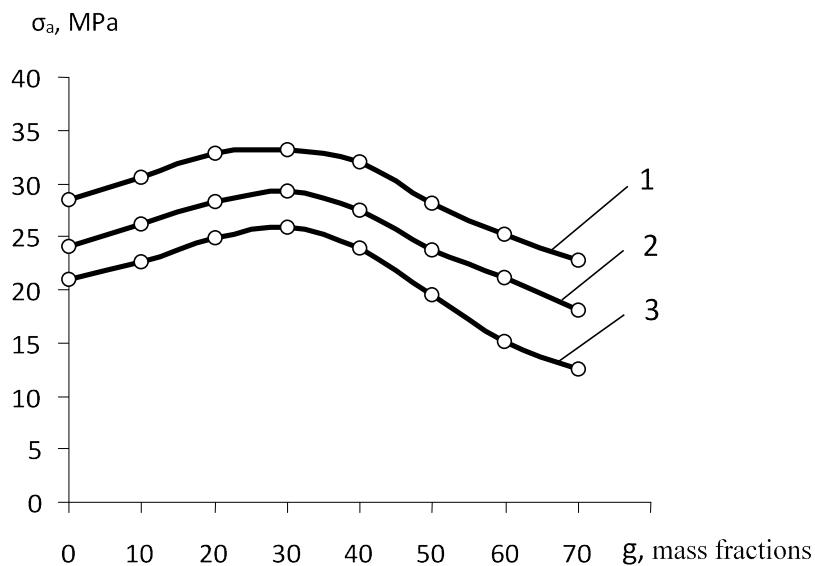


Fig. 4.19 The effect of KO-921 modifier on adhesive strength of epoxy polymers with PEPA hardener content: 1-12 mass fractions, 2-13 mass fractions, 3-11 mass fractions.

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 in the matrix, and at the higher content of the hardener, the defective structure with high internal tensions (0.61 MPa) is formed.

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 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 polymethyl 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 [21, 22, 134, 137]. 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 pos-

sible 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 (Fig. 4.20).

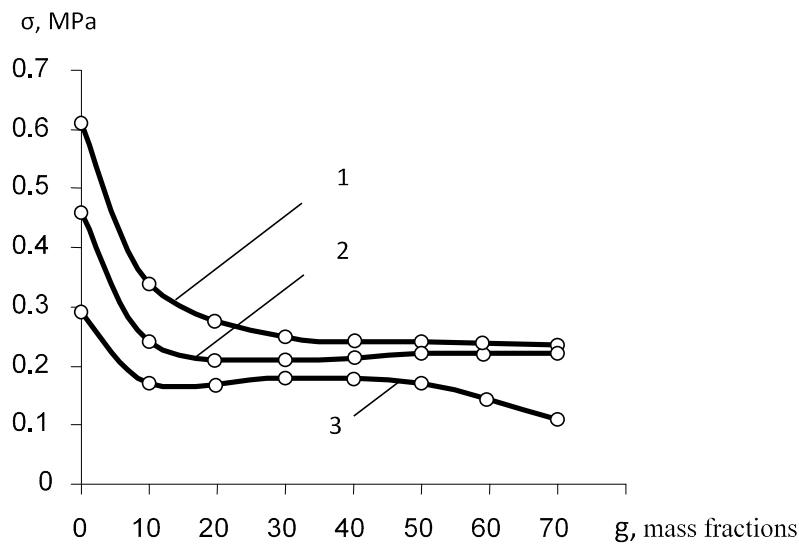


Fig. 4.20 The effect of KO-921 modifier on internal tensions of epoxy polymers with PEPA hardener content: 1-13 mass fractions, 2-12 mass fractions, 3-11 mass fractions.

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 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 had epoxy silicon-organic polymers with modifier of the concentration of 30 mass fractions.

CF surface is normally inert [6]. The PTFE-composition with CF is a complex heterogeneous system with numerous surfaces of phase distribution. Physicochemical processes in boundary layers during forming of composition make a significant contribution to structure forming and, thus, to major operating properties in such compositions [10, 23, 24]. The formation of reaction surfaces of PTFE-matrix and CF is an important scientific and practical task and its solving guarantees obtaining and reproducing the planned properties of the composite.

It was suggested to modify the surface of carbon fiber by different methods in order to provide technological combining of carbon fiber with the polymer matrix in PTFE-based anti-friction composite materials [12, 13, 25, 26, 67, 78, 89]. Such filler processing allows increasing composite materials characteristics, which depend a lot on adhesive bonds of carbon fiber and PTFE-matrix [13, 17, 28, 45, 67].

The carried out research has shown that the most widespread method of carbon fiber surface modification with the purpose of improvement of the PTFE adhesion to CF is thermal-oxidation of fibers surface. The thermal-oxidative treatment of CF surface results in an increase of specific surface and multimolecular adsorption [27, 29, 67, 71, 79].

The peculiarities of thermal (before milling) and thermomechanical (during milling) modification of fiber surface were studied according to the results of experiments. Table 4.12 contains the research results of wear resistance of CFRP containing heat-treated fiber, which prove the effectiveness of thermal (an increase of wear resistance up to 100 %) and thermomechanical modification (an increase of wear resistance up to 130 %) of CF.

Table 4.12
Wear intensity of CFRP ($I \cdot 10^{-7} \text{ mm}^3/\text{m}$) at the introduction of CF
after thermal and thermomechanical modification

Modification	Control	Temperature °C					
		100	200	300	400	500	600
Thermal	12.5	12.0	10.0	8.0	6.0	12.5	13.0
Thermomechanical		11.0	9.0	7.0	5.5	11.5	-

The most effective thermal and thermomechanical modification is at 400 °C (the temperature of crystallites melting PTFE is 325-350 °C), it happens as a result of supermolecular structure change, because of flexibility increase of PTFE macromolecules.

The increase of strength by 50 % and wear resistance by more than 2 times is observed for CFRP containing CF after thermomechanical modification.

In order to intensify the energy effect during milling of CF, the mechanical modification was carried out in a vacuum ($p = 0.073 \text{ MPa}$). It was found out that strength of CFRP containing fiber modified in a vacuum increased almost by 50 % and wear resistance increased by 100% while milling of CF in a vacuum (Table 4.13).

Modern material science widely uses synergistic approach to the issue of increasing the strength of composites, thus, the research of combined influence of thermomechanical processing and vacuum processing of CF on physicomechanical and tribotechnical properties of CFRP was performed (Table 4.14).

Table 4.13
Physical and mechanical properties of CFRP depending on the conditions
of grinding fiber (grinding time 15 min, vacuum $p = 0.073$ MPa)

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 $I \cdot 10^{-7} \text{ mm}^3/\text{m}$	12.5	7.0	6.0	7.1	6.5

Table 4.14
Properties of CFRP at thermomechanical modification of grinding fiber
under the vacuum conditions ($p = 0.073$ MPa)

Parameter	Control	Temperature processing $^{\circ}\text{C}$				
		100	200	300	400	500
Tensile strength MPa	15.0	24.8	24.9	25.2	26.0	24.4
Wear intensity $I \cdot 10^{-7} \text{ mm}^3/\text{m}$	12.5	4.4	4.4	4.2	4.0	4.5

As it was shown in Table 6, the strength of CFRP increased by more than 75 % and wear resistance increased by more than 3 times, as compared with the not modified sample during thermomechanical modification of fibers at 400°C for 15 min in a vacuum ($p = 0.073$ MPa).

Thus, having analyzed the series of experiments, revealing the effectiveness of influence of different technological methods on composite properties, it turned out that the thermal vacuum technology of CF modification, which allowed increasing the strength of PTFE composite by 18-22 % and its wear resistance by 20-25 % was the most effective; all these presented practical interests for industrial implementation.

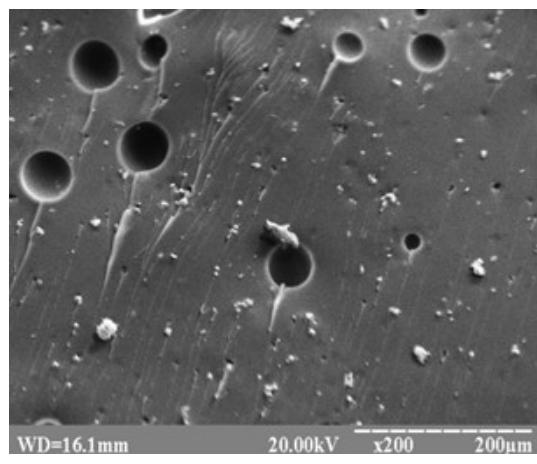
Adhesive epoxy capacity is much higher compared with thermoplastics, so it is not necessary to conduct special preparatory operations connected with activation of fillers. In this regard, it is appropriate to perform an operation of powders drying in order to remove moisture at 100°C temperature for 1 hour, which allows raising the mechanical properties to 30-40 %.

The perfection of obtaining a method of carbon filler is possible due to the successive milling of CF in the presence of PTFE powder, allowing binding of fiber with the length less than «critical» in CFRP agglomerate and preventing «agglutination» with longer fibers. Such qualitative and chemically reactive carbon-fiber filler increases strength and resistance to wear of PTFE-composite [8, 12, 30, 56, 71, 74]. The structure of CF, prepared *in situ*, is studied with the help of scanning electron microscopy.

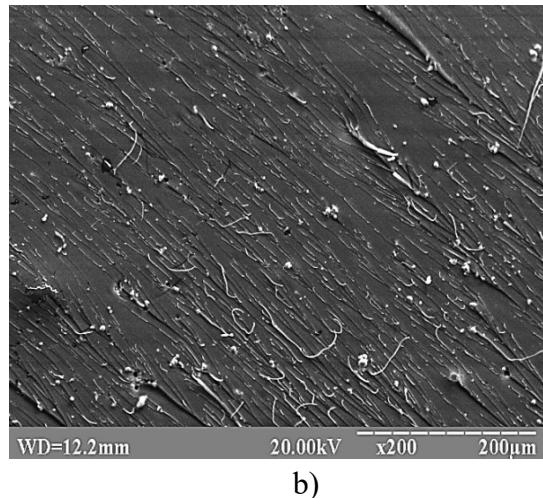
The research analysis of experiments of composition with CF, prepared according to the above mentioned scientific and technical solution [17, 22, 31, 56, 76, 78] and the known technological process [8, 27, 32, 67, 82], shows that PTFE-based compositions obtained with the help of such filler increase the breaking strength by 10-20 % and resistance to wear by 17-40 %.

The effect of the increase of composite operational properties due to the developed scientific-technological method consists in the mechanical combining of small (powdery) CF with PTFE powder, which results in the creation of disperse composite product before the creation of composition in general. The composition will consist of three fractals at the end of volume structured skeleton formation. The first fractal is flour particles of CF bonded with PTFE powder, the second is longer CF coated by PTFE (Figure 3), the third is unbound mass of matrix PTFE. According to the percolation theory [16, 25, 33, 39, 67, 85], such structure of polymer composite is a prerequisite for the creation of an infinite cluster of filler (CF) in a polymer matrix (PTFE). Thus, the thermodynamic bond of small particles of fiber with necessary and sufficient volumes of PTFE powder results in obtaining the more reactive filler, which has higher thermodynamic compatibility in comparison with a mechanical mixture of components in analogous 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 (Fig. 4.21, a).



a)



b)

Fig. 4.21 Fracture fractograms of epoxy composites filled with iron dispersed particles:
a) without treatment, b) ultrasound treatment of composition ($\times 200$).

Epoxy composites surface after treatment of composition at the stage of ultrasound treatment (Fig. 4.21, b) is characterized by a large number of distinct microscopic chipping lines, which have significant branchings that define the system structuredness of hightension state. In epoxy composites, the compositions of which were treated by ultrasound, the minimal value of residual tensions ($\sigma = 0.48$ 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.

According to the analysis of research data, it was found out that moisture absorption of the composite with CF had to be adjusted by molding technology, which defines the structure, properties, and durability of the composite material. The main ways of composite moisture absorption and preservation of its service properties with the help of the obtained technology were grounded. These are the selection of optimal molding conditions; previous processing of CF with PTFE particles; introduction of processing aids into CFRP.

The complexity of formation of epoxy composites is connected with presence of the air inclusions 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 Fig. 4.22 a and Fig. 4.22 b it is evident that fraction fractograms of epoxy composite material have a smooth surface since they are absent of sharp drops of relief.

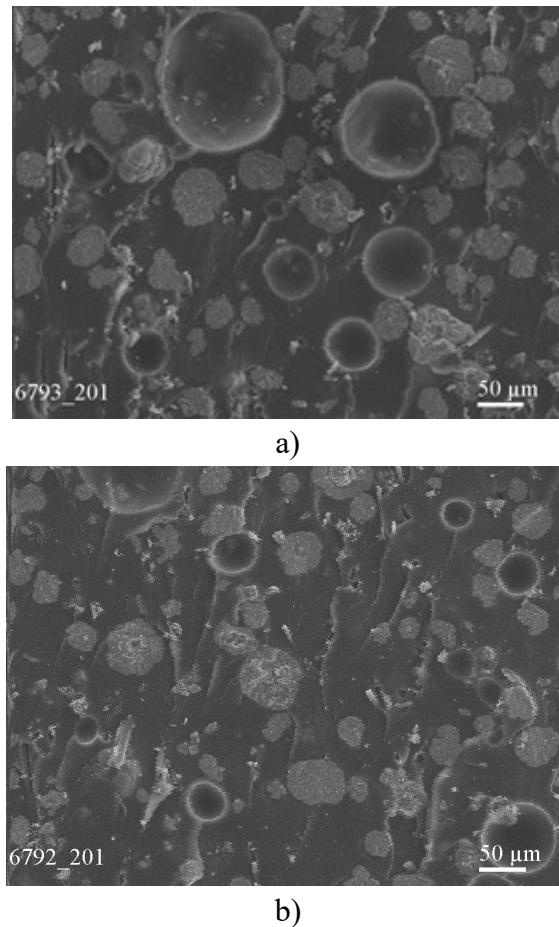


Fig. 4.22 Fracture fractograms of epoxy composite material formed under the pressure of
a) 150 MPa, b) 300 MPa.

Because of the presence of insignificant appearances 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.

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.

Service life of the composite details depends on the heat exposure during their manufacture. The lack of sufficient information and summarized data about the impact of heat exposure on the properties of polymeric materials complicates the choice of optimal modes for production and heat treatment of PTFE-composites [11–16, 34, 35, 37–42].

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 [23–27, 36].

The main type of thermal effect on PTFE and its composition is sintering, which consists in heating of half-finished product up to the temperature of 360–380 °C, exposure at this temperature (1 hour for 1 mm thickness) and rapid cooling at a temperature range from 327 °C to 350 °C [7, 9, 12, 37, 37–40].

The exposure time of the material during quenching has a significant effect on properties of the final products. This is due to the change in the polymer structure of macromolecules configurations and to an increase of number of straight sections which become PTFE cooling crystallization centers.

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 [41, 42]. 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. At the same time, orientation of the molecules fragments takes place that allows forming of more homogeneous supermolecular structure and stable composite properties in the whole volume. As a result, strength characteristics and wear resistance of the composite are increased.

The cascade mode of sintering with hour exposure at each step of cascade allows removal of uncompensated tension of molding and provides complete structural transformations in composite volume during transition through characteristic temperature points of phase transformations, which prevents damage of the composite integrity during cooling (cracking) and formation of necessary correlation of polymer matrix phases. All these allow forming of the structure of CFRP of high homogeneity and stable properties of the composite. This results in an increase in the strength and resistance to wear of the composite (by 25 and 50 % respectively) and it can be recommended for the production of construction materials of general and antifriction designation able to operate at high temperatures and also in chemically active media.

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 re-

duction 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.

In works [43-46] 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 [24, 33, 30-38, 43, 44, 134].

The highest values of adhesive strength ($\sigma_a = 39.2$ MPa) were obtained for epoxy silicon-organic polymers, thermally treated at 210 °C, that registered the lowest internal tenses (0.17 MPa) (Fig. 4.23).

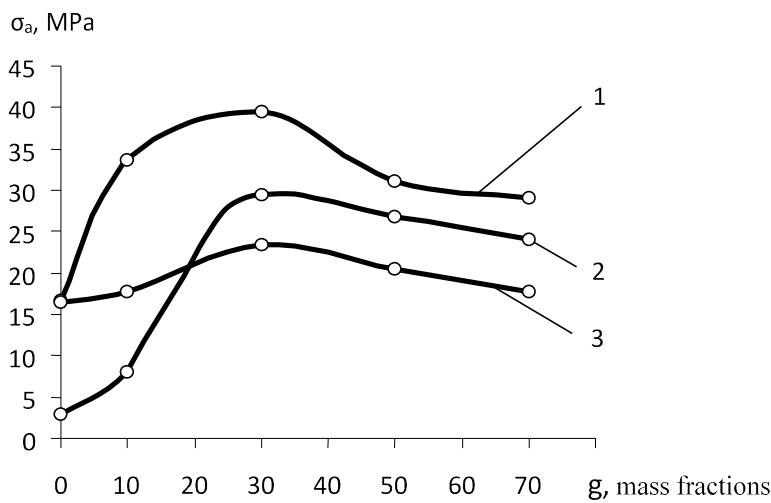


Fig. 4.23 The effect of KO-921 modifier on adhesive strength of epoxide matrix at final thermal treatment temperature: 1-210 °C, 2-240 °C, 3-180 °C.

Thermal treatment at $T_k = 180$ °C does not provide sufficient thermal effect on the structuring processes in the presence of silicon-organic additive, and a high temperature of 240 °C 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 in comparison to the other modes, as evidenced by the deterioration of physical and mechanical properties of the epoxy organic silicon matrix processed at $T = 240$ °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 of 7 K/min during 4 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.

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, 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 [56, 67, 78, 83].

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 [67, 72, 84, 86].

4.7 Peculiarities of Composition sintering Technologies

The service life of composite details depends on the heat exposure during their manufacture. The lack of sufficient information and summarized data about the impact of heat exposure on the properties of polymeric materials complicates the choice of optimal modes of the production and heat treatment of PTFE-composites [45, 67, 78, 132].

The technology of PTFE-composites thermal processing is a thermal process of impact on the material that starts with the drying of the initial material and ends with the cooling of the heat-treated product.

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Thus, the technological modes of heat processing define the degree of crystallization and, as a result, they define physicomechanical properties of the material. The crystallinity degree of sintered PTFE ranges from 50 to 70 % and depends on the molecular weight and the speed of cooling. The majority of PTFE mechanical properties worsen with the increase of crystallinity degree [45].

The research is based on the task to increase the breaking strength and wear resistance of PTFE-based composite material, reinforced with CF, due to varying sintering modes.

The assigned task is fulfilled due to the fact that composite material sintering is carried out in the cascade heat treatment mode, taking into consideration the time of phase transition and critical points of such transition of the composite material (Fig. 4.24).

During the sintering of billet material at the stage of the particles fusion of polymer and carbon fiber filler, the chemical, physicomechanical, physicochemical, and electrical properties of the future product are formed in the composite. After applying the cascade heat treatment mode to the composite during sintering, which includes heating at different speeds and different time exposures with slow cooling, the shift of alternate disordered orientation and the structure stabilization at the molecular level take place. At the same time, the molecules fragments orientation takes place that allow forming a more homogeneous supermolecular

structure and stable composite properties in the whole volume. As a result, the strength characteristics and wear resistance of the composite are increased.

The cascade mode of sintering with an hour exposure at each step of cascade allows removing the uncompensated tension of molding and provides complete structural transformations in the composite volume during the transition through characteristic temperature points of phase transformations, which prevents damaging the composite integrity during cooling (cracking) and the formation of necessary correlation of polymer matrix phases.

All these allow forming the structure of CFRP of high homogeneity and stable properties of the composite. As a result, the strength and wear resistance characteristics of the composite are increased (by 25 and 50 % respectively) and it can be recommended for the production of construction materials of general and antifriction designation able to operate at high temperatures and also in chemically active media.

Conclusions

The experience of lot of theoretical and practical works concerning the technology of PTFE-composites formation, accumulated by many prominent specialists and author's in this sphere has been analyzed and systematized. The results of this work were published in many scientific editions, but the continuation of the search for the optimal technology of PTFE-composites creation presents scientific and practical interest.

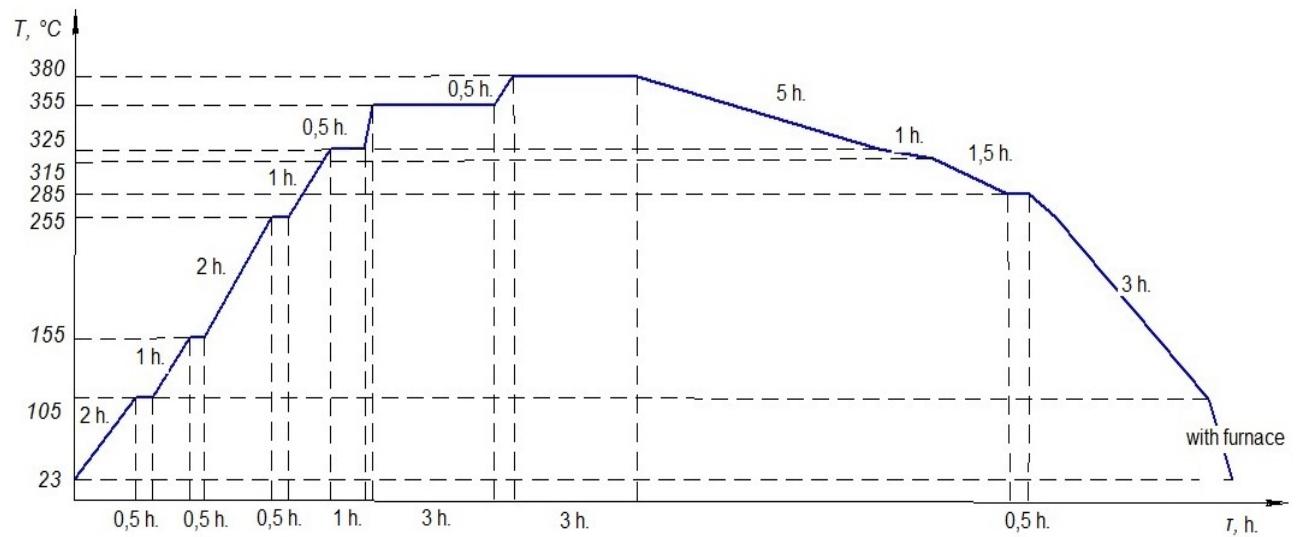


Fig. 4.24 Graph of cascade heat treatment during sintering PTFE-composite.

The research results defined the operation regimes of process equipment: after the processing, the PTFE-composites have increased operation properties in comparison with basic ones and can be most effectively used for industrial implementation:

- energy impact on the uncompounded PTFE results in an increase in parameters of deformation and strength characteristics (breaking strength by 2.6 times, breaking elongation by 4.3 times) while preserving high tribotechnical characteristics;

- it turned out that the thermal and vacuum technology of CF modification allowing the increase of PTFE – composite strength by 18-22 % and its wear resistance by 80 % – was the most effective;
- while manufacturing the PTFE-composition with CF using the two-stage mode, the level of strength characteristics of carbon-filled plastic in comparison with the control sample increases by 45% and wear resistance increases by 80 %;
- the optimum molding modes were found, which provide a stable phases interaction between the PTFE-matrix and CF with minimal moisture absorption (less than 15-25 % in comparison with the analogue) and high operation properties (compression strength is higher by 15–25 %, wear resistance is higher by 40-45 %);
- the cascade mode of sintering the PTFE-composite allowed obtaining the PCM, which is characterized by an increased strength and wear resistance (25 and 50 % respectively) in comparison with the analogue.

It is shown that under the action of mechanical activation, an ordered spherulite supramolecular structure of the matrix PTFE, which is characterized by micro and nanosizes and contributes to the growth of the thermostability of the modified polymer on (293-353) K., is established that mechanical activation does not lead to a marked destruction of the PTFE molecular chain but occurs conformational changes, which consist in increasing the concentration of valence and finite groups of CF_2 , which can lead to an increase in the physico-mechanical and tribotechnical properties of the polymer.

Thus, PTFE-composites are a bright illustration of material science triad – “composition – structure – properties”. Although, the processes of strengthening such materials cannot be described with the use of the universal theory, the technology of the PTFE-composites of tribotechnical designation has taken its place and is one of the main ones.

Modified PTFE is a further development of PTFE with improved characteristics compared with the standard PTFE as a result of chemical modification (incorporation of a modifier in the polymer chain).

It is established for the first time 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 is observed at this, but the concentration free CF_2 groups to (4-8) times. Using the quantitative estimates of the relationship between the parameters of mechanical activation, the structure of composite materials and the level of their operational properties, the theoretical basis for predicting the latter was formulated for the first time. A fundamentally new technology for the progressive preparation of the matrix and fillers is developed, which consists in the separate mechanical activation of the ingredients before mixing under different modes of equipment, for obtaining PTFE composites with maximum wear resistance while maintaining a sufficient level of physical and mechanical properties.

CHAPTER V

MATHEMATICAL SIMULATION AND OPTIMIZATION OF COMPOSITE STRUCTURES BASED ON POLYTETRAFLUOROETHYLENE FOR ENSURING HIGH WEAR-RESISTANCE PROPERTIES

The influence of the mechanochemical activation of the matrix, fillers and composition on the physical, mechanical and tribotechnical properties of the composite has been investigated by methods of mathematical modeling. The optimum content of fibrous and dispersed fillers in the composition volume and the parameters of the production technology that provide maximum wear resistance of the composite while maintaining a sufficient level of physical and mechanical properties are found.

The experience of using wear-resistant composite materials on the basis of polymers in the friction knots of different applications of technological equipment has shown [56, 89, 138] that maximum success can be achieved, only scientifically based approach to the design of products made of composite materials. It is necessary to take into account the peculiarities of constructing models of these materials on the basis of the mechanics of composite materials and the peculiarities of the technological process of their production.

The task of modeling the optimal wear-resistant composite material is the selection of physical and mechanical characteristics of a polymer matrix, which is reinforced with short fibrous filler and dispersed inclusions of various shapes. This will ensure the reliable work of manufactured structures from this material at minimum technological costs. In modeling, it is necessary to take into account the multifactorial dependence of the wear resistance of the composite material on its properties, which describe the deformation processes within the elasticity, viscosity and plasticity. The thermophysical properties of the composite are important because friction processes cause an increase in temperature, which causes the appearance of thermal fields in the material and affects the change in the macroscopic characteristics. The effects of temperature and plastic deformation can even change the structure of the material.

One of the ways to solve the problem is to establish the functional dependencies of the physical and mechanical properties of the composite material on the volumetric composition, the layout of the arrangement, the geometric form and the physical and mechanical characteristics of the components from which the composite material is composed. Such studies require the solution of the boundary-value problems of the mechanics of composite materials describing certain processes of deformation.

A polymer material should have high resistance to viscoplastic and plastic deformations, hardness and fluidity limit and at the same time it should be plastically deformable. Thus, there appears a task to calculate mechanical characteristics of three-component polymer composites with a binary filler according to the properties of the initial ingredients.

The authors of the article [9, 45, 67, 83] suggest that the characteristics describing the ability of the material to be worn during friction should be the correlation of its hardness H to the elasticity modulus of E, in the paper [10, 123] the hardness is substituted with the viscosity.

One of the ways to solve the given task is to establish functional dependence of composite material physico-mechanical properties on spatial distribution, arrangement scheme, geometrical forms and physico-mechanical characteristics of components of which it consists. Such investigations require solving some boundary value problems of composite material mechanics that describe these or those deformation processes. Another approach that is applied in this paper allows to employ variation principles pf mechanics of a solid body and formulate boundary value problems as the condition of minimality of functionality $\Phi(v)$ on the set of possible shifts v or their velocities [11, 12, 123, 137]. Such an approach is the reflection of the fundamental energetic principle which states that some functionality of an energetic type takes the minimal value only on the values of variables that are solutions of a boundary value problem.

The basic structures for investigation are three-component composite materials whose structure is constituted by the matrix (PTFE) that is statistically homogeneously reinforced with the inclusions of different geometrical forms (Fig. 5.1).

It should be noted that the actual abrasive-resistant composite materials have a random structure, due to the incorrect form of inclusions, and their random placement in the matrix. The technological process of constructing structures adds additional complexity to the structure, for example, the presence of porosity (capture of air during sintering) or the wide distribution of lengths of inclusions, fibers obtained from carbon fabric by grinding in mill-mills. This distribution of lengths of inclusions is most often described by a gamma-function (gamma-distribution in the theory of probabilities) [3, 45, 67, 89, 90]. Note that strictly derived theories in the mechanics of composite materials are based on some assumptions or hypotheses that determine the limits of the application of the results obtained and the possible correction of theoretical models in the form of conducting experimental studies. This again confirms the significance of the combination of theoretical and experimental research in solving the problem of optimal design of composite materials.

The monograph studies the possibilities to create three-component tribotechnical materials on the basis of PTFE whose fillers can be carbonic and basalt fibers as well as dispersed particles – kaolin or coke. The starting data were physico-mechanical and geometrical characteristics of the material components. The task consists in designing composite materials of different structure that combine necessary properties of elasticity, viscosity, plasticity with high wear resistance that enables the application of these materials for the products of tribotechnical purpose.

The relations of coherence of elastic and plastic properties are taken as the criteria that describe the ability of the composite material to abrasive wear resistance:

$$T = k^*/E^*, \quad (5.1)$$

where k^* is the limit of the composite material plasticity, E^* is the modulus of elasticity.

Then the task to design wear-resistant materials will consist in determining such structures of composites under which this criterion takes the maximal value. The basic variable parameters are spatial concentrations of fillers.

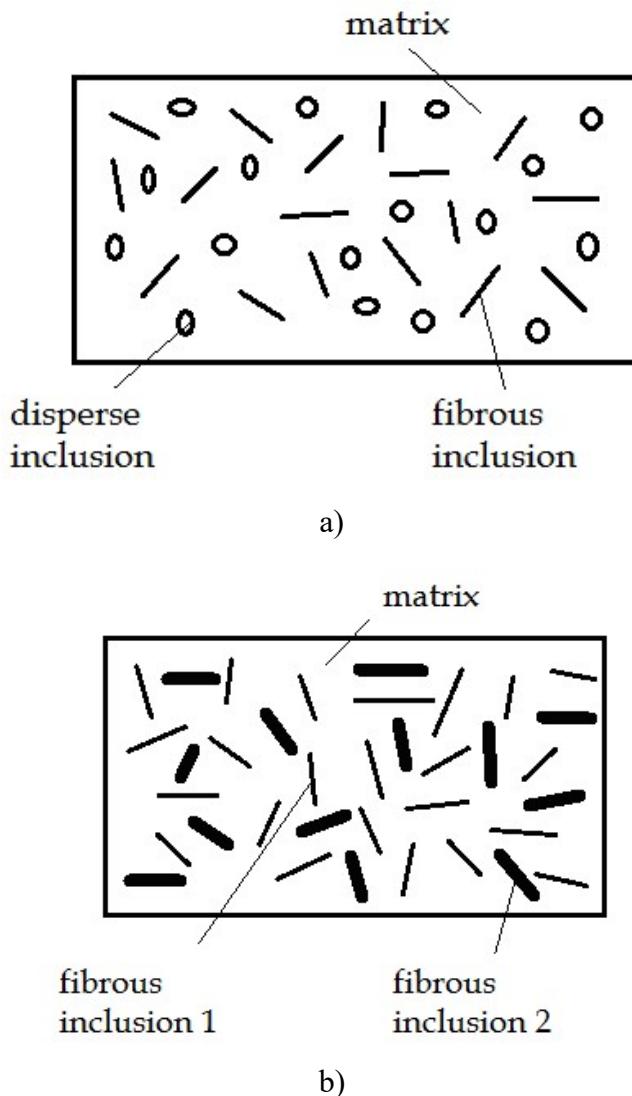


Fig. 5.1 Structure of three-component material based on PTFE filled:
a) disperse and fibrous inclusions; b) fibrous inclusions of two types

5.1 Choice of a model and methods of investigation

Consider the two-phase composite material of random structure, which consists of a polymer continuous matrix, reinforced by the random distribution of discrete inclusions in it. The choice of two-phase material as a research object somewhat simplifies (in comparison with the three-component composite) mathematical calculations and, at the same time, contains all the hypotheses and the initial preconditions for further research. In addition, this approach allows us to consider some well-studied two-component structures - materials with spherical inclusions and materials, reinforced with short fibers. For example, in Fig. 5.2 shows the structure of two-component material, inclusions in which there are short fibers, in Fig. 5.3 - inclusions are particulate particles.

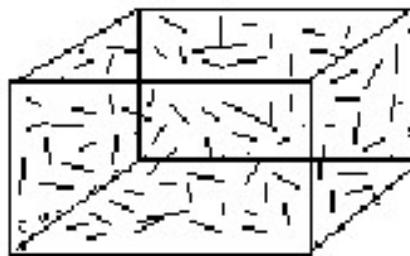
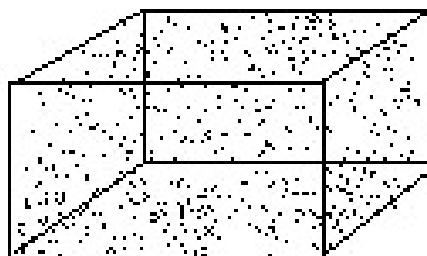


Fig. 5.2 Structure of the two-component material based on polytetrafluoroethylene reinforced with carbon fibers



b)

Fig. 5.3 Structure of the two-component material based on polytetrafluoroethylene reinforced with dispersed particles

Composite material with random structure can be presented as an environment whose physical-mechanical characteristics are random functions of coordinates.

In such a formulation a three-component composite can be presented as a hierarchical structure [10, 11, 45, 67, 89, 90]:

- the first level – matrix conglomerate – the matrix with the inclusions of the first type;
- the second level – the structure of a composite - the matrix conglomerate with the inclusions of the second type.

We design inclusions with the ellipsoid of revolution with the half-axes a and b that allows us to show different geometrical forms – both the inclusions in the form of dispersed spherical particles ($a=b$) and the matrix reinforced with short fibers (the correlation of half-axes a/b of the ellipsoid determines the ratio of the fiber length to the diameter – $a/b \approx l/d$, where l is the average length of the fibers, d is their diameter).

Let us apply the hypothesis of ergodicity according to which averaging the random variables as to the material volume V coincides with the statistical averaging (as to the ensemble of realizations) and average values as to the volume will be marked V . The average values in volume V of any quantities (\bullet) will be marked with angular brackets and determine the following:

$$\langle (\bullet) \rangle = \frac{1}{V} \int_V (\bullet) dV . \quad (5.1)$$

The geometrical structure of the material is described with indicator random functions of the coordinates $\chi_n = (x_1, x_2, x_3)$ that take the value of one around the inclusions of the n -direction and a zero – otherwise. In this case

$$\langle \chi_n \rangle = \frac{1}{V} \int_V \chi_n dV = \frac{1}{V} \int_{V_n} dV = \frac{V_n}{V} = c_n, \quad (5.2)$$

where c_n – concentration of the inclusions oriented in the n -direction.

Suppose we have the set L_k - inclusion of k-th direction for which χ_k is given. Given that the sets do not intersect, we obtain $\langle \chi'_n \chi'_k \rangle = c_n (1 - c_k)$.

Random fields of tensions, deformations, shifts and indicator functions will be presented as a sum of mathematical expectations and fluctuations:

$$\begin{aligned} \sigma_{ij} &= \langle \sigma_{ij} \rangle + \sigma'_{ij}, \quad e_{ij} = \langle e_{ij} \rangle + e'_{ij}, \\ u_i &= \langle u_i \rangle + u'_i, \quad \chi_n = \langle \chi_n \rangle + \chi'. \end{aligned} \quad (5.3)$$

In accordance with the consistent variation approach we investigate the deformation of a composite material within elasticity and viscoplasticity, determine macroscopic properties and determine the material structure based on the assumed criterion of wear-resistance.

5.2 Determination of macroscopic properties of elasticity

We will assume that both phases (matrix and inclusion) in the composite material are isotropic, firmly connected at the boundary of division (the continuity of displacements in the transition through the interface) and those subordinate to the Hooke law, which binds the stresses and deformations by the relations:

– for inclusions

$$\sigma_{ij} = 2\mu_1 e_{ij} + \lambda_1 \delta_{ij} e_{ll}; \quad (5.4)$$

– and matrix

$$\sigma_{ij} = 2\mu e_{ij} + \lambda \delta_{ij} e_{ll}, \quad (5.5)$$

where $\mu, \lambda, \mu_1, \lambda_1$ – coefficients of the Lame matrix and inclusions respectively, the index l indicates the values belonging to the inclusions.

With the help of indicator functions, the connection of stresses with deformations for a composite material will be presented in the form

$$\sigma_{ij} = 2\mu e_{ij} + \lambda \delta_{ij} e_{ll} + \sum_n (2\bar{\mu}_1 \chi_n e_{ij} + \bar{\lambda}_1 \delta_{ij} \chi_n e_{ll}), \quad (5.6)$$

where $\bar{\mu}_1 = \mu_1 - \mu$, $\bar{\lambda}_1 = \lambda_1 - \lambda$.

The functions χ_n , the stress σ_{ij} and the deviation e_{ij} are considered to be random statistical homogeneous coordinate functions and, in accordance with the condition of ergodicity of their averaging over the ensemble, coincides with the averaging over the characteristic volume.

In the case of statistical homogeneity, the average body mass (in all volume V) is equal to the average for any characteristic volume.

Random fields of stresses, deformations, displacements and indicator functions will be presented as a sum of mathematical expectations and fluctuations:

$$\begin{aligned}\sigma_{ij} &= \langle \sigma_{ij} \rangle + \sigma'_{ij}, & e_{ij} &= \langle e_{ij} \rangle + e'_{ij}, \\ u_i &= \langle u_i \rangle + u'_i, & \chi_n &= \langle \chi_n \rangle + \chi'_n.\end{aligned}\quad (5.7)$$

In so doing

$$\langle \chi_n \rangle = \frac{1}{V} \int_V \chi_n dV = \frac{1}{V} \int_{V_n} dV = \frac{V_n}{V} = c_n, \quad (5.8)$$

where c_n is the concentration of inclusions oriented in the n th direction.

To relations $\langle e_{ij} \rangle_1$ and $\langle e_{ij} \rangle$ we have a relation

$$\langle e_{ij} \rangle_1 = \langle e_{ij} \rangle + \langle \chi' e'_{ij} \rangle / c_1. \quad (5.9)$$

The calculation of the properties of the elasticity of a composite material involves the determination of a stress-strain state under load conditions and the calculation of macroscopic properties of elasticity.

The averaged equation defines the law of deformation (Hooke's law) in the context of material continuity

$$\langle \sigma_{ij} \rangle = 2\mu \langle e_{ij} \rangle + \lambda \delta_{ij} \langle e_{ll} \rangle + 2\bar{\mu}_1 \chi_n \langle e_{ij} \rangle_1 + \bar{\lambda}_1 \delta_{ij} \chi_n \langle e_{ll} \rangle_1 \quad (5.10)$$

$$\sum_n c_n = c_1, \quad \sum_n c_n \langle e_{ij} \rangle_n = c_1 \langle e_{ij} \rangle_1, \quad (5.11)$$

in general, is an relationship

$$\langle \sigma_{ij} \rangle = \lambda^{*}_{ijkl} \langle e_{kl} \rangle, \quad (5.12)$$

where λ^{*}_{ijkl} is the tensor of the macroscopic modulus of elasticity.

Comparison of the last two expressions shows that the finding of macromodules is related to the establishment of the relationship between the field of mean deformations in the inclusions and the macro-deformations of the entire material. Given the properties it is necessary to find a functional connection between the correlation moment and the mean deformations:

$$\langle \chi'_r e'_{ij} \rangle = \phi \langle e_{ij} \rangle . \quad (5.13)$$

To solve the problems we use the variational principle, according to which the absolute minimum of elastic deformation energy, determined for all kinematically possible distributions of deformations, corresponds to the real field of displacements (or deformations, following the Cauchy law).

For a composite material we formulate the following: the elastic energy of material deformation reaches a minimum on the set of statistical displacement fields u_i with given mean deformations $\langle e_{ij} \rangle$.

Let us consider both phases (matrix and inclusions) in the composite material isotropic, tightly connected along the interface (continuous shifts during transition across the interface) and we will indicate the elastic deformation energy correlated with the volume V as

$$\langle W \rangle = \frac{1}{V} \left(\int_{V-V_1} W_1 dV + \sum_n \int_{V_n} W_2 dV \right), \quad (5.14)$$

where $W_1 = \mu e_{ij} e_{ij} + \frac{1}{2} \lambda e_{ll}^2$, $W_2 = \mu_1 e_{ij} e_{ij} + \frac{1}{2} \lambda_1 e_{ll}^2$.

Or, using the meanings above, we get

$$\langle W \rangle = \mu \langle e_{ij} e_{ij} \rangle + \frac{1}{2} \lambda \langle e_{ll}^2 \rangle + \sum_n (\bar{\mu}_1 c_n \langle e_{ij} e_{ij} \rangle_n + \frac{1}{2} \bar{\lambda}_1 \langle e_{ll}^2 \rangle_n). \quad (5.15)$$

Let us go over to the markers of the average values accepted above and introduce some limitation to the field of possible kinematic deformations making the following assumption in the functionality $\langle e_{ij} e_{ij} \rangle_n \approx \langle e_{ij} \rangle_n \langle e_{ij} \rangle_n$, and we will get.

This approximation corresponds to the case $e_{ij} e_{ij} = const$ in the field of inclusions of the n-th type, avoids the difficulties associated with the nonlinearity of the statistical problem.

As a result of the proposed assumption, the functional will pick up a kind

$$\langle W \rangle = \mu \langle e_{ij} e_{ij} \rangle + \frac{1}{2} \lambda \langle e_{ll}^2 \rangle + \sum_n (\bar{\mu}_1 c_n \langle e_{ij} \rangle_n \langle e_{ij} \rangle_n + \frac{1}{2} \bar{\lambda}_1 \langle e_{ll}^2 \rangle_n). \quad (5.16)$$

The variation of the functionality on the independent fluctuations of the shifts $\delta u'_i$ contributes to the minimality of functionality (5.16) condition

$$2\mu e'_{ij,j} + \lambda e'_{ll,i} + \sum_n (2\bar{\mu}_1 \chi'_{n,j} \langle e_{ij} \rangle_n + \bar{\lambda}_1 \chi'_{n,i} \langle e_{ll} \rangle_n) = 0. \quad (5.17)$$

The acquired system of differential equations determines fluctuations of the field of composite deformations. After multiplying by χ'_m and averaging of the acquired value according to the volume V its answer determines the necessary functional connection.

When there is some spatial statistically homogeneous reinforcement one can apply the procedure of the transition to isotropic properties [1, 5, 56, 78, 89], then the obtained formulae of moduli of elasticity are given below.

The equation is solved by the Fourier integral transform method. Spectral expansions of the fluctuations of random functions will be distinguished by specifying the argument ξ , which serves as a Fourier transform parameter. The solution in the variables space has the form

$$\begin{aligned} \mu'_{ij}(\xi) = & \frac{\lambda + \mu}{\lambda + 2\mu} \cdot \frac{\sum_n (2\bar{\mu}_n \chi'_n(\xi) \langle e_{kl} \rangle_n + \bar{\lambda}_n \chi'_n(\xi) \langle e_{rr} \rangle_n \delta_{kl})}{\xi^4} \xi_i \xi_j \xi_k \xi_l - \\ & - \sum_n \bar{\mu}_n \chi'_n(\xi) \langle e_{il} \rangle_n \frac{\xi_l \xi_j}{\xi^2} - \sum_n \bar{\lambda}_n \chi'_n(\xi) \langle e_{jl} \rangle_n \frac{\xi_l \xi_i}{\xi^2} - \\ & - \sum_n \bar{\lambda}_n \chi'_n(\xi) \langle e_{rr} \rangle_n \frac{\xi_i \xi_j}{\xi^2}. \end{aligned} \quad (5.18)$$

We solve the relation (5.18) for a transversally isotropic medium, when the inclusion has the same direction.

Multiplying by χ'_m and averaging, we arrive at the relations

$$\langle e_{12} \rangle_1 = \frac{\langle e_{12} \rangle}{1 - (4R\mu'A - 2L\mu')/C_1}, \quad \langle e_{i3} \rangle_1 = \frac{\langle e_{i3} \rangle}{1 - (4R\mu'(A+B) - \mu'(2L+M)/C_1)}, \quad (i=1,2),$$

$$\langle e_{11} \rangle_1 = X_1 \langle e_{11} \rangle + Y_1 \langle e_{22} \rangle + Z_1 \langle e_{33} \rangle, \quad \langle e_{22} \rangle_1 = X_2 \langle e_{11} \rangle + Y_2 \langle e_{22} \rangle + Z_2 \langle e_{33} \rangle,$$

$$\langle e_{33} \rangle_1 = X_3 \langle e_{11} \rangle + Y_3 \langle e_{22} \rangle + Z_3 \langle e_{33} \rangle,$$

$$X_1 = \frac{a_1 a_5 - a_3 a_4}{\Delta}, \quad Y_1 = \frac{a_3 a_4 - a_2 a_5}{\Delta}, \quad Z_1 = \frac{a_2 a_3 - a_1 a_3}{\Delta},$$

$$X_2 = Y_1, \quad Y_2 = X_1, \quad Z_2 = Z_1, \quad X_3 = \frac{a_2 a_4 - a_1 a_4}{\Delta}, \quad Y_3 = X_3, \quad Z_3 = \frac{a_1^2 - a_2^2}{\Delta},$$

$$R = (\lambda + \mu)/(\lambda + 2\mu), \quad a_1 = 1 - [R(6\mu'A + \lambda'L) - \lambda'L - 2\mu'L]/C_1,$$

$$a_2 = -[R(2\mu'A + \lambda'L) - \lambda'L]/C_1, \quad a_3 = a_2 - 2\mu'RB/C_1,$$

$$a_4 = -[R(2\mu'A + 2\mu'B + \lambda'(L+M)) - \lambda'(L+M)]/C_1,$$

$$a_5 = 1 - [R(6\mu'A + 12\mu'B + 2\mu'C + \lambda'(L+M)) - \lambda'(L+M) - 2\mu'(L+M)]/C_1$$

$$\Delta = (a_1 - a_2)(a_5(a_1 + a_2) - 2a_3a_4).$$

The substitution of the relations in the function of elastic energy W allows us to establish the law of deformation of the composite material. In general, the law will be presented as follows

$$\langle \sigma_{11} \rangle = C_{11} \langle e_{11} \rangle + C_{12} \langle e_{22} \rangle + C_{13} \langle e_{33} \rangle,$$

$$\langle \sigma_{22} \rangle = C_{12} \langle e_{11} \rangle + C_{11} \langle e_{22} \rangle + C_{13} \langle e_{33} \rangle,$$

$$\langle \sigma_{33} \rangle = C_{13} \langle e_{11} \rangle + C_{12} \langle e_{22} \rangle + C_{33} \langle e_{33} \rangle,$$

$$\langle \sigma_{12} \rangle = 2\mu_{12}^* \langle e_{12} \rangle, \quad \langle \sigma_{13} \rangle = 2\mu_{13}^* \langle e_{13} \rangle, \quad \langle \sigma_{23} \rangle = 2\mu_{13}^* \langle e_{23} \rangle, \quad (5.19)$$

where $C_{11}, C_{12}, C_{13}, C_{33}, \mu_{12}^*, \mu_{13}^*$ effective properties of elasticity of a composite. For example, the displacement modules μ_{12}^*, μ_{13}^* are equal

$$\mu_{12}^* = \mu + \frac{\bar{\mu}_1 C_1}{1 - (4R\mu' A - 2L\mu') / C_1}, \quad (5.20)$$

$$\mu_{13}^* = \mu + \frac{\bar{\mu}_1 C_1}{1 - [(4R\mu'(A+B) - \mu'(2L+M)) / C_1]}.$$

The modulus of elasticity of the composite E^* for the structure of a composite material with short fiber inclusions is defined by the formula

$$E^* = E / [1 + (1 - c_f) / (Qc_f) + E / (E_f - E)], \quad (5.21)$$

where E, E_f – modulus of elasticity of the matrix and fiber inclusions, c_f – volume content of fibers in the composite material, Q – function of geometrical parameters of fibers that is de-

fined through the parameter $\alpha = \sqrt{1 - z^2}$, $z = \frac{d}{l}$ where d – the fiber diameter, l – its length.

$$Q = 2\{1 + 0,1 / [6R_2 + E / (E_f - E)]\}, \quad (5.22)$$

$$R_1 = \frac{1-\alpha^2}{4\alpha^5} \left[(3-\alpha^2) \frac{1}{2} \ln \frac{1+\alpha}{1-\alpha} - 3\alpha \right], \quad R_2 = \frac{3}{8} [1 - 4R_1 - R_3], \quad R_3 = \frac{1-\alpha^2}{\alpha^5} \left[(1-\alpha^2)\alpha + \frac{1}{2}(1-\alpha^2) \ln \frac{1+\alpha}{1-\alpha} \right].$$

For the structure of the composite material whose matrix is reinforced with inclusions of the spherical form the modulus of elasticity of the composite E^* is defined by the formula

$$E^* = E \{1 + Q_I c_s / (1 - c_s)\}, \quad (5.23)$$

$$Q_I = 1 / [E / (E_s - E) + 0,4], \quad (5.24)$$

where E, E_s – modulus of elasticity of the matrix and dispersed inclusions, c_s – volume content of dispersed inclusions, Q_I – the function of elastic properties.

5.3 Determination of visco-plastic and thermophysical properties

Consider the two-phase structure of a composite material consisting of visco-plastic components subordinated to the Bingham rheological equation that determine the relationship between stresses σ_{ij} and deformation rates ε_{ij}

$$s_{ij} = k \frac{\varepsilon_{ij}}{\sqrt{\varepsilon_{kl}\varepsilon_{kl}}} + \eta \varepsilon_{ij}, \quad s_{ij} = \sigma_{ij} - \frac{1}{3} \sigma_{ll} \delta_{ij}, \quad (5.25)$$

where k the boundary of the plasticity of the material; η viscosity of the material.

We will formulate the variational problem of determining the visco-plastic properties of a two-component composite material by analogy with the statement of problem 5.1 as a condition for the extremality of the functional W^* , which is the dissipation of energy [4, 56, 78, 89]

$$W^* = \frac{1}{V} \int_{V-V_1} (k \sqrt{\varepsilon_{ij}\varepsilon_{ij}} + \frac{1}{2} \eta \varepsilon_{ij}\varepsilon_{ij}) dV + \frac{1}{V} \int_{V_1} (k_1 \sqrt{\varepsilon_{ij}\varepsilon_{ij}} + \frac{1}{2} \eta_1 \varepsilon_{ij}\varepsilon_{ij}) dV \quad (5.26)$$

where the index 1 marks values that belong to inclusions, k – the limit of material plasticity, η – the material viscosity, ε_{ij} – deformation rate.

Let the structure of the material be described again by the isotropic function χ , which acquires value 1 on inclusions, and 0 in the matrix. Obviously, $\langle \chi \rangle = c_1 = V_1/V$ and have a correlation

$$(1 - c_1) \langle \varepsilon_{ij} \varepsilon_{ij} \rangle_2 = \langle \varepsilon_{ij} \varepsilon_{ij} \rangle - c_1 \langle \varepsilon_{ij} \varepsilon_{ij} \rangle_1, \\ \langle \chi' \varepsilon'_{ij} \rangle = c_1 (\langle \varepsilon_{ij} \rangle_1 - \langle \varepsilon_{ij} \rangle), \quad (5.27)$$

where the index 2 denotes the averaging over the matrix, the stroke - the fluctuations of random variables. Let's introduce the designation: $I_0^2 = \langle \varepsilon_{ij} \rangle \langle \varepsilon_{ij} \rangle$; $I_1^2 = \langle \varepsilon_{ij} \rangle_1 \langle \varepsilon_{ij} \rangle_1$; $I^2 = I_0^2 + \langle \varepsilon'_{ij} \varepsilon'_{ij} \rangle - c_1 I_1^2$. Then (5.26) we will submit as

$$W^* = k \sqrt{1 - c_1} I + k_1 c_1 I_1 + \frac{1}{2} \eta I^2 + \frac{1}{2} \eta_1 c_1 I_1^2. \quad (5.28)$$

The functionality minimization according to (5.27) along fluctuations ε'_{ij} under the fixed values $\langle \varepsilon_{ij} \rangle$ lead to the parameter $W^*(\langle \varepsilon_{ij} \rangle)$ calculation that will finally determine the value of tensions $\langle \sigma_{ij} \rangle = \partial W^* / \partial \langle \varepsilon_{ij} \rangle$.

Formulas for calculating invariants form a system of equations

$$\begin{aligned} I_1(1-2(1-c_1)A/5) &= I_0; \\ I^2 = I_0^2 - c_1 I_1^2 + 2c_1(1-c_1)A^2 I_1^2/5; \quad (5.29) \\ A &= (\eta_1 + k_1/I_1)/(\eta + k\sqrt{1-c_1}/I). \end{aligned}$$

Depending on the tensions $\langle\sigma_{ij}\rangle$ the deformation process is possible when the inclusions behave as stiff particles. For such a state of deformation ($I_1 = 0$) we have [2]

$$\begin{aligned} W^* &= k\sqrt{1-c_1}I + \frac{1}{2}\eta I^2, \\ I_0 &= \frac{2}{5}(1-c_1)\frac{k_1}{\eta + k\sqrt{1-c_1}/I}, \quad (5.30) \\ I^2 &= I_0^2 + \frac{2}{5}c_1(1-c_1)k_1^2/(\eta + k\sqrt{1-c_1}/I)^2. \end{aligned}$$

The relations (5.31) make it possible to determine the dissipation function in the case of rigid inclusions

$$W^* = k\sqrt{1+\frac{3}{2}c_1}I_0 + \frac{1}{2}\eta\frac{1+\frac{3}{2}c_1}{1-c_1}I_0^2. \quad (5.31)$$

It is easy to establish, depending on (5.28), the values of the limits of plasticity and viscosity of composite material with rigid inclusions. The critical values of intensity I^{*0} of deformation, in which the stresses in the inclusions reach the limits of plasticity, follow from (5.30)

$$k_1 = \frac{5}{2}\left(\frac{k}{\sqrt{1+\frac{3}{2}c_1}} + \frac{\eta}{1-c_1}I_0^*\right). \quad (5.32)$$

Let us assume for the purpose of simplifying that the inclusions (both fibers and dispersed particles) are absolutely solid in comparison with the matrix (PTFE). Then the functional dependency of the plasticity limit of the composite with the dispersed particles will acquire such a type

$$k^* = k\sqrt{1+1.5c_s}, \quad (5.33)$$

and in the case of short fiber inclusions

$$k^* = k \sqrt{1 + (Q_2 - 1)c_f},$$

$$Q_2 = \frac{1 - \frac{2(1 - 8R_1 - 7R_2)}{5(1 - 4R_1 - 5R_2)} + \frac{2(R_1 - R_2)}{15R_2}}{2(2R_1 + R_2)} \quad (5.34)$$

The Voltaire visco-elastic analogy method allows us to obtain relationships that determine the viscosity of a composite material. Taking into account the absolute stiffness of the inclusions compared to the matrix for the composite material of the first level (the matrix is dispersedly reinforced with inclusions of round shape), we observe

$$\eta^* = \eta(1 + 2, 5c_s / (1 - c_s)) \quad (5.35)$$

and for the composite material of the second level (a composite conglomerate of the first level in which the stochastically homogeneously placed short-fiber inclusion)

$$\eta^k = \eta^*(1 + Qc_f / (1 - c_f)). \quad (5.36)$$

In formulas (5.35 – 5.36), η is the matrix viscosity; c_s – volume content of dispersed particles; c_f is the volume content of the fiber filler; Q – is determined by the relation (5.21).

The thermophysical properties are important for determining the practical value of polymer materials.

Such details of technical devices as sealing structures and many others that work in non-stationary thermal fields require knowledge of the thermophysical characteristics of the applied polymer materials.

The coefficient of thermal conductivity of composite material β^* is a physical parameter characterizing heat-inertial properties of a physical object. The larger its value, the faster the alignment of temperature occurs at all points of the body. Accordingly, the lower the value of β^* , the better the heat insulator is the material.

Knowledge of temperature conductivity is necessary in view of the technological purpose for evaluating the cooling time of products obtained from the melt of a polymer or its softened blank to evaluate the behavior of a polymeric component in non-stationary thermal fields.

The three-phase composite material, which occupies volume V , one of which components is continuous, is considered, two others are in the form of discrete inclusions, distributed statistically homogeneously in the first phase. We will assume that all the components in the material are isotropic, have different thermophysical properties, have an ideal thermal contact at the interface (the continuity of the temperature field and the heat flux when passing through the boundary) and obey the Fourier law, which binds the flux of heat q_i and temperature gradient T_j :

$$q_i = -\beta_{ij} T_j \quad (5.37)$$

where β_{ij} is the coefficient of thermal conductivity tensor.

Effective coefficients of thermal conductivity of a composite material β_{ij}^* are defined as the coefficients included in the ratio

$$\langle q_i \rangle = -\beta_{ij}^* \langle T_j \rangle \quad (5.38)$$

Here and in subsequent angular brackets mean average in volume (5.1).

Again, the geometric structure of the material is given by the indicator random functions of the coordinates $\chi_n = (x_1, x_2, x_3)$, which acquire the value of the unit in the field of n inclusion and zero - otherwise.

The thermophysical properties of the components of the composite material (heat conduction coefficients) are considered to be given, inclusion of the composite material will be considered close to the spherical ones.

The calculation of the thermophysical properties of a composite material offers a definition of the distribution of temperatures in the structure of the material and the calculation of macroscopic thermophysical properties (coefficients of thermal conductivity).

To solve the problems we will use the variational principle according to which the absolute minimum of thermal energy, determined for all possible temperature distributions, corresponds to the actual temperature field.

For a composite material this principle is formulated as follows: the thermal energy of a material reaches a minimum on the set of statistical temperature fields at given average temperature gradients.

Let us represent a functional for a thermal field, assigned to volume V in this way

$$\langle U \rangle = \frac{1}{V} \left(\int_{V-V_1} U_1 dV + \sum_n \int_{V_n} U_2 dV \right), \quad (5.38)$$

where $U_1 = \beta E_i E_i$, $U_2 = \beta_k E_i E_i$, ($\kappa = 1, 2$), $E_i = T_{,i}$ – temperature gradient; β, β_k – coefficients of thermal conductivity of the matrix and inclusions.

In the macro volume V, the random fields of temperature T and the indicator functions are statistically homogeneous, and we apply the hypothesis of ergodicity. Using the definition of averages and replacing the temperature states of inclusions on the average in volume, we get

$$\begin{aligned} \langle U \rangle &= \beta \langle E_i E_i \rangle + \bar{\beta}_k c_k \langle E_i \rangle_k \langle E_i \rangle_k, \\ \bar{\beta}_k &= \beta_k - \beta, c_k = V_k / V. \end{aligned} \quad (5.39)$$

The variational formulation of the heat conduction problem involves $\langle E_i \rangle$ searching for a statistically homogeneous field of temperature fluctuations T' , which corresponds to the minimum value of the functional (5.39).

Варіаційна постановка задачі теплопровідності передбачає відшукування при заданих середніх $\langle E_i \rangle$ статистично однорідного поля флюктуацій температур T' , яке відповідає мінімальному значенню функціонала (5.39). From the condition of extremity it follows that

$$\beta E'_{i,i} + \bar{\beta}_k \langle E_i \rangle_k \chi'_{k,i} = 0. \quad (5.40)$$

For the connection of the temperature fields in the inclusions with the temperature fields of the composite there is a correlation

$$\langle E_i \rangle_k = \langle E_i \rangle + \langle \chi'_k E'_i \rangle / c_k. \quad (5.41)$$

Applying the Fourier transform method and multiplying it by χ'_1 a χ'_2 , we obtain the averaging

$$\begin{aligned} \langle \chi'_1 E'_i \rangle &= (-\beta'_1 \langle E_i \rangle_1 c_1 (1 - c_1) + \beta'_2 \langle E_i \rangle_2 c_1 c_2) / 3, \\ \langle \chi'_2 E'_i \rangle &= (-\beta'_1 \langle E_i \rangle_1 c_1 c_1 + \beta'_2 \langle E_i \rangle_2 c_1 (1 - c_2)) / 3, \end{aligned} \quad (5.42)$$

where $\beta'_k = \bar{\beta}_k / \beta$.

Solving compatible equation, we get

$$\begin{aligned} \langle E_i \rangle_{i_1} &= (1 + \beta'_2 / 3) \langle E_i \rangle / L, \quad \langle E_i \rangle_{i_2} = (1 + \beta'_1 / 3) \langle E_i \rangle / L, \\ L &= (1 + \beta'_1 (1 - c_1) / 3) (1 + \beta'_2 (1 - c_2) / 3) - \beta'_1 \beta'_2 c_1 c_2 / 9. \end{aligned} \quad (5.43)$$

Simplify the functional (5.39), using (5.43). The summation of the latter from T' averaging leads to the equation

$$\beta \langle E'_i E'_i \rangle + \bar{\beta}_k \langle E_i \rangle_k c_k (\langle E_i \rangle_k - \langle E_i \rangle) = 0,$$

the substitution of which in (5.39), taking into account (5.42), will lead to a functional appearance

$$\langle U \rangle = \beta \langle E_i \rangle \langle E_i \rangle + (\bar{\beta}_1 c_1 (1 + \beta'_1 / 3) / L) \langle E_i \rangle \langle E_i \rangle + (\bar{\beta}_2 c_2 (1 + \beta'_2 / 3) / L) \langle E_i \rangle \langle E_i \rangle. \quad (5.44)$$

From equation (5.44) follows the formula for determining the effective coefficient of thermal conductivity of the three-phase composite material

$$\beta^* = \beta + \bar{\beta}_1 c_1 (1 + \beta'_1 / 3) / L + \bar{\beta}_2 c_2 (1 + \beta'_2 / 3) / L. \quad (5.45)$$

The resulting formula determines the dependence of the coefficient of thermal conductivity of the three-phase composite material on the properties of the components that make up this composite and their volumetric composition. Inclusions in the form are close to spherical ones.

The heat equation mathematically describes the relationship between the average (by volume) values of the heat flux and the temperature gradient. To find the temperature field, that is, the temperature distribution in the structure of the composite material, it is necessary to use the resulting relations and set the boundary conditions.

5.4 Determination of the strength of a polymer material chaotically reinforced with short fibers

Forecasting of the properties of strength is related to the analysis of processes occurring in the structure of the composite material in the occurrence and spread of cracks.

The mechanics of composite materials [6, 7, 56, 78, 120, 130] consider mainly unidirectionally reinforced materials with a polymeric or metallic matrix that has a finite deformation than fibers. This leads to the fact that the destruction of the composite begins with a cliff of fibers.

Crossing the surface of the crack of the fiber creates resistance to its opening, which leads to an increase in the strength of the composite.

Consider the composite material, which is a polymer matrix chaotically reinforced with short carbon fibers. It has a flat, discoidal crack with a radius a intersected in different directions with fibers in the structure.

At infinity, perpendicular to the crack, there is a tensile stress σ° (Fig. 5.4).

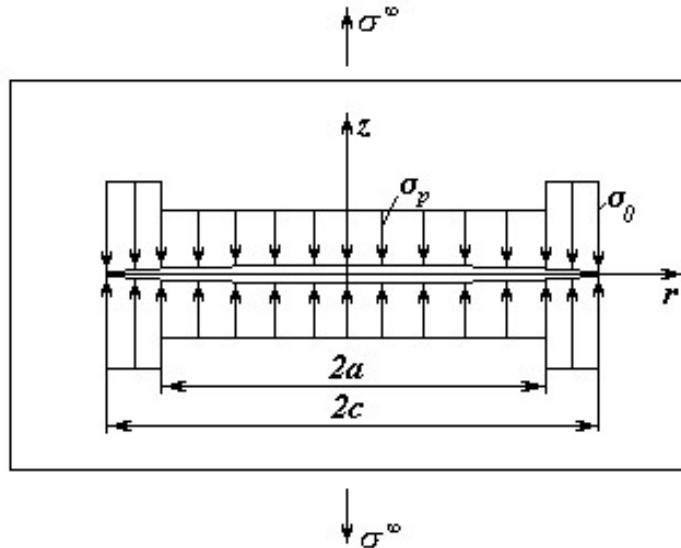


Fig. 5.4 Scheme of a composite with a macrocrack

Let r – polar radius of a point. The domain $0 \leq r \leq a$ corresponds to the torn bonds between the particles of the matrix. We replace the action of fibers that hold open the crack uniformly distributed over its surface by tensions σ_p . According to the Leonov-Panasyuk model [8], in the annular domain $a \leq r \leq c$ the opposite edges of the crack are attracted with a constant voltage σ_0 if the distance between them does not exceed the limiting value of the opening of the crack δ_k .

The value σ_0 is equal to the strength of the composite. The condition for the crack propagation has the form [8]

$$2w(a,0) = \delta_k, \quad (5.46)$$

where $w(r, z)$ – moving along the Z-axis with coordinates (r, z) .

The displacement of material points on the surface of the crack relative to the plane $z = 0$ can be calculated by the formula [8, 34, 56, 78, 57]:

$$w(r,0) = B_k \int_0^{\pi/2} d\alpha \int_{r \sin \alpha}^{c \sin \alpha} \frac{q(\rho) d\rho}{\sqrt{\rho^2 - r^2 \sin^2 \alpha}},$$

$$B_k = \frac{4(1-\nu_k^2)}{\pi E_k},$$

$$q(r) = \begin{cases} \sigma^\infty - \sigma_p, & 0 \leq r \leq a, \\ \sigma^\infty - \sigma_0, & a < r \leq c, \end{cases}$$

$$c = a \left[1 - \left(\sigma^\infty - \sigma_p \right)^2 / \left(\sigma_0 - \sigma_p \right)^2 \right]^{-1/2}, \quad (5.47)$$

where ν_k, E_k – Poisson's coefficient and Young's modulus of composite.

Calculating the internal integral, we obtain

$$w(r,0) = B_k (\sigma_0 - \sigma_p) \int_{\arcsin(a/c)}^{\pi/2} \sqrt{a^2 - r^2 \sin^2 \alpha} d\alpha, \\ 0 \leq r \leq a, \quad (5.48)$$

$$w(r,0) = B_k (\sigma_0 - \sigma^\infty) \int_{\arcsin(a/c)}^{\arcsin(a/r)} \sqrt{a^2 - r^2 \sin^2 \alpha} d\alpha, \\ a < r \leq c.$$

For $r = a$ from the formula (5.42) determine the displacement of points on the line separating the zone of adhesion and the zone of torn bonds:

$$w(a,0) = B_k (\sigma_0 - \sigma_p) a (1 - a/c). \quad (5.49)$$

Using the criterion (5.42), we find the external boundary voltage

$$\sigma_*^\infty = \sigma_p^* + (\sigma_0 - \sigma_p^*) \sqrt{\frac{2a_*}{a}} \sqrt{1 - \frac{a_*}{2a}}, \quad a \geq a_* = \frac{\pi E_k \sigma_k}{8(1 - \nu_k^2)}, \quad (5.50)$$

where a^* – critical size of the crack. For $a = a^*$ the greatest value of the composite strength is achieved

$$\sigma_*^\infty = \sigma_p^* + \sigma_m^*, \quad (\sigma_m^* = \sigma_0 - \sigma_p^*). \quad (5.51)$$

With a further increase in the radius of the crack ($a > a^*$), the boundary voltage decreases σ_*^∞ , therefore, it is σ_*^∞ a destructive load for a composite material with a disc-shaped crack with a radius of $a \geq a^*$. The composite with a cracked radius $a < a^*$ has the strength of a defect-free material.

Consider the elastic cylindrical fiber length L , which is extracted with the force P of the elastic matrix, which fills the half-space $z \geq 0$ (Fig. 5.5).

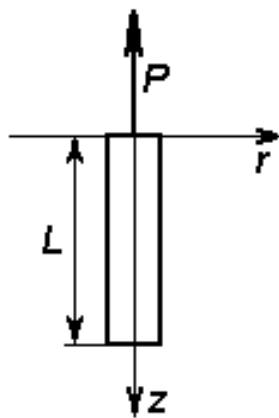


Fig. 5.5 Scheme of pulling fiber from matrix

We find the distribution along the fiber of the contact stresses τ_{rz} and stresses σ_z^f in the fiber.

In the paper [62] the problem is reduced to a numerical solution of the integral equation. To obtain an approximate analytic solution, we use the theory outlined in [6, 34, 56].

Equation for matrix:

$$\frac{\partial^2 w}{\partial r^2} + \frac{\partial w}{r \partial r} = 0, \quad \sigma_z = E_m \frac{\partial w}{\partial z}, \quad \tau_{rz} = G_m \frac{\partial w}{\partial r}, \quad (5.52)$$

where $w(r, z)$ – moving along the Z-axis of the matrix with coordinates (r, z) ; E_m , G_m – Young's modulus and matrix material bias.

The equilibrium equation of the fiber element will be presented in the form

$$\frac{d\sigma_z^f}{dz} = -\frac{2}{R} \tau_{rz}, \quad (5.53)$$

where σ_z^f – stress in the fibre; τ_{rz} – extreme shearing stress on the surfaces separating fibres with matrix; R – radius of the cross-section of the fiber.

Denoting r^* is the radius of the boundary layer zone, $W(z)$ – moving the fiber point with coordinate z and using Hooke's law

$$\sigma_z^f = E_f \frac{dW}{dz}, \quad (5.54)$$

as well as the condition of the generality of the deformations of the fiber and the matrix, we obtain

$$\frac{d^2W}{dz^2} + k^2 W = 0, \quad k^2 = 2G_m \left[E_f R^2 \ln \frac{R}{r_*} \right]^{-1}. \quad (5.55)$$

The solution of an equation satisfying boundary conditions $\sigma(0) = P/\pi R^2$, $\sigma(l) = 0$ has the form

$$W(z) = -\frac{P \operatorname{ch}[k(l-z)]}{k \pi R^2 \operatorname{sh}(l)} \quad (5.56)$$

The ratio (4.53 - 4.56) allows you to find the desired tension

$$\sigma_z^f(z) = \frac{2\tau_0 \operatorname{sh}[k(l-z)]}{k R \operatorname{ch}(kl)}, \quad \tau_{rz}(z) = \tau_0 \frac{\operatorname{ch}[k(l-z)]}{\operatorname{ch}(kl)}, \quad \tau_0 = \tau_{rz}(0). \quad (5.57)$$

For both $r_* = 8R$ и $E_f / E_m = 4$ the stress σ_z^f , is determined by the formula (4.57), coincides with the accuracy of 4 % with the numerical solution given in [9, 34, 45, 67, 78,].

With increasing force P , the maximum tensile stress increases, reaching some limit value $\langle \tau \rangle$ at which there is a detachment of the fiber from the matrix.

Assuming that on the segment of the separation operates a uniformly distributed on the surface of the fiber tangential strain of friction τ_s , we obtain the following laws of change $\tau_{rz}(z), \sigma_z^f(z)$, the fiber that was detached to a depth h :

$$\tau_{rz}(z) = \begin{cases} \tau_s, & 0 \leq z \leq h, \\ \sqrt{(1+\nu_m) \frac{E_f}{E_m} \ln \left(\frac{r_*}{R} \right)}, & \langle \tau \rangle \operatorname{ch}[(l-z)/(\chi R)] / \operatorname{ch}[(l-h)/(\chi R)], \end{cases} \quad (5.58)$$

$$\sigma_z^f(z) = \begin{cases} 2\langle \tau \rangle \chi \operatorname{sh}[(l-z)/(\chi R)] / \operatorname{ch}[(l-h)/(\chi R)], & h \leq z \leq l, \\ 2\tau_s(h-z)/R + 2\langle \tau \rangle \chi \operatorname{th}[(l-h)/(\chi R)], & 0 \leq z \leq h. \end{cases} \quad (5.59)$$

From (5.58), (5.59) we find an extension of a part of the fiber in the segment of detachment

$$W(h) - W(0) = \left\{ \tau_s h^2 / R + 2\langle \tau \rangle \chi h \operatorname{th}[(l-h)/(\chi R)] \right\} / E_f. \quad (5.60)$$

To determine $W(h)$ we use the solution of the Mindlin problem [11], which allows us to calculate the field of displacements caused by the action of the concentrated force applied at some point in an elastic half-space.

Assuming that on the section $0 \leq z \leq h$ along the Z-axis, the running stress is valid on the matrix $\tau_s 2\pi r$, and at the point $z = h$ the concentrated force equal to the total effort perceived by the non-layered fiber segment is obtained for $W(h)$, which after linearization for h will look like

$$W(h) = -\frac{R}{2G_m} \left\{ \left(1 - \frac{h}{l}\right) \langle \tau \rangle \chi \operatorname{th} \left(\frac{l}{\chi R} \right) + \tau_s \frac{h}{l} \ln \left(\frac{l}{R} \right) \right\}. \quad (5.61)$$

The connection of the voltage in the fiber with the displacement $W_0 = |W(0)|$ looks like

$$\begin{aligned} \sigma_z^f(0) &= 2\tau_s h/R + 2\langle \tau \rangle \chi \operatorname{th}[(l-h)/(\chi R)], \quad l > l_0, \\ \sigma_z^f(0) &= 2\tau_s l/R, \quad l \leq l_0 = \sqrt{RW_0E_f/\tau_s}. \end{aligned} \quad (5.62)$$

For a fiber immersed in a matrix at depth l at an angle θ to the Z axis (Fig. 5.6), the relations analogous to (5.62) will be written as

$$\begin{aligned} \sigma_z^f(0) &= \left\{ 2\tau_s \sqrt{VE_f \cos \theta / (R\tau_s)} + 2\langle \tau \rangle \chi \operatorname{th}[(l-h_\theta)/(\chi R)] \right\} \cos \theta, \\ l_0 \leq l \leq L, \quad 0 \leq \theta \leq \theta_* &, \quad \sigma_z^f(0) = 2\tau_s l \cos \theta / R, \\ 0 \leq l < l_0 &= \sqrt{RVE_f \cos \theta / \tau_s}, \quad 0 \leq \theta \leq \theta_*, \\ \sigma_z^f(0) &= E_f V \cos^2 \theta \operatorname{th}(l/(\chi R)) / (\chi R), \\ \theta_* \leq \theta < \pi/2, \quad 0 \leq l &\leq L. \end{aligned} \quad (5.63)$$

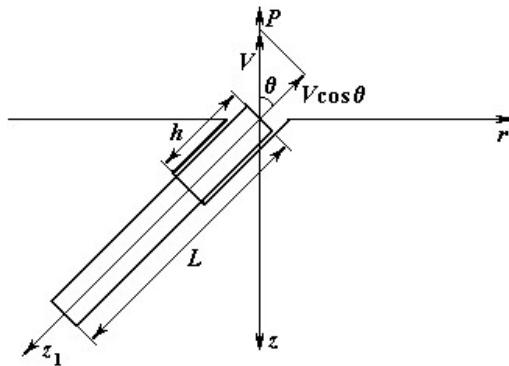


Fig. 5.6 Extracting the fiber from the matrix

Here $2L$ is the length of the fiber; $h_\theta = \sqrt{RV \cos \theta E_f / \tau_s}$,

$$\theta_* = \arccos \left[\langle \tau \rangle R \ln(r/R) / (VG_m) \right]$$

– the boundary angle (at $0 \leq \theta \leq \theta_*$ the fibers are exfoliated, when $\theta_* \leq \theta < \pi/2$ the fiber does not expand). Then suppose that $\theta_* = \pi/2$.

The averaging of the ratio (5.63) according to orientations and depths of immersion will give the possibility of obtaining the value of the average voltage $\langle \sigma_f \rangle$ in the fiber crossing the crack.

For example, when it is statistically homogeneous in the plane of reinforcement, it is equal

$$\langle \sigma_f \rangle = \frac{4}{\pi L} \int_0^{\pi/2} d\theta \int_0^L \sigma_z^f(l, \theta) dl = \frac{8\tau_s}{\pi} \left\{ 0,8741 \sqrt{\frac{VE_f}{R\tau_s}} + \chi \frac{\langle \tau \rangle}{\tau_s} - \frac{\pi}{8} \frac{VE_f}{L\tau_s} \right\}. \quad (5.64)$$

The relations (5.51), (5.52), (5.64) make it possible to establish the dependence of the strength of the composite material on the geometrical and mechanical characteristics of its components.

The number of N fibers crossing the crack surface with the area F at a statistically homogeneous bulk reinforcement is determined by the formula $N = c_f F / (2S)$ for plane reinforcement $N = c_f F / (2\pi S)$, where c_f is the volume content of the fibers in composite material; S - cross-sectional area of the fiber.

Multiplying the average voltage in a fiber $\langle \sigma_f \rangle$, which corresponds to the limiting opening δ_k of the crack on N , we obtain the total force acting on the edge of the crack of the fibers.

Dividing this effort into the surface of the crack, we find σ_p^* . The dependence of the composite strength $\sigma_k = \sigma_*^\infty$ on c_f , the strength margin of the matrix on the stretching σ_m , and the averaging over the orientations and depths of the anchoring of the voltage in the fiber $\langle \sigma_f \rangle$, will be given as

– for bulk reinforcement

$$\sigma_k = \langle \sigma_f \rangle c_f / 2 + \sigma_m (1 - c_f); \quad (5.65)$$

– for plane reinforcement

$$\sigma_k = \langle \sigma_f \rangle c_f / \pi + \sigma_m (1 - c_f). \quad (5.66)$$

Using the constructed model for finding the limit values of strength requires knowledge of some of the experimentally determined characteristics.

We will show its application for materials that have the required characteristics for calculations.

5.5 Creation of criteria for optimal design of composite material structure

The wear of the composite depends on how effective the microstructure of the composite material can resist the different processes of separating the material. Therefore, during the design of abrasion resistant composite that deforms and wears out, it is necessary to take into account its plastic and elastic behavior, the change in the physical and mechanical characteristics of the properties, the effect of the concentration, shape and relative sizes of the two-component filler particles on the hardness, the modulus of elasticity and deformation of the composite, epoxy and elastic properties, abrasive stability and thermophysical properties. Thus, the problem arises of calculating the mechanical characteristics of three-component polymer composites with a binary filler on the properties of the original ingredients.

In many works, the main criteria for wear resistance when abrasive wear are mechanical characteristics of the material, which are determined experimentally. The analysis of these works shows that the abrasive wear resistance of polymer composites depends on their physical, mechanical, rheological and deformation properties. Therefore, the development of a criterion of optimization of a filled polymer for these characteristics, which would be theoretically determined by the properties of the initial ingredients at the technological stage of composite manufacturing, has practical value, since it allows to reduce the high-value experimental work. The regularities of abrasive wear of materials are given in the works [1, 6, 12, 45, 67, 78, 120, 134].

Studies indicate the specific limits of the plasticity of the composites depending on the concentration of the fillers: the linear nature of the dependence (for the case of the plastic state of the filler particles) or the law of the square root (for the case of a rigid state of the particles).

In the general case, it is necessary to determine four sections on the deformation curves of the composite:

- matrix and particulates of deformable elastic fillers;
- the matrix, which deforms plastically, particles, - elastic;
- matrix and particles that are deformable plastic;
- one of the components that begins to collapse.

The process of destruction of the composite, which is a consequence of the destruction of one of the components, depends on the concentration of fillers.

For the case when the ellipsoidal particles are destroyed, we use the method that (by analogy with the theory of elastic composites) leads to the expression

$$H_k = H_0 \sqrt{1 + \frac{1}{\frac{1-c_f}{c_s Q_f} + \frac{\sigma_f^2}{\sigma_f^2 - \sigma_0^2}}}, \quad (5.67)$$

where the function is determined by the formula

$$Q_f = \frac{1 + \frac{4(R_1 - R_2)}{5\sigma_0^2(\sigma_f^2 - \sigma_0^2)^{-1} - 1 + 6R_2}}{\sigma_0^2(\sigma_f^2 - \sigma_0^2)^{-1} + 2(R_1 - R_2)}. \quad (5.68)$$

The task of optimal design of a three-component abrasive-resistant composite is as follows: it is necessary to choose the composition of a composite based on a polymer and a two-component filler simulated by spherical and ellipsoidal particles, which provides maximum abrasion resistance for given mechanical properties of the polymer matrix and fillers.

Let the structure of the composite material be formed by a polymer matrix and filler particles, visco-elastic, plastic and strength properties of which are known. The components of the composite are homogeneous and firmly bound to the matrix at the interface between the phases. The matrix, in addition to the elastic properties of the elastic modulus E_0 , has a viscosity η_0 and a plasticity limit τ_0 , which are subject to the Mises flow conditions and Maxwell's visco-elastic equation.

The indexes in the symbols of the quantities belong to the spherical (s) and ellipsoidal (f) particles, the matrix (o), respectively. Assume that elastic deformations are small compared with plastic ones. The fields of deformation velocities ε_{ij} and stress σ_{ij} are statistically homogeneous and satisfy the conditions of ergodicity.

To select the optimization criterion, which can reliably assess the abrasion resistance of the filled polymers, it is necessary to take the characteristics of the composite, which are reliably determined by the characteristics of the original components.

The criteria for the maximum permissible wear of the composite should characterize the initial manifestations of the process of catastrophic abrasive wear (for example, fluidity, limiting deformation), preceding the complete destruction of the composite.

Thus, in connection with such a broad interpretation of the criterion of the limiting state and abrasive wear, it is practically impossible to characterize it with a sufficient degree of determination.

The boundary state of a polymer is often referred to as a stressful state in which further tension increase is accompanied by a process of forced strain.

By combining in one analytical expression the conditions of fragile destruction and forced highly elastic deformation, one can create generalized criteria of extremely stressed state.

The need for the development of such generalized criteria arises in connection with the fact that when the state of stress changes the state of the composite.

We take a known position according to which the yield strengths of the matrix σ_0 and the composite σ_k are proportional to their hardness H_0 and H_k , respectively.

Boundaries of fluidity are considered as limits of strength. We proceed from the conditions that the process of destruction of the polymer during abrasive wear is accompanied by significant plastic deformations, and the fragile character of the fracture is brought by the fibers and spherical particles.

The achievements of the particles of the filler of stresses at which their destruction occurs can be expressed by the conditions when the strength of the particles of the filler σ_1 is equal to the value of the stress calculated for the non-destroyed hard particles of the filler.

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The coordination of elastic and plastic properties and, accordingly, the maximum abrasive resistance of the composite is achieved with a certain optimum content of the filler.

According to Fig. 5.7. The relative modulus of elasticity increases, and the relative deformation decreases with increasing s_f and c_s .

Among the calculated parameters of the abrasion resistance, we choose the material's viscosity η and the elastic modulus during tension E , using the methods of the theory $T=\eta/E$, which has the physical content of the relaxation time of the stresses.

To exclude dimensions from the criterion of harmonization and wear resistance, we use the concept of relative characteristics (Fig. 5.8)

$$\tau = \frac{T_0}{T_k} = \frac{\eta_0}{E_0 \frac{\eta_k}{E_k}} = \left(\frac{\eta_0}{\eta_k} \right) \cdot \left(\frac{E_k}{E_0} \right);$$

$$j = \frac{J_k}{J_0} = \frac{I}{I_k \frac{I}{I_0}} = \frac{I_0}{I_k}, \quad (5.69)$$

where τ is the relative criterion for the elastic and plastic properties of the composite; T_0, T_k - criteria of coordination of elastic and plastic properties of polymeric matrix and composite, respectively; J_0, J_k - abrasive wear resistance of the polymer matrix and composite respectively; I_0, I_k - intensity (or specific intensity) of abrasive wear of a polymeric matrix and composite respectively; j - relative abrasive wear resistance of the composite.

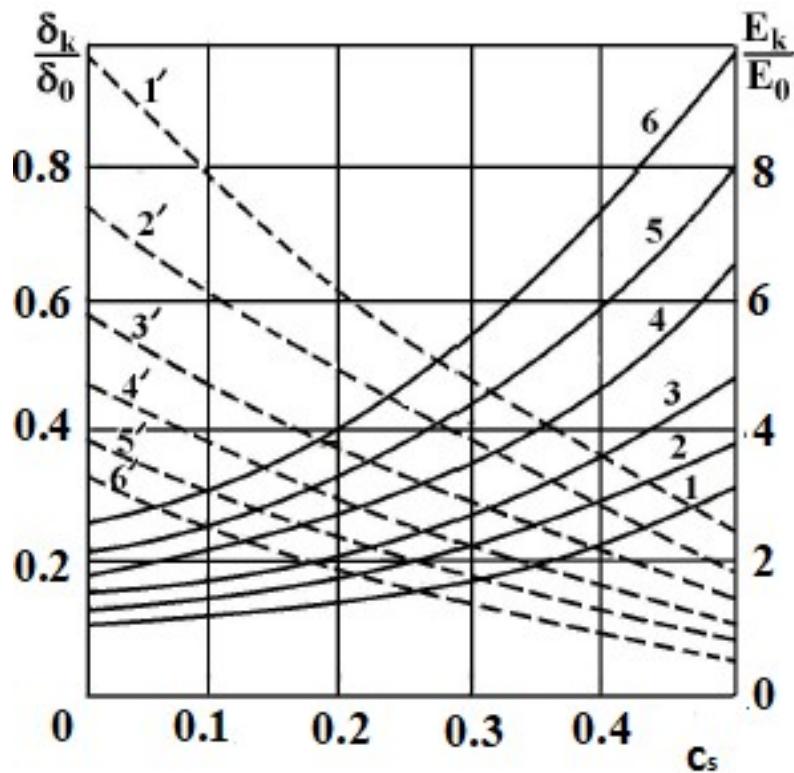


Fig. 5.7 Dependence of the relative elasticity modulus E_k/E_0 (1 – 6) and the relative deformation δ_k/δ_0 (1' – 6') of the three-component composite on the volume fraction of spherical C_s particles with a volume fraction of ellipsoidal particles C_f : 1.1' – 0; 2.2' – 0.05; 3.3' – 0.10; 4.4' – 0.15; 5.5' – 0.20; 6.6' – 0.25

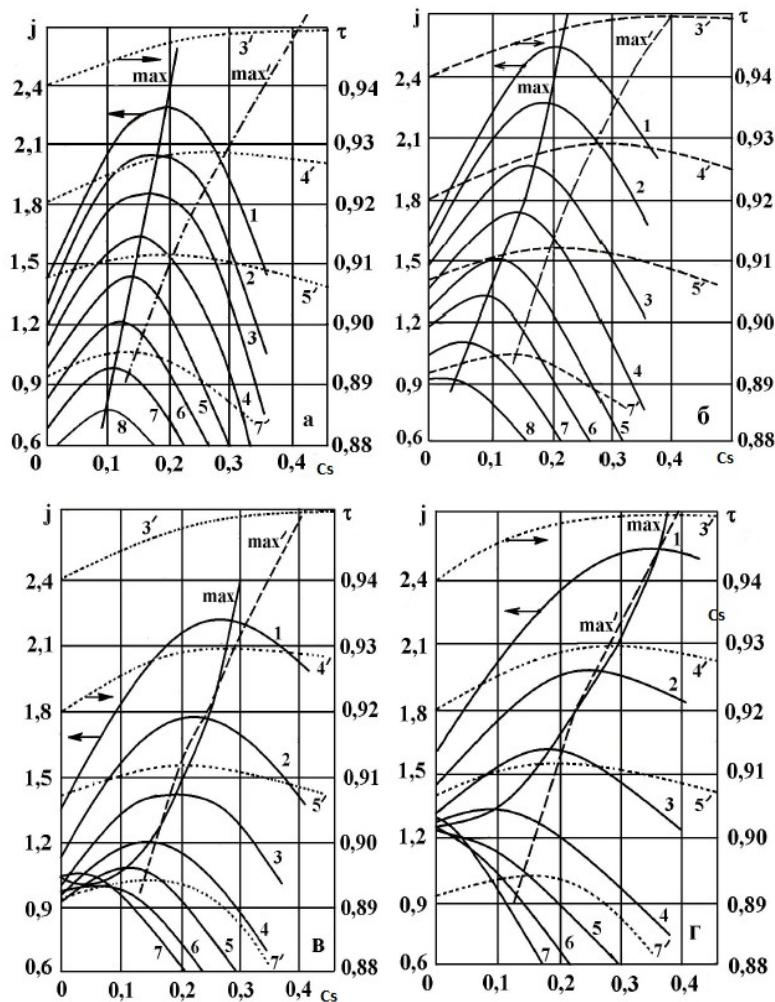


Fig. 5.8 Dependence of relative abrasion wear resistance I_0/I_k (1 – 8) under normal load $N = 20 \text{ N}$ (a), 50 N (b), 105 N (c), 160 N (g), like the relative criterion of matching the plastic and the elastic properties T_0/T_k ($3' - 5', 7'$) of a three-component composite based on PTFE on the volume fraction of titanium carbide powder (C_s) with a volumetric fraction of carbon fiber PTFE-matrix (C_f): 1 – 0; 2 – 0.05; 3.3' – 0.10; 4.4' – 0.15; 5.5' – 0.20; 6 – 0.25; 7.7' – 0.30; 8 – 0.35.

It was established that the greatest increase in wear resistance while maintaining high values of the physical and mechanical properties of PTFE composites is observed at the synergistic effect from the application of mechanical activation of the matrix, fillers, their mixing in a two-stage mode, and also the use of binary filler of different chemical nature. At the same time, the best performance indicators are observed at the following concentrations of ingredients (mass%): 1) 10 CF and 10 CBF; 2) 14 CF and 6 kaolin; 3) 5 CF and 15 cu; 4) 15 CF and 5 graphite.

The model and algorithm of search of structures of three-component composite materials with a polymeric matrix on the basis of PTFE are offered, which provide high indexes of durability according to the criterion of coordination of properties of plasticity and elasticity. The basis of the properties calculation is the single variational approach. It is shown that when designing a three-phase structure of composite material based on PTFE, reinforced with volu-

metric content of CF (10-20) wt. %, the second component (disperse particles of coke) should be taken in an amount (20-22) wt. %, which will provide, according to the accepted criterion, the maximum durability.

5.6 Calculations of effective properties of composite materials and comparison with the results of other studies

Consider the three-component composite material as a hierarchical structure, which is distributed at the following levels:

- the first level - a matrix conglomerate consisting of a polymer matrix and statistically homogeneously distributed in it inclusions of the first type;
- the second level is a matrix conglomerate of the first level, in which statistically homogeneously distributed inclusions of the second type.

Its constituents are PTFE-matrix that has the modulus of tension $E_m = 410$ MPa; carbonic fibers with the ratio $d/l = 0, 0,85$ and the modulus of tension $E_f = 35$ GPa; dispersed particles of coke with the diameter (10-50) μm and the modulus of tension $E_s = 500$ MPa.

In the graph (Fig. 5.9) we observe a slight decrease E^* with increasing length of reinforced fibers.

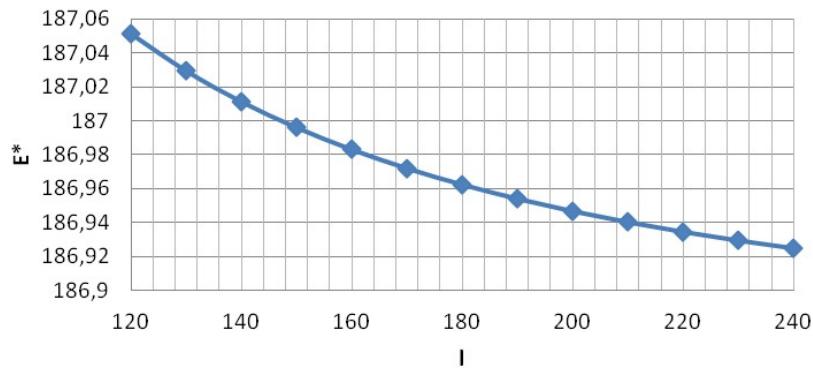


Fig. 5.9 Young's dependence of the composite on the length of the fiber

If the length of the fiber became (it was assumed that $l = 150 \mu\text{m}$), and its diameter varied in the range of 5 - 17 μm , there is a slight increase in E^* (Fig. 5.10).

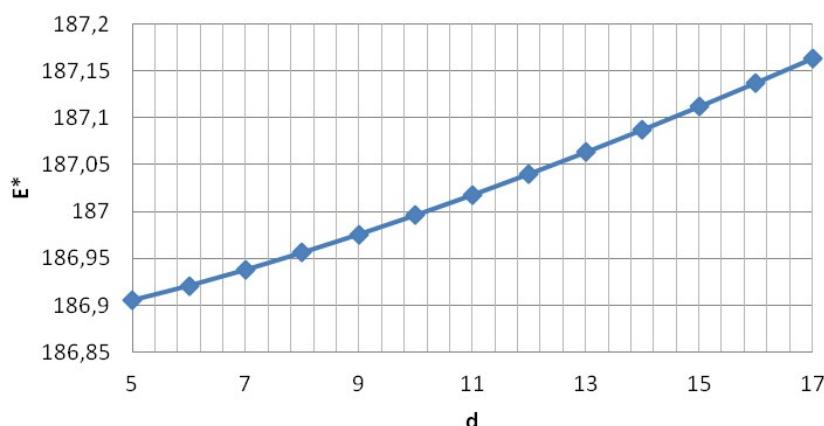


Fig. 5.10 Dependence of the Young's modulus of the composite on the diameter of the fiber

In Fig. 54.11 calculations of the relative elastic modulus of the composite material E_k/E_m are presented, the structure of which consists of: a matrix - PTFE having $E_m = 410$ MPa; carbon fiber $E_f = 35$ GPa; disperse particles of coke $E_s = 500$ MPa.

Figure 5.12 shows the calculations of tension and viscoplasticity of the three-component structure under investigation.

The calculation choice of structure components that ensures high wear-resistance according to the criterion of coherence of properties is shown on Fig. 5.13 In this research fiber composite content is fixed (the values are given in the legend on the charts), depending on the content of dispersed particles (coke) the maximum of the criterion of coherence of properties is searched.

The data analysis (Fig. 5.11) has shown that while designing the three-phase structure of a composite material on the basis of PTFE reinforced with the volume content of carbonic fibers in quantity $c_f = 0,2$ (20 wt%) a6o $c_f = 0,1$ (10 wt%), another component (dispersed coke particles) should be taken in quantity $c_s = 0,2$ as to the volume content (20 wt%) that will ensure the maximum of wear-resistance according to the accepted criterion.

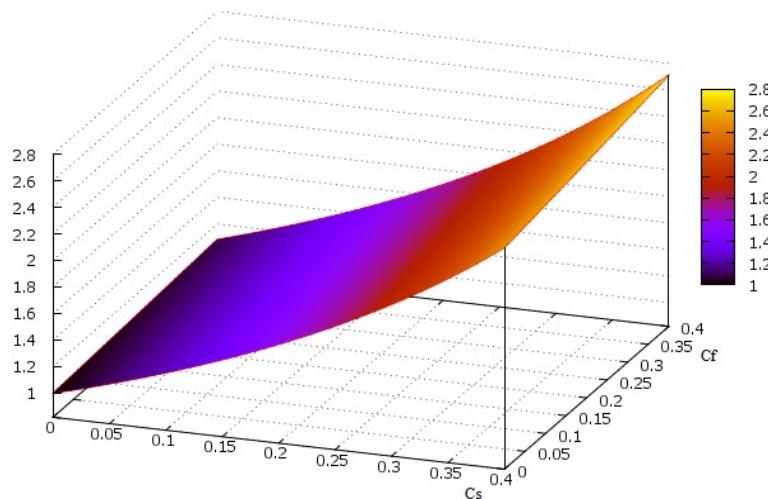


Fig. 5.11 Dependence of Young's modulus of composite material on the volumetric composition of carbon fibers and disperse reinforcement

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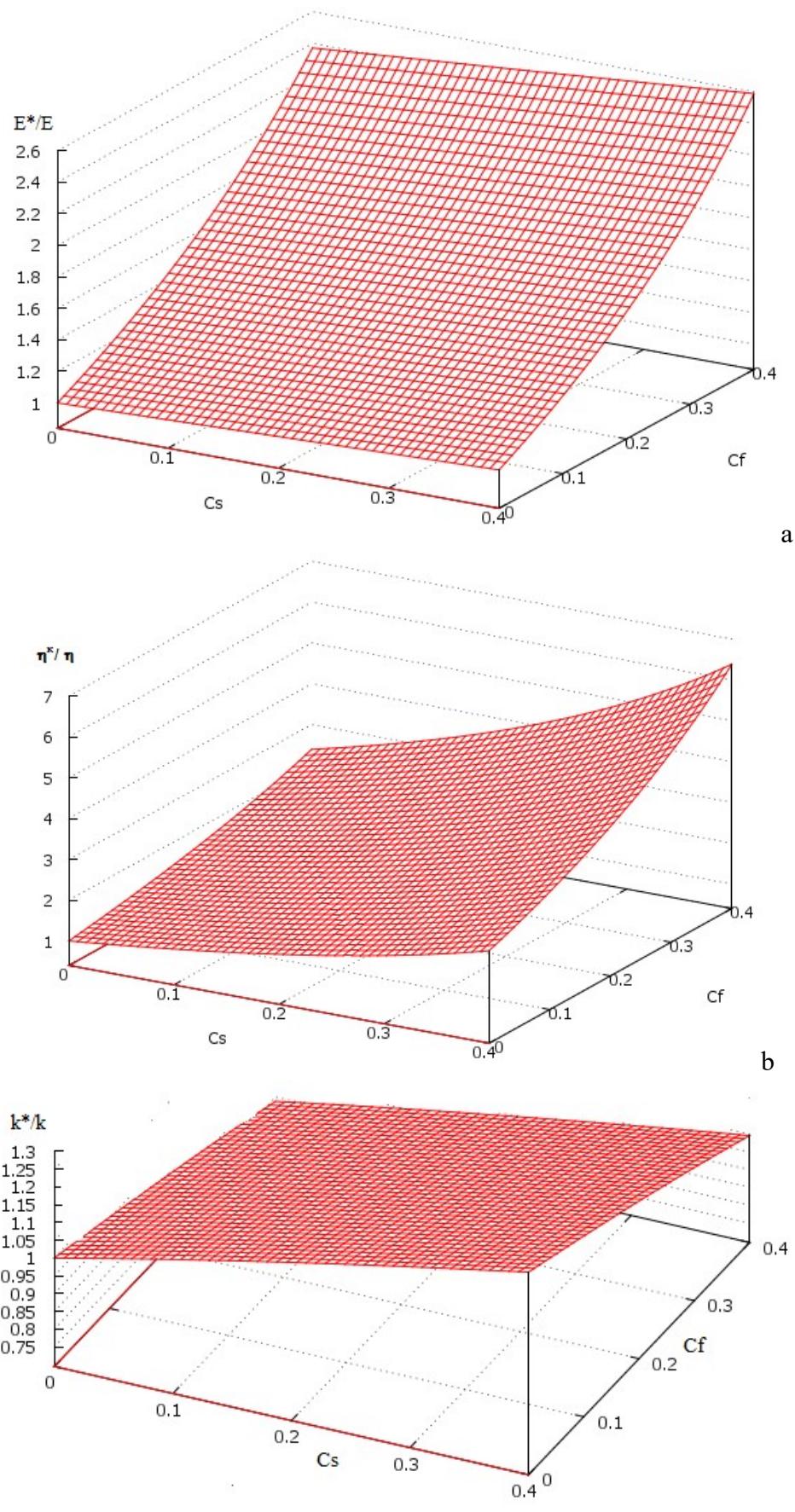


Fig. 5.12 Dependence of elasticity (a), viscosity (b) and plasticity (c) of a three-component PTFE-composite

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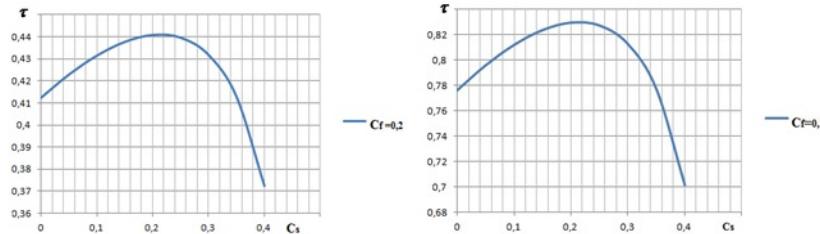


Fig. 5.13 Criterion of coherence of properties

Conclusions from Section 4

Using the variational method of the theory of composite materials, the elastic and visco-plastic behavior of the material is studied. The method of testing on three-component composite materials, the inclusion of which is geometrically and physically and mechanically different (they are in the form of short fibers or close to spherical ones). Calculations of elastic and visco-plastic properties are compared with the results of other studies.

In the mathematical procedure for optimizing the composition of composite material, the criterion of abrasive stability, which agrees with plastic and elastic properties, is the ratio of dynamic viscosity to the elastic modulus. The calculations are based on this criterion. The process of destruction of a composite material under the influence of stress is studied. The strength limit of composite material reinforced with short fibers is determined, depending on the geometrical and mechanical characteristics of its components.

The proposed mathematical modeling is tested on the calculations of real three-component three-component materials used in nodes of friction, which showed its efficiency and applicability in the tasks of creating and designing new materials.

CONCLUSIONS

Optimization of technological regimes of manufacturing and processing of PTFE composites allows to achieve economically significant results and increase their competitiveness.

An important factor in this approach to PTFE-composites technology is the realization of the principle of "reasonable sufficiency" when choosing the composition, component ratio, material fabrication technology and its processing into products with given performance characteristics.

This approach allows to provide the optimum combination of strength properties and tribotechnical characteristics of the product, as well as technical, economic and technological parameters for the production of materials adapted to specific industrial conditions and practical applications.

The content of the monograph reflects the results of many years of research and development in the field of the creation of new composite materials for tribotechnical purposes on the basis of polytetrafluoroethylene, technologies of structural modification of antifriction materials, the development of new metal-polymer tribosystems (bearings, sealing devices).

The results make it possible to characterize the physicochemical processes during the frictional interaction in the tribosystems of metallic polymers.

The results of the research, the formulation of the concept of the creation of antifriction materials based on PTFE, are of practical value for the reliable operation of equipment and process equipment in conditions of intense wear.

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