The concept of energetic and technological compliance of components in materials science of fluorine composites

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Abstract: *The structural and technological aspects of the polytetrafluoroethylene-matrix composites formation are shown. It is shown that due to the existence of inert components in the process of interfacial interaction with the degree of filling in the traditional technological paradigm implemented structural paradox manifests itself in proportion to the reduction of the parameter of tensile strength with increasing degree of filling. According to the concept of energy and technological compliance of components the technological principles to eliminate the negative impact of the structural paradox fluorine composites are proposed.*
KEYWORDS: *POLYTETRAFLUOROETHYLENE, FLUORINE COMPOSITE, METHODOLOGICAL PRINCIPLES, STRUCTURAL PARADOX, ENERGY AND TECHNOLOGICAL COMPLIANCE*

1. Introduction

Polytetrafluoroethylene (PTFE) and composite materials based on it are widely used for the manufacture of products for sealing, tribological purposes, as well as for protection against the effects of aggressive technological environments and high temperatures [1–5]. The features of the PTFE macromolecule structure contribute to the parameters of the supramolecular structure that determine the mechanisms of friction, wear, deformation under the action of static and dynamic loads and inertness in the processes of interaction with technological media. In particular, it applies to the processes of interfacial interaction with components of different composition, structure and dispersion, which are used as functional modifiers of composite materials in the manufacture of products for various purposes.

A review of the scientific literature on the study of physical, chemical and technological aspects of the production and processing of functional fluorine composites indicates that traditional methodological approaches based on the classical concepts of polymer materials science, physical chemistry and technology of plastics and composite materials have been established [1–3, 6]. The essence of these approaches is the application of methods for regulating the composite supramolecular structure by using fragments of organic and inorganic fibers - glass, oxalonic, basalt, carbon.

In all their diversity of fluorine composites grades (materials of the series "Flubon", "Fluvis", F4K20, F4G10, etc.) and its production, a general technological principle of formation and processing into products is implemented. This principle involves a combination of operations for components mixing in specified ratios, cold pressing of semi-finished products and its hot sintering (monolithization) in an air atmosphere according to a given temperature – time regime. This technological principle, which is close in essence to that used in the technology of powder metallurgy, currently dominates in the literature, patent and commercial sources, becoming the basis of the technological paradigm of functional fluorine composites [1–5].

The using of various types of this technology, consisting in the introduction of highly dispersed fillers (carbon- and silicon-containing particles: UDD, zeolites, etc.), including nanosized and mechanically activated fillers [1–8], as well as reinforcing fibers (carbon (CF), glass, basalt, aramid) or their combinations [9], while maintaining the traditional sequence of technological operations to obtain blanks (products) does not allow achieving fundamentally new effects of increasing the parameters of stress-strain, thermophysical and tribological characteristics.

The manifestation of a structural paradox for fluorocomposites is generally recognized, which consists in a significant decrease in the values of most important parameters (tensile strength σ_t, friction coefficient f, density ρ) under introducing of high-strength reinforcing fillers (for example, CF) [6, 9].

The purpose of this work was to develop principles for improving the technology of functional fluorine composites based on the concept of multilevel modification.

2. Materials and research methods

Such commercially produced polytetrafluoroethylene (PTFE) grades as Ф-4ПН, Ф-4ПН90, Ф-4ТМ that differ in the average size of the powdered fraction (HaloPolymer, Russia), were used as the base binder in the preparation of fluorine composites. Fragments of carbon fiber (CF) obtained by a mechanical fragmentation of carbon tape of ЛО-1-12Н brand (SvetlogorskKhimvolokno OJSC, Belarus) with a size of fractions of less than 200 microns, were used for the reinforcement of the PTFE. The targeted modification of PTFE was carried out by introducing into the composition of carbon black (CB) grades П234 and П803 with an average particle size of 20 and 80 nm, ultrafine PTFE (UPTFE), commercially available under the Forum trademark (Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences, Russia) that are a polymer-oligomeric products of thermogasdynamic synthesis of polytetrafluoroethylene, and fluorine-containing oligomers "Foleox" and "Epilam". In addition, dispersed particles of semi-finished products of organic and inorganic origin - clays, tripoli, metal oxides, carbon nanotubes, ultradispersed carbon-containing products of explosive synthesis (detonation nanodiamond (DND), also known as ultradispersed diamond (UDD) produced by Scientific and Production Closed Joint-Stock Company «SINTA», Belarus), etc. were used as modifiers of the PTFE structure.

The parameters of the stress-strain (tensile strength σ_t, compressive strength at 10% linear deformation $\sigma_{c10\%}$, Young's modulus under compression E_c, hardness HB) and tribological (wear rate I, friction coefficient f) characteristics were determined according to the standard methods recommended in the regulatory documentation, using the МР-200, ComTen 94C, Р-0,5, ХП-250, СМЦ-2, ХТИ-72 friction machines. The analysis of the physical and chemical properties and structure of the samples was carried out based on the data of IR spectroscopy (Tensor-27), atomic force (Nanotop-III), optical microscopy (Micro200T-01), scanning electron microscopy (LEO1455VP) and X-ray diffraction analysis (Dron-2.0).

3. Results and discussion

A systematic analysis of the effect of the structure of fluorine composites on the mechanisms of deformation, fracture and wear of products made of them under various conditions of loading and operation made it possible to identify the main factors influencing the manifestation of the structural paradox in the implementation of traditional technologies for their manufacture at the molecular, supramolecular, phase and interphase levels.

In a number of literary sources, it is noted that it is impossible to preserve some of the initial parameters of the properties (for example, tensile strength σ_t, Charpy impact strength a) of the PTFE matrix polymer or to its increase with the introduction of fillers of any composition and dispersion, including high-strength ones, especially in the case of an increased content of fillers [2, 3, 5]. The manifestation of a structural paradox is the feature of fluorine composites. The structural paradox consists in a significant decrease in the values of a number of the most important parameters of fluorine composites (density ρ, tensile strength σ_t, friction coefficient f) upon the introduction of reinforcing fillers (for example, carbon fibers CF). The introduction of more than 20 wt.% of any filler, including high-strength filler, into the composite is not advisable, because in this case there is a significant decrease of the parameter σt that determines the field of application of products made of it.

The experimentally observed negative effect of a decrease in the values of a number of the most important parameters of fluorine composites modificated by high-strength fillers cannot be explained from the point of view of classical ideas about the role of the structure at the supramolecular and interphase levels in the implementation of the deformation and destruction mechanisms of products made of it under the influence of operational factors.

A systematic analysis of the structure of fluorine composites influence on the mechanisms of deformation, destruction and wear of products made of its under various conditions of loading and operation made it possible to identify the main factors (at the molecular, supramolecular, phase and interphase levels) that affect the manifestation of the structural paradox in the implementation of traditional technologies of its manufacture (Fig. 1).

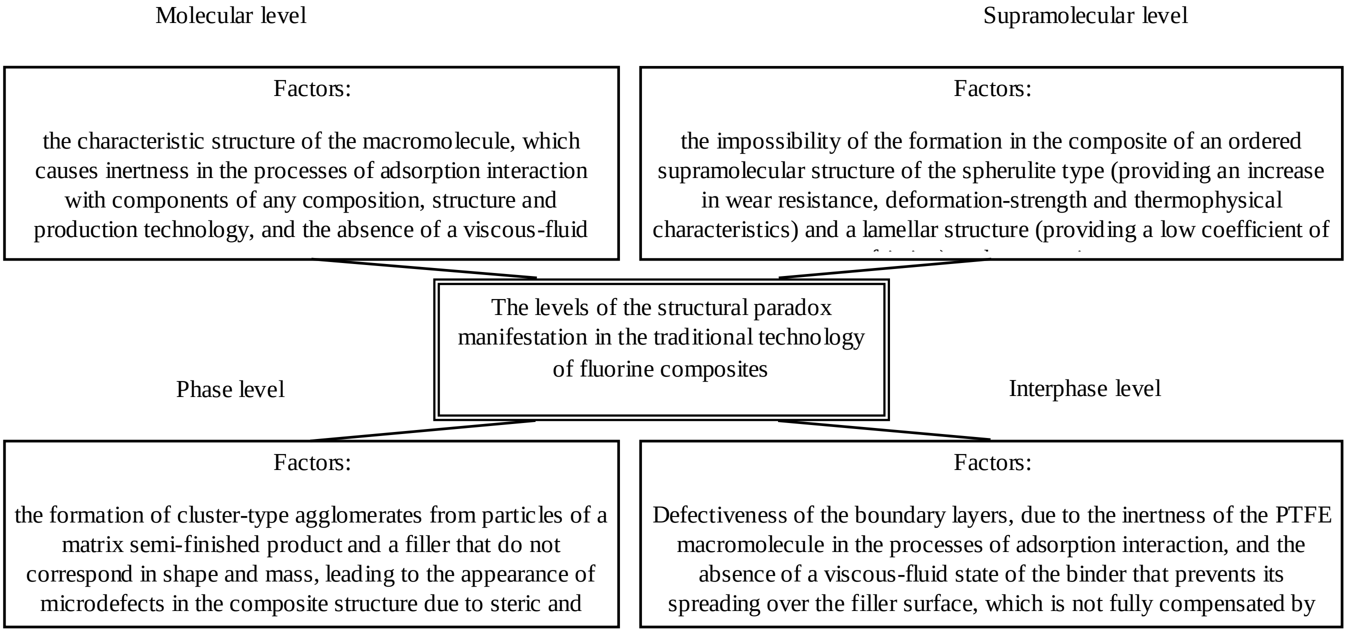

Fig. 1. *The main factors influencing the manifestation of the structural paradox during the formation of fluorine composites according to the technological paradigm*

The imperfection of the structure of fluorine composites at the *molecular level* is predetermined by the specific structure of the PTFE macromolecule, which causes the absence of a viscous-fluid state. The molecular structure of PTFE dictates the need to use special technological methods that ensure the formation of a low-defect structure under temperature impact on the compacted sample. The most effective method is the introduction into the interparticle boundary layer of thermodynamically compatible with PTFE modifiers that play the role of a high molecular weight plasticizer.

At the *supramolecular level* of the formation of the fluorine composite structure, the paradox manifests itself in the impossibility of obtaining a gradient structure with a lamellar structure of the surface layer of the product that provides low shear resistance, and a disperse spherolite-like structure of the matrix in the bulk that causes increased parameters of stress-strain characteristics, at the same time. The formation of the optimal supramolecular structure in the filled PTFE matrix during monolithization is difficult due to the low mobility of the binder macromolecules. Therefore, the greatest importance has been the activity of the dispersed particle in the processes of recrystallization of the initial structure of the PTFE matrix particles.

With the dispersed modifiers particles activity growth, which can be achieved through the use of special technologies for the formation of nanoscale fractions [1], mechanical or thermal action on a semi-finished product [1, 2], the effectiveness of its action on the process of supramolecular organization increases that provides the necessary modification effect with a significant lower filler concentrations [1, 4]. Therefore, nanosized modifiers (DND, zeolites, sialons, etc.) treated by mechanical activation provide a significant increase in the parameters of deformation-strength and tribological characteristics of fluorine composites at a content of up to 1 wt.% [1].

At the *phase level*, the formation of an imperfect structure of a fluorine composite is due to the formation of cluster-type agglomerates during mixing of matrix polymer and filler particles that cause the appearance of microdefects in the sample after cold pressing and persist after sintering the semi-finished product due to the action of interparticle friction forces, steric and rheological obstacles to filling the cavities of clusters with a binder.

The *interphase level* of the PTFE composite materials structure imperfection leads to a decrease in the parameters of its service characteristics and realizes due to the defectiveness of the boundary layers in the "matrix - filler" system that causes its low strength, which is predetermined by the inertness of PTFE macromolecules in the processes of adsorption interaction and the absence of a viscous-flowing state of the binder that prevents its spreading over the filler surface. Therefore, in composites filled by dispersed fragments of carbon, glass, and other fibers, their strength parameters are not fully realized that in other thermoplastic matrices with high melt fluidity lead to a significant increase in the values of the σ_t and σ_c parameters. For example, the tensile strength parameter σ_t for carbon-fiber reinforced plastics and fiberglass-reinforced plastics based on polyamide 6 with a filler content of 20 wt. % has a value of 110 and 130 MPa, respectively, with an initial σ_t value for a matrix polymer of 60–65 MPa.

It was established by the SEM method that, regardless of the individual parameters of dispersed particles (composition, structure, and production technology), they are characterized by clustering during production and storage (Fig. 2), as well as the presence in micro-sized particles (mechanically dispersed silicon, silicate glasses, formate copper, tripoli, clays, metal oxides, PTFE, UPTFE, etc.) the nanoscale components in the surface layer of particles

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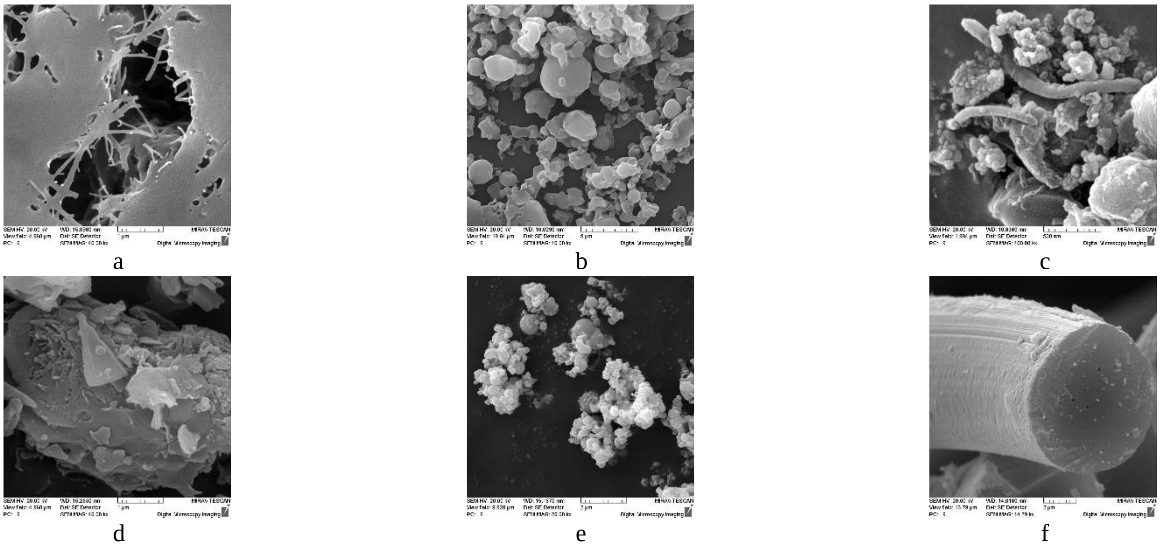

Fig. 2. *Typical morphology of particles of PTFE (a), UPTFE (b), carbon nanotubes (c), tripoli (d), metal oxides (e), carbon fiber (f) in the as-received condition*

Analysis of the spectra of thermally stimulated currents (TSC) of modifiers of different composition, structure and production technology indicates not only its active state, but also different temperature ranges of manifestation of this state [1]. Considering that dispersed particles of predominantly micrometer dimension (50-200) microns were chosen for modification, obtained by mechanical shredding of natural semi-finished products (shungite, tripoli, clay) and thermodynamic synthesis during ablation of a PTFE block (ultrafine polytetrafluoroethylene under the "Forum" trademark) clustering processes, it should be assumed that the structural components of the surface layer, which are in the nanostate, have a significant effect on the manifestation of energy activity. Therefore, to increase the efficiency of the modifying action of dispersed components, it is advisable to use technological methods that determine the formation of the morphology of the surface layer with nanosized components, which ensure the formation of the optimal structure of composites at the supramolecular and interphase levels of organization. This morphology will promote not only the processes of orientation of the binder macromolecules under the action of the energy field of the nanocomponents, but also the formation of an interphase layer with increased adhesion due to the filling of the particle relief irregularities with the binder.

The nanostate of dispersed particles of condensed media with various composition, structure and production technology is determined by a combination of factors, which are shown in Fig. 3.

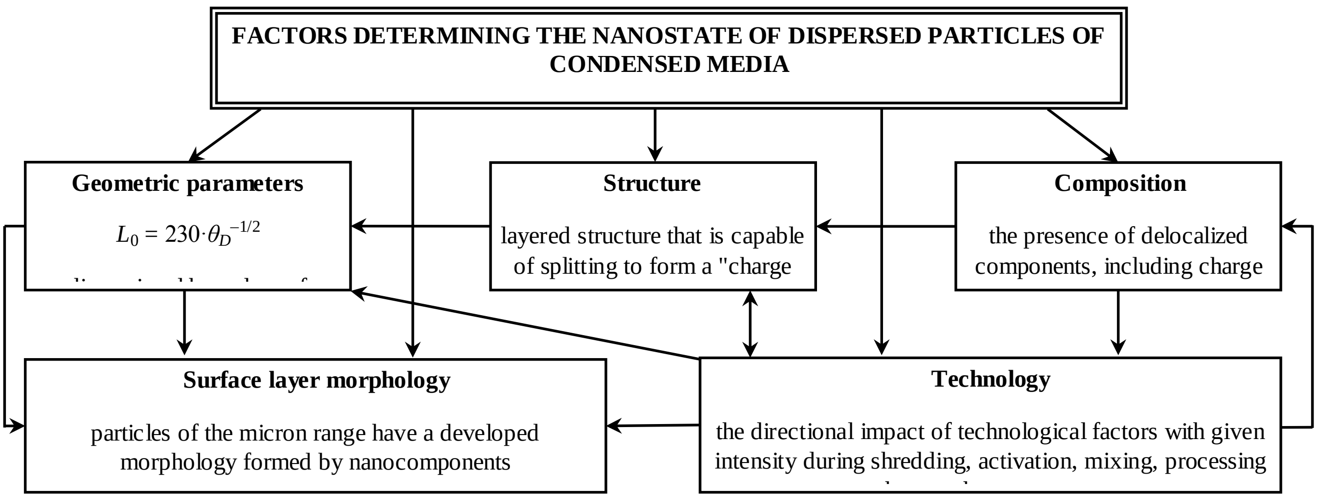

Fig. 3. *Factors determining the nanostate of dispersed particles of condensed media*

A combined analysis of the factors causing the manifestation of the structural paradox, leading to the occurrence of a negative effect of a decrease of the parameters of stress-strain and tribological characteristics of fluorine composites under increasing the amount of modifiers, indicates the prevalence of factors associated with the technology of obtaining a matrix binder (powdered PTFE) and a reinforcing filler (mainly CF), which aggravate the unfavorable processes that prevent the formation of the optimal structure of the composite. Therefore, to increase the values of the strength and wear resistance parameters of composite materials based on PTFE with a filler content of more than 20 wt. %, identified it as highly filled, it is necessary to change the traditional approaches that formed the technological paradigm [7, 9].

The essence of these changes is as follows:

– it is necessary to carry out the technological preparation of the components, which makes it possible to achieve the optimal parameters of the geometric characteristics of the prevailing fraction and to reduce the negative influence of the unstable molecular weight distribution of the matrix polymer on the parameters of the stress-strain, rheological characteristics and interparticle interaction;

– it is necessary to apply technologies for combining material components, ensuring the destruction of cluster structures formed by PTFE and filler (CF) particles during mixing;

– the characteristic morphology of the matrix PTFE particles makes it possible to use components with high thermodynamic compatibility as target modifiers, which increase the plasticity of the matrix during cold pressing and monolithization due to the plasticization effect. An effective modifier of this type is oligomer and polymer-oligomer products of chemical and thermogas dynamic synthesis – fluorine-containing oligomers (FCO), ultrafine polytetrafluoroethylene (UPTFE);

– the cluster structure, which is formed at the stage of combining the components, makes it possible to implement the principle of multilevel modification using a combination of components with different dispersion, habit and energy state, which provide an optimal structuring effect at various levels of the organization;

– the technological parameters of the composite monolithization process should ensure the possibility of not only reducing the number of structural defects, but also achieving an optimal ratio of the energy characteristics of the matrix and filler for the implementation of the prevailing interphase process, which ensures the formation of a boundary layer with increased characteristics of adhesive interaction.

Evaluation of the effectiveness of the practical application of the developed methodological principles of the highly filled fluorine composites technology (Fig.) indicates the feasibility and validity of the existing paradigm shift [9].

The methodological approach based on the establishment of the dominant physicochemical (in particular, tribochemical) reaction made it possible to establish a functional relationship between the parameters of the components and the energy state of the systems.

To characterize the *energy state* a complex parameter was used, which is the cumulative result of transformation of the initial individual parameters (structure, composition, morphology, habit, size) of the components under the influence of technological and operational factors. The feature of the proposed methodological approach is the possibility of a targeted intensification of the dominant interfacial reactions through the implementation of the energy state of components with certain parameters of electrical and physical characteristics. Under certain conditions a material object acquires a special state (nanostate), which can manifest itself when the dimensional parameters are reached both by a single particle and by components of the surface layer morphology of a particle or substrate with micro- and macro-sizes [3, 4].

The priority principle of the choice of components and methods of its activation is to ensure the necessary ratio of the parameters of the energy characteristics at a certain stage of the formation of the structure of the composite, product, metal-polymer system, that is, when exposed to specific technological parameters.

The conducted research and analysis of literature sources devoted to the material science of polymer composites made it possible to substantiate the concept of energy and technological compliance of components for the formation of systems with optimized parameters of structural characteristics at various levels of organization.

The energy compliance of the components implies the possibility of its reaching a total energy state, which corresponds to the activation energy of the dominant physicochemical process, which ensures the formation of the optimal structure of the interphase layer in composites or metal-polymer systems.

To implement the principle of energy compliance of components, it is necessary not only a certain combination of initial parameters (thermophysical, dimensional, electrophysical, structural, elemental, etc.), but also the possibility of their change in the specified ranges of values under technological influences on the components (deformation, temperature, ionizing , laser, etc.). When choosing an adequate technology for obtaining, preparing, mixing components or processing composites into products, conditions are created for changing the initial energy state and achieving a nanostate directly in the interphase interaction zone, which ensures the dominant physicochemical process of forming the optimal structure of the boundary layer.

The formation of an interfacial (boundary) layer with an optimal structure indicates the technological correspondence of the components of functional materials and metal-polymer systems, which is understood as the possibility of achieving the specified energy parameters of the components at a certain stage of the formation of a composite, product or construction, ensuring the manifestation of the dominant mechanism of interphase interaction. The absence of such a state does not allow realizing the potential of individual components in the selected technological process of manufacturing the system, since it can manifest itself in various ranges of temperature, mechanical, physicochemical and other effects, without ensuring the achievement of the required value of the activation energy at a specific technological stage, leading to the structural paradox.

4. Conclusion

Thus, the implementation of the phenomenon of the nanostate of dispersed particles in the structure of fluorine composites on the basis of the concept of energy and technological compliance of components provides a decrease in the prerequisites for the demonstration of a "structural paradox" and the possibility of achieving a synergistic combination of parameters of tress-strain and tribological characteristics using the developed technological principles of production and processing.

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