# THE CONDITIONS FOR OBTAINING SELF-ORGANIZED STRUCTURES ON THE TRIBOLOGICAL SURFACES OF COMPOSITE MATERIALS BASED ON POLYTETRAFLUOROETHYLENE WHICH IS USED IN AUTOMOTIVE AND OTHER DEMANDING TECHNOLOGIES

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The paper discusses a self-organization phenomenon, physical and chemical aspects of friction, and the methods of friction control using advanced polymer composites based on polytetrafluoroethylene (PTFE). The article also concerns a generic physical and an engineering approach to the development of new wear-resistant polymer composites with modified fibers filler. 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. Determine the properties of the composite based on the properties of the matrix and the filler. In this case, determining the distribution of the particles of the filler by size and the particles of different sizes in the volume of the composite.

**KEYWORDS**

wear, composite material, principles of self-organization and nonequilibrium thermodynamics, physical and mechanical properties, polytetrafluoroethylene.

## 1 INTRODUCTION

The scientific novelty of the obtained results consists in the development of theoretical foundations of friction modeling. Interaction of the surface layers of materials is considered as an open system. The state of the surface layers of a material is determined by the kinetics of phase transitions. In contrast to existing approaches, the patterns of self-organization in the process of friction are described. Differential equations of the evolution of the order parameter, the connected field and the control parameter having an equal character determine the conditions for the formation of the emergence properties. This makes it possible to develop practical recommendations for the design and use of polytetrafluoroethylene based polymer composites, taking into account the phenomena of self-organization. Friction is a well-known issue to be taken into account in reliability engineering and it's a highly complex phenomenon that should be studied thoroughly by means of modern physics that deals with complexity. The most common idea considering the complexity of natural processes is the concept of self-organization. Creation, research and usage of new tribomaterials, coating and surface strengthening technologies increase the machinery reliability [Elsayed 2012, Myers 2010, Verma 2016, Finkelstein 2013, Wessels 2015, Zaborowski 2007, Janekova 2014, Lesso 2014, 2016, Monkova 2013, Mrkvica 2012, Rimar 2016, Sebo 2012, Straka 2013, Vojtko 2014, Valicek 2016, Zaborowski 2007].

The polytetrafluoroethylene (PTFE), which is the most notable tribological polymer because of its excellent frictional properties, has the greatest capacity for sustaining wear after reinforcement of a filler. From a structural viewpoint, there are two major categories of material response critical to applying PTFE to automobiles. These are fatigue (durability) and wear resistance. In addition, there is another critical vehicle requirement, ride quality, which is usually defined in terms of noise, vibration, and ride harshness, and is generally perceived as directly related to vehicle stiffness and damping. Tribotechnical properties play a significant role in this category of vehicle response. Polytetrafluoroethylene (PTFE) composites are widely used in friction units and seals in various kinds of machinery and equipment due to its molecular and supramolecular structure which conditions a certain combination of deformation and strength, thermophysical, tribotechnical, anticorrosive and other characteristics and identifies the field of the products implementation [Avdeychik 2012].

Features of operation of products with the PTFE composites usually lead to the transformation of the primary structure for a short time. Formed under the influence of external factors the new structure is significantly different from the primary and determines the resource of the products in actual use. Influence of the primary structure of PTFE composite on the kinetics of formation the distributing layer with a structure that more effectively resists acting on tribosystem the energy parameters needs a more detailed study and consideration of the interaction of components in determining the composition of PTFE composite.

Influence of the primary structure of PTFE composite on the kinetics of formation the distributing layer with a structure which more effectively resists degradation processes acting on tribosystem is originally studied more thoroughly in this paper. Interaction of components in order to determine the composition of PTFE composite is also considered. Surface layers morphology modified with the filler particles is studied and energy influence on the processes of adsorption and chemical adsorption interaction is analyzed [Sawyer 2014, Nosonovsky2009, Balara 2018, Janekova 2014]. Thus special methods of active influence on the composition, primarily mechanochemical and energy, are required here [Nosonovsky 2010, Fox-Rabinovich 2007, Pogrebnjak 2015, Berladir 2016, Panda 2017].

Analysis of literary sources showed that the potential opportunities of conventional technologies of PTFE composites preparation are not implemented in full because of underestimation of significant factors at recycling the composite into products. In this paper, we present a model of the self-organization phenomenon, physical and chemical aspects of friction, and the methods of friction control using advanced polymer PTFE composites.

## 2 MATERIALS AND METHODS

The non-equilibrium open systems are characterized with their interaction with the environment and the exchanged mass, energy and information flows. In addition, self-organization is often a consequence of coupling of friction and wear with other processes, which leads to modification of the primary structure in the tribosystem.

The research of non-equilibrium open complex systems shows that, representation of the self-organizing system is reduced to the description of time dependences of an order parameter, a conjugate field and an operating parameter. As efficiency of application of PTFE composites is defined at their operation, it is necessary to label the change of entropy of frictional PTFE composites (dS) as an order parameter. As shown in detail in [Fox-Rabinovich 2007], the change of entropy of frictional PTFE composites (dS) is:

$$dS = dS_i + dS_e + dS_m + dS_f - dS_w \quad (1)$$

After differentiation with respect to time, Equation (1) in a stationary condition looks like:

$$dS/dt = dS_i/dt + dS_e/dt + dS_m/dt + dS_f/dt - dS_w/dt \quad (2)$$

or:

$$dS_w/dt = dS_i/dt + dS_e/dt + dS_m/dt + dS_f/dt \quad (3)$$

where:

dSi/dt is the entropy production as a result of the distribution of heat and other flows within a material surface;

dSe/dt is the flow of entropy due to external interactions, which could be changed due to the transition of heat from a frictional layer with a higher temperature into a layer with a lower temperature, resulting in an entropy increase;

dSm/dt is the change of entropy due to the formation of chemical compounds on the PTFE composites surface due to the entropy of the matter particles transferred from the contacting frictional layer;

dSf/dt is the change of entropy due to formation the distributing layer as a result of the primary surface modification;

dSw/dt is the change of entropy due to the wear process. The change of entropy, dSf/dt, could be positive if there are equilibrium processes [Nicolis 1989, Olemskoĭ 2007, Gershman 2004, Mah 1983]. As follows from (2), lower entropy production corresponds to a lower dSw/dt value. Taking into account that entropy is an additive value, we can conclude that the lower dSw/dt, the lower the wear rate of the PTFE composites surface. Therefore, the entropy decrease leads to wear rate reduction. Non-equilibrium processes on the surface (dSf/dt < 0) and the formation of lubricating distributing layer due to matter particles transfer from the workpiece with its further chemical adsorption (dSm/dt < 0), with all other conditions being equal, can also lead to a wear rate decrease.

Accordingly, the conjugate field represents the mechanical activation (*G*) of preparation of PTFE composites. Dispersity of PTFE powdered product depends on the technology of the PTFE preparation (pressing with subsequent sintering) and largely determines the effective resistance to degradation processes and its effective recycling. The dominant value of the conjugate field is at creation of PTFE compositions with the fillers of different nature and morphology.

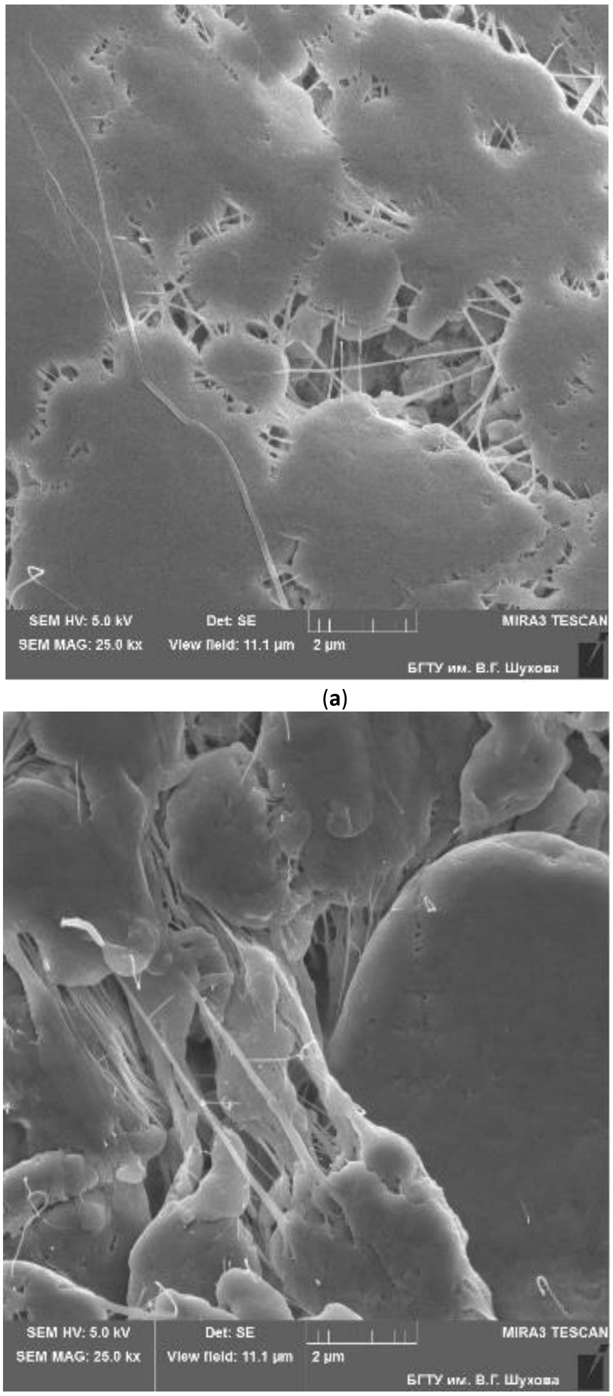
Scientifically substantiated and practically proved that effective way to improve physical-mechanical and tribotechnical properties of PTFE is its mechanical activation in which the supramolecular structure of PTFE undergoes significant changes - from lamellar disordered in the structure with higher ordering until the spherulitic [Budnik 2009]. As a result of energy-active mechanical impact is chemical mechanical destruction of macromolecules of polytetrafluoroethylene with the formation of radical fragments and formation of inter-factional elements of PTFE which that form the structures that more actively resist wear and provide higher physical and mechanical properties.

By IR spectroscopy method it was found that in case of the PTFE modification as a result of mechanical activation, a transition of the polymer into dispersed, nanodispersed and other structural states occurs [Budnik 2015]. In the IR spectra of these formations, the bands that characterize the vibrations of individual fragments and whole chain even under intense energy impact are preserved. This allows assuming that the external mechanical influence does not result in noticeable destruction of polytetrafluoroethylene molecular chain, but in some cases, certain changes occur at the molecular level, which leads to enhanced physical, mechanical and service properties of the polymer and reveals the possibility to use activated PTFE as a matrix of fluoropolymer composites of various applications. It was found that the activated PTFE has the optimal ratios of physical-mechanical and tribotechnical properties in mode of $n$ = 9·103 $\text{min}^{-1}$ and $\tau$ = 5 minutes: breaking strength $\sigma_b$ =24.8 MPa, relative elongation $\delta$ = 415 %, wear intensity I = $610 \cdot 10^{-6}$ $\text{mm}^3/\text{N}\cdot\text{m}$ [Brown 2006, Joyce 2003, Brown 2005]. Methods of electron microscopy have shown the grinding of structural components of PTFE with value of 250-300 microns in the nonactivated polymer to 10-50 microns by length and diameter from 10 to 100 nm in an activated polymer (Figure 1) [Rae 2004, 2005].

The degradation and healing processes usually have characteristic scale lengths and thus belong to different hierarchy levels, as was discussed above. The generalized degradation and healing forces are external forces that are applied to the system, and flows are related to the forces by the governing equations.

The operating parameter *F* characterizes dependence upon a micro/nanostructure parameter of the material (structural parameter), such as the size distribution or the concentration of microparticles embedded in a composite material. The problem of optimum design of a self-healing system can be seen as finding an optimum value of for the minimization of micro/nanostructure parameter the degradation parameter. For any self-healing mechanism, the following scheme is suggested. First, micro/nanostructure parameters critical for the self-healing mechanism, as well as relevant degradation and healing parameters are identified. Then thermodynamic flows and forces are related to the microstructure. Initially, nanoparticles may have been proposed to address the abrasion problem, as nanoparticles have a characteristic dimension (<200 nm) smaller than the transfer film thickness. However, nanoparticles can be extremely hard, and nanoparticle abrasion can polish the counter surface to promote transfer film stability.

Furthermore, nanoparticles have high number densities and ratios of surface area to volume. A nanocomposite has one thousand times the filler surface area and one billion times the number of particles of a comparable microcomposite (i.e., 20 nm versus 20 µm average filler diameter). Although polymers and fillers are often inert and are expected to have weak interfaces, the likelihood for chemical interaction increases with an increased ratio of surface area to volume [Basu 2007].



(**a**)

(**b**)

**Figure 1.** (**a**) Structure of PTFE before mechanical activation in mode $n = 9 \cdot 10^3$ min$^{-1}$ and $\tau = 5$ minutes; (**b**) Structure of PTFE after mechanical activation in mode $n = 9 \cdot 10^3$ min$^{-1}$ and $\tau = 5$ minutes

The mechanical properties of PTFE depend strongly on its crystallinity, crystalline phase, and crystalline morphology [Lillehei 2009], all of which may be strongly influenced by interactions at the polymer/nanoparticle interface. PTFE has a unique crystalline structure that is often described as banded, and this banded structure contains intermittent bands of crystalline polymer and amorphous polymer [Luo 2008]; the viscoelastic properties of this banded structure are related to its friction and wear responses [Luo 2008]. Within crystalline regions, lamellar slices are composed of folded PTFE chains. An individual chain is a fully fluorinated carbon backbone in a helical conformation, the twist of which dictates the phase. The influence of the nanoparticles on the polymer is limited by how well the particles have been dispersed. High surface area per unit volume, the very property that makes nanoparticles special, also encourages them to stick or agglomerate. This behavior results in a competition between the potential for mechanical enhancement and difficulty of dispersion. Although many proposed methods [Navarchian 2009] characterize a property of the distribution of particles (a strategy with virtually endless possibilities), the experience with tribological nanocomposites suggests that the characteristic size of the unreinforced polymer domain is the feature that matters most; he was named termed this the free-space length, $L_f$ [Pegel 2009, Khare 2010]. As $L_f$ decreases, the influence of the interface region (Figure 2) increases along with the reinforcement effect. We would therefore expect smaller, better dispersed, and higher loadings of fillers to improve the properties. Figure 2 illustrates the effect of dispersion quality on $L_f$ for a 6% nanocomposite.

The obtained system of equations is dependent upon *F* and should be optimized by *F* for the minimization of degradation. As a result, the problem is reduced to an expression of micro/nanostructure parameter the specified quantities change rates through their values. Considering that the behaviour of order parameter is a key one and is subordinate to behaviour of the conjugate field and the operating parameter, we will accept expression for its change rate *dS* in the linear form

$$\tau_S dS = -S + A_S G \tag{4}$$

Here the first summand in the right part considers a relaxation of the entropy of a PTFE composites to zero value for time $\tau_S$, the second − describes linear reaction of the change rate dS to field increase *G* ( $A_S > 0$ − a communication constant). The equation for the conjugate field is accepted as

$$\tau_G dG = -G + A_G SF \tag{5}$$

where the first sum again has a relaxation nature with the characteristic time $\tau_G$, the second - represents a positive feedback of the entropy of a PTFE composites and a gain of operating parameter *F* with the change rate of the conjugate field ($A_G > 0$ - the communication constant). This communication causes increase of the conjugate field (the mechanical activation (*G*) of making system), which is at the bottom of self-organizing.

Last equation of evolution of the system describes the relaxation of the gain of the free-space length $L_f$, which is playing a role of the operating parameter *F*

$$\tau_F dF = \left(F_e - F\right) - A_F SG \tag{6}$$

Unlike (4), (5) the first summand in (6) describes a relaxation of parameter *F* not to zero, but to final value $F_e$, which is set by external influence ( $\tau_F$ - corresponding characteristic of relaxation, $A_F > 0$ − a communication constant). According to (6) negative feedback of the conjugate field and parameter of an order with speed of a gain of operating parameter, according to a principle of Le-Shatele, results to reduction of this parameter.

According to [Olemskoi 2002, Yushchenko 2009, Haken 2004] system of synergistic equations (4) - (5) is the elementary field scheme representing effect of self-organizing. For the analysis of this system it is convenient to make use of dimensionless variables by scaling time *t*, the order parameter *S*, conjugate field *G* and internal status parameter *F*

$$\begin{aligned} &\tau_S, S_c \equiv \left(a_G a_F\right)^{-1/2}, \\ &G_c \equiv \left(a_S{}^2 a_G a_F\right)^{-1/2}, \qquad (7) \\ &F_c \equiv \left(a_S a_G\right)^{-1} \end{aligned}$$

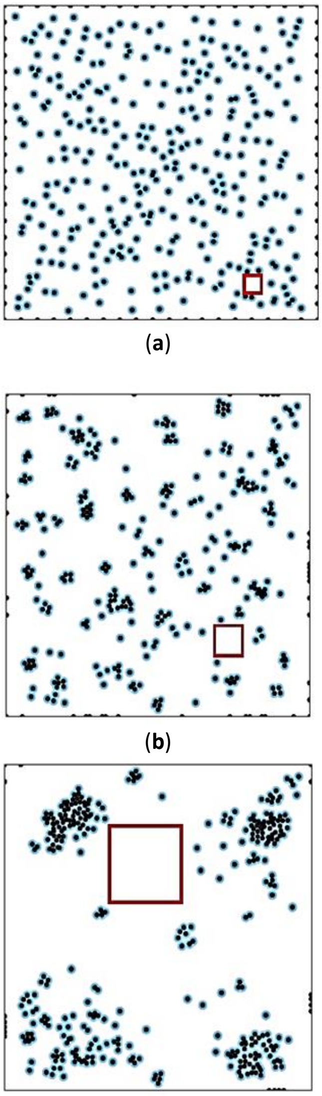
Then the behaviour of PTFE composites is represented by dimensionless system of the equations

$$\mathrm{dS} = -\mathrm{S} + \mathrm{G}, \qquad (8)$$

$$\sigma\mathrm{dG} = -\mathrm{G} + \mathrm{SF}, \qquad (9)$$

$$\delta\mathrm{dF} = \left(\mathrm{F_e} - \mathrm{F}\right) - \mathrm{SG} \qquad (10)$$

where relations of characteristic times $\sigma \equiv \tau_G / \tau_S$ and $\delta \equiv \tau_F / \tau_S$ are entered.


(a)

(b)

(c)

**Figure 2.** Schematic illustrations of the effects of nanoparticle dispersion on the free-space length $L_f$ for a 6% nanocomposite; the dispersion quality deteriorates, and $L_f$ increases from 75 nm (*a*) to 106 nm (*c*). The polymer is shown in white, the nanoparticle is shown in black, and the interface region is shown in blue at the interface of the particle and the polymer. Red boxes represent the free-space length of each dispersion

Within the frames of the elementary picture the evolution of self-organizing systems is represented by adiabatic approach $\tau_G, \tau_F \ll \tau_S$, according to which the conjugate field *G*(*t*) and the operating parameter *F*(*t*) change so quickly that they have time to be arranged under slow change of parameter of an order *S*(*t*). Thus system evolution has the monotonous character described by the equation of Landau-Halatnikov. According to [37], for reflexion of nonmonotonic evolution of system, it is necessary to weaken a standard principle of hierarchy [38], accepting that not one, but two variables possess the greatest time of relaxation. As a result a system of two differential equations represents a transition and the problem comes to research of possible scenarios of continuous transition. The elementary picture of continuous transition, which is traditionally related to the second kind, is realized provided that characteristic time of parameter of an order $\tau_S$ does not depend on its value *S*. In adiabatic approach characteristic time of change of the order parameter much more surpasses corresponding scales for the conjugate field of the making system and a gain of internal status parameter

$$\tau_G, \tau_F \ll \tau_Q \qquad (11)$$

As dimensionless rates *dS*, *dG*, *dF* have an identical order, conditions (10) allow to neglect the left parts of the equations (8) and (9) that lead to parities

$$\begin{aligned} &\mathrm{G} = \mathrm{F_e}\frac{\mathrm{S}}{1+\mathrm{S}^2}, \\ &\mathrm{F} = \frac{\mathrm{F_e}}{1+\mathrm{S}^2} \end{aligned} \qquad (12)$$

Substitution of the first of equalities (13) by (8) gives the equation of evolution of system in the form of the equation of Landau-Halatnikov:

$$dS = -\frac{\partial V}{\partial S} \qquad (13)$$

Its kind is defined by synergistic potential, which is measured in units $S_c^2$.

$$V = \frac{S^2}{2} - \frac{F_e}{2}\ln\left(1+S^2\right) \qquad (14)$$

At small values of intensity of external influence $F_e$ dependence *V*(*S*) has monotonously increasing type with a minimum $S_0 = 0$, which answers inefficient realization of PTFE composites. With growth of $F_e$ to the values exceeding critical level of $F_c$, there appears minimum

$$S_0 = \sqrt{F_e - 1} \qquad (15)$$

which answers the effective realization of PTFE composites.

The consideration shows that the use of the system (8) - (10) allows to present the self-co-ordinated picture of transition between various modes of realization of PTFE composites.

## 3 RESULTS

There are significant efforts dedicated to the research and development of low friction, low-wear solid lubricants with traditional particle and fiber fillers, many of which have successfully transferred to application. In this particular composite, a soft PTFE film is preferentially drawn from the composite to separate the surfaces, protecting the relatively soft polymeric material from direct asperity contact, and providing a low shear friction reducing film to accommodate the sliding motion. This is called a transfer film. Friction coefficients for unfilled PEEK were relatively high and noisy with average values of $\mu$ = 0.37. The addition of PTFE reduced the friction coefficient for all loading conditions.

These data are plotted against filler loading in Figure 3. In the context of polymer tribology and in particular the tribology of polytetrafluoroethylene (PTFE) films, molecular dynamics (MD) simulations have been used to investigate atomic-scale friction at interfaces of self-mated PTFE constructs [39]. The initial structure of the bottom surface is shown in panel a. The sequence in panel b illustrates the evolution of the bottom surface during sliding when the chains on the top (not shown) and bottom surfaces are oriented parallel to one another. In contrast, the sequence in panel c illustrates the evolution of the bottom surface when the chains on the top (not shown) and bottom surfaces are oriented perpendicular to one another. In the latter case, the simulations predict molecular-scale wear of the PTFE surface. In particular, the chains on the bottom surface deform, break, and are in the process of reorienting to line up with the direction of sliding, as indicated by the schematics of the numbered chains in panel *d*.

Sliding of chains oriented parallel to the chain backbones resulted in low friction forces and in low barriers to interfacial slip and molecular reorganization at the surface. In contrast, sliding of chains oriented perpendicular to the chain backbones resulted in high friction forces and wear in the form of molecular reorientation and chain scission. These predictions were examined and validated by complementary experiments on oriented transfer films of PTFE [Jang 2007, Krick 2012, Vail 2011].

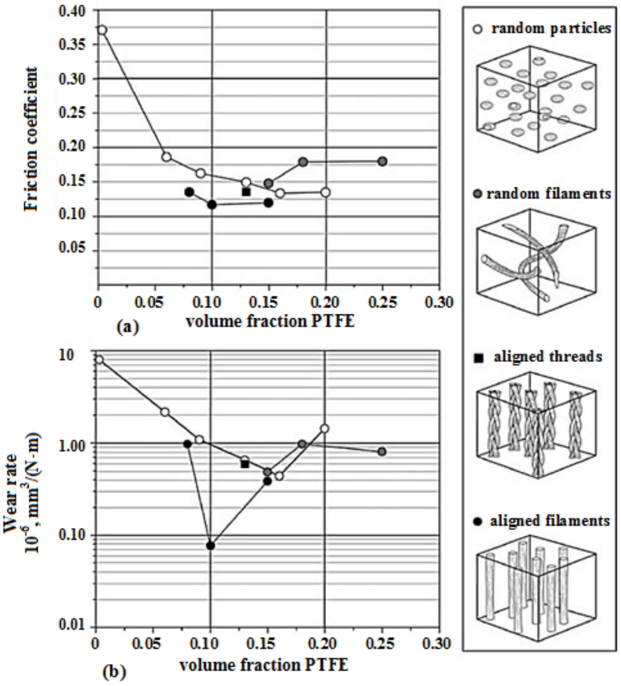


**Figure 3**. **(a)** Friction coefficient versus PTFE filler loading; **(b)** steady state wear rates plotted against PTFE filler loading

Figure 3 shows that at low loadings of aligned ePTFE filaments, the friction coefficient was slightly less than that of the powder filled composites at similar. Composites with expanded PTFE filaments aligned normal to the sliding direction demonstrated the best wear rates; the performance of randomly oriented filaments was similar to the powder PTFE filled PEEK composites loadings.

It was found out that trace quantities of nanofillers can reduce the wear of PTFE by four to five orders that cannot be explained through traditional reinforcement mechanisms. The work is underway to elucidate the responsible mechanisms for nearly a decade and have found a number of potential contributing factors. Although we have not pinpointed exact mechanisms, they appear to be nanoscale in nature and to feedback into one another. Low loadings of well-dispersed nanoscale fillers maximize the interaction area between the filler and the matrix and minimize the characteristic length scale of the unreinforced polymer. These interactions, when sufficiently strong, may have long-range effects on the polymer and on its mechanical response at the nano-, micro-, and macroscales. Interestingly, wear rates, debris morphology, and transfer film properties are relatively unaffected by the particles during the early stages of sliding, which suggests that the reinforcement effect is primarily indirect.

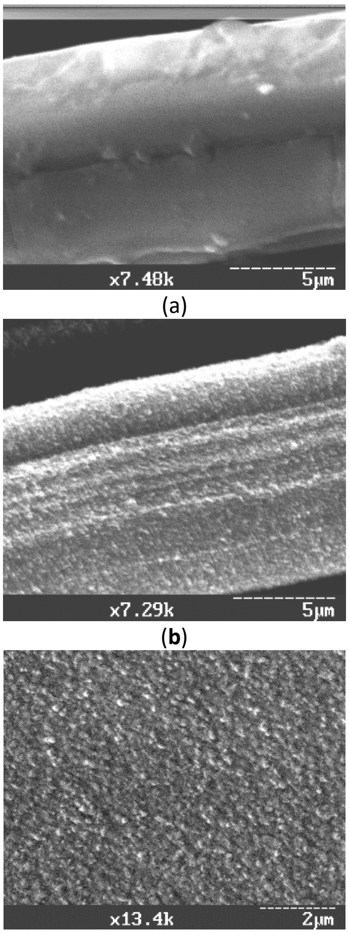
Debris are initially compositionally identical to the bulk and do not adhere to the counter surface. The wear rate and debris size of all PTFE nanocomposites decrease with continued sliding, but only ultralow-wear PTFE exhibits marked degradation at the interface.

These chemical modifications lead to harder, more brittle (possibly through cross-linking and conjugation), and more-wear-resistant polymer surfaces. We can disrupt ultralow wear by removing the environmental water vapor necessary to form the chelating reaction products, supporting the importance of tribochemistry. The nanoparticles may reduce the barriers to PTFE defluorination and chain scission to promote this tribochemistry. Whereas debris size and wear rates reach moderate steady-state values, the wear rates of ultralow-wear materials continue to decrease until debris become optically undetectable. At this point, chemically degraded nanoscale PTFE fragments transfer and strongly adhere to the countersurface; nanoscale phenomena are likely involved in accelerating reactions and increasing adhesive strength. During the transition phase, frictional input continues to chemically and mechanically degrade the surfaces until the first significant posttransition wear event occurs. Unlike debris from the run-in phase, debris from the steady-state phase degrade, adhere strongly to the countersurface, and coalesce to form a continuous and stable transfer film that is eventually worn and replenished at equal rates. Although nanofillers typically improve mechanical properties only modestly, we have shown that trace quantities of nanofillers can increase the wear resistance of a polymer by 10,000 times; to our knowledge, this is the most extreme example of nanofiller reinforcement in the polymer nanocomposites literature. The model we describe here remains a hypothesis but is consistent with nearly a decade of work by our group and others in the field to elucidate the responsible mechanisms. Although the specific nanoparticle surface property responsible for activating the ultralow-wear mechanism in PTFE has not been isolated, the observation that wear resistance can be switched on and off with only subtle filler changes has exciting implications for the future of tribomaterials design and for other areas of polymer science and engineering.

## 4 DISCUSSION

Previous studies of structure and properties composites based on activated PTFE matrix and carbon fibers was found that carbon fillers in relation to PTFE show structural activity and affect the morphology and the degree of ordering of the modified polymer matrix. The character and efficiency of this influence depend on reducing the sizes of elements structure, dimension of the particles and concentration of the filler. The optimum concentration of fibrous filler (20 wt. %) which corresponds to the formation of a homogeneous composite structure and the necessary physical-mechanical and tribotechnical properties was found. The task of increasing the breaking strength and wear resistance of the polymer composition by preliminary mechanical activation matrix (PTFE) and fillers before their mixing was posed as the basis of this work. The task was achieved by improving the technology of preparation of the filler and mixing modified ingredients of composition by the energy impact. Fragments of CF were activated in high-speed mill in mode $n = 7{\cdot}10^3$ $min^{-1}$ and $\tau = 9$ minutes. Activated fragments of CF (20 wt. %) were mixed with the previously activated by the author technology powder PTFE (80 wt. %) in the high-speed mixer in mode $n = 7{\cdot}10^3$ $min^{-1}$ and $\tau = 5$ minutes. Electron microscopic studies of the fragment of CF after such mechanical activation showed (Figure 4) that the character of the fiber surface before grinding (Figure 4a) is significantly different from the character of the surface of activated fiber (Figure 4b): fiber structure becomes «fluffier», its area increases (Figure 4c) and this contributes to a more active interaction between PTFE and fragments of CF and increasing their mutual adhesion.

Obviously, this is due to the fact that the structure of the fragments of CF is a fibrous. Fibrils are composed from the ribbon graphite layers of the condensed carbon (Figure 4 b). These layers are separated by a long (20.0 – 30.0 nm) and narrow pores (diameter 1.5 – 2 nm), the orientation of which coincides with the orientation of the fibrils. The total volume of pores in the carbon fiber is ranging from 5 to 30%. Mechanical activation of the fragments of CF leads to the explosive disturbance these pores and appearance on the fiber surface «plowed» relief.



(a)

(**b**)

(**c**)

**Figure 4.** Microphotographs of the surface of the fragments CF before (a) and after (b, c) mechanical activation in mode $n = 7{\cdot}10^3$ $min^{-1}$ and $\tau = 9$ minutes

For prevention the formation of free radicals the chemical bonds on the surface of grinding filler and its deactivation it was suggested to perform the grinding filler in situ, – that is, in the presence of small impurities (about 1 wt. %) of PTFE. Then necessary quantity was added for compounding with PTFE (1:4 optimal). As result of this technological reception was received modified carbon fiberfill coated with a layer of activated PTFE (Figure 5).

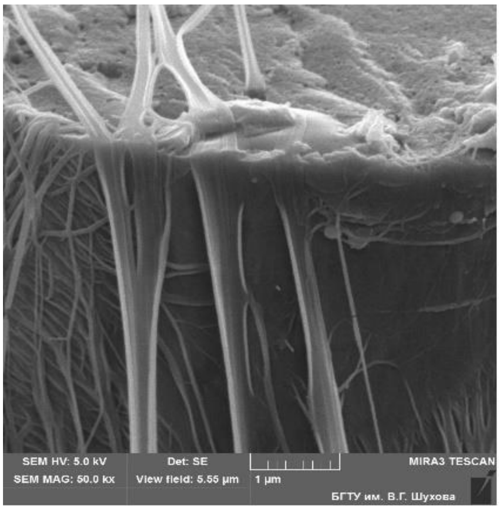
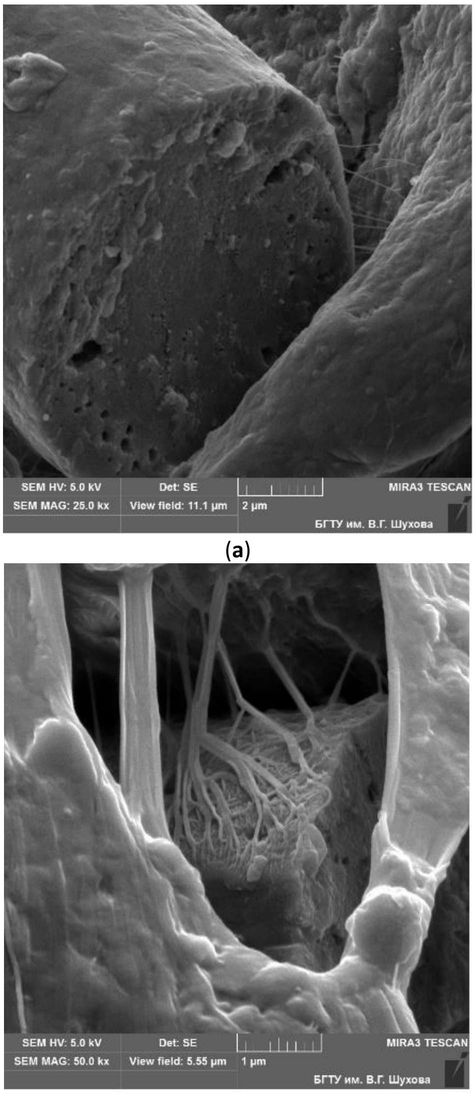


**Figure 5.** Microphotograph of the surface of the fragments CF modified by technology in situ

Thus, in the process of the energy impact on the composition as a result of mechanical sequential activation of the ingredients before their combination (mixing) there is a growth of free surface energy, dispergating and changing their shape. Mechanical load leads to appearance of the metastable conditions surface layers. All these phenomena cause the appearance on the surface of the filler particles uncompensated valences, which promote interaction of the filler particles with a matrix and initiating the polymerization reaction of monomers or the formation of chemical bonds with polymer radicals.

Simultaneously with the activation process of the fillers, takes place the chemical mechanical destruction of macromolecules polytetrafluoroethylene with the formation of radical fragments. Availability, on the one hand, the active surface of fillers and with another - free radical of the polymer macromolecule can initiate the reaction of vaccination of polymer to the filler. Although such reactions with the formation of chemical bonds between polymer and filler surface are passing only on the active centers and have the probable character, however their contribution to the creation of the strengthened composite material quite substantial.

Methods of electron microscopy (Figure 6) was established the formation on the surface of the fragments of CF more stable intermediate layer of polytetrafluoroethylene (Figure 8b), than without their activation (Figure 6a), that «cures» the defects of the fillers and promotes the formation of a stable spacious cluster of filler in the volume of matrix composition. Constructional fibrous composites based on PTFE during its formation as a composition absorb the nanostructured components of CF, which go beyond fiber and penetrate into the interphase boundary of partition and the matrix. This allows achieving maximum reinforcing effect and, thus, increasing the strength characteristics of the composite and its wear resistance (Table 1).



(**a**)

(**b**)

**Figure 6.** Microphotographs of the composite structure according to technology of obtaining: (**a**) activated PTFE + fragments of CF; (**b**) activated PTFE + activated fragments of CF

**Table 1.** Influence of mechanical activation the ingredients composition on its mechanical-physical and tribotechnical properties

| **Composition of composite materials** | **Density $\rho$, g/cm³** | **Breaking strength $\sigma_b$, MPa** | **Relative elongation $\delta$, %** | **Wear intensity $I \cdot 10^{-6}$, mm³/N·m** |
|---|---|---|---|---|
| 80 % PTFE (activated) + 20 % fragments of CF (activated) | 1.97 | 24.2 | 154 | 3.5-6.5 |
| 80 % PTFE (activated) + 20 % fragments of CF | 1.98 | 22.1 | 145 | 16-38 |
| 80 % PTFE + 20 % CF (control) (TC 301-05-16-89) | 1.98 | 12-13 | 20 | 75-85 |

Thus, mechanical activation method of obtaining composite greatly transforms weekend particle of the fragments of CF transforming them into a structure that are covered with a thin, nanoscale layer of PTFE. These formations are active nanofillers of PTFE, which significantly (by 20-45 %) increase its physical-mechanical and performance properties.

## 5 CONCLUSIONS

Theoretical modeling and nanoscale experimentation have shown that friction is fundamentally driven by intermolecular forces.

In the offered work the phenomenological scheme is investigated. In the framework of this scheme evolution of self-organizing systems can be represented in a self-coordinting way, and possible variants of continuous transition between modes of PTFE composites realisation can be considered.

The conducted researches show that Lorentz's system ((7) - (9)) allows to present in the self-coordinating way the basic features of transition from the mode of inefficient realization of PTFE composites to the mode of its effective realization. The phenomenological description is reached due to dependence of synergistic potential from the entropy of frictional PTFE composites. In case of continuous transition this dependence is defined by the characteristic value of intensity of the external influence $F_e$ a monotonously increasing dependence $V(S)$ with a minimum in a point $S_0 = 0$, which answers inefficient realization of PTFE composites, is received at $F_e < 1$. And at $F_e > 1$ there is a minimum $S_0 \neq 0$, which corresponds to a mode of effective realization of PTFE composites.

The results of research allowed making the following conclusions:

1. Studies have opened the possibility of using nanostructured activated PTFE as a matrix of fluoropolymer composites of fluoropolymer composites in order to obtain a composite material with high physical and mechanical properties for friction joints of machinery and equipment for various purposes.
2. Performed obtained modes of process technological equipment, which after processing on it activated PTFE with nanoscale structure has elevated the performance properties compared to the baseline, and may be used to produce composites based on it with maximum efficiency.
3. It was established that the formation of the optimal nanostructure of PTFE composite with fragments of CF is completed after mode $n = 7 \cdot 103$ min$^{-1}$ during $\tau = 9$ minutes.
4. It is shown that modification of nanofiller by its surface processing of PTFE activated powder in obtaining in situ improves the physical-mechanical and tribotechnical properties of the composite by increasing adhesion ability of the filler.

Therefore, optimization of technological modes of production and recycling of PTFE composites using available equipment allows achieving economically significant results and increases their competitiveness among the analogs.

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