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Nanostate Factor in Materials Science of Functional Nanocomposite Materials

Avdeychik S.V.[1], Antonov A.S.[2*], Struk V.A.[2], Prokopchuk N.R.[3], Zhang R.[4]
[1]Francisk Skorina Gomel State University, Gomel, Belarus
[2]Yanka Kupala State University of Grodno, Grodno, Belarus
[3]Belarusian State Technological University, Minsk, Belarus
[4]Zhejiang International Scientific and Technological Cooperative Base of Biomedical Materials and Technology, Zhejiang Engineering Research Center for Biomedical Materials, Laboratory of Advanced Theranostic Materials and Technology, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, People's Republic of China
*corresponding author

Abstract. Based on the system analysis of the features of the morphological and energy parameters of dispersed components of condensed matter of various compositions, their structure and production technology, methodological approaches to the implementation of the nanostate phenomenon in the formation of the optimal structure of composite materials and metal-polymer systems at different levels of organization have been developed. The concept of energy and technological compliance of the components of functional composite materials and systems has been developed, consisting in the implementation of the parameters of their energy characteristics adequate to the value of the activation energy of the prevailing structural process, which determines the optimal parameters of stress-strain, adhesive and tribological characteristics, under technological effects on the components in the process of obtaining a composite and its processing. Scientifically based principles for the creation of nanocomposite materials with high parameters of stress-strain, adhesive and tribological characteristics based on industrial thermoplastics for functional metal-polymer systems and effective technologies for their manufacture and processing into products, the novelty of which is confirmed by patents for inventions are proposed.

Keywords: nanostate phenomenon, nanocomposite structure, concept of energy and technological compliance of components, principles of obtaining and processing nanocomposites, industrial thermoplastics

Introduction

In the brand range of modern engineering materials, a special place belongs to nanocomposites based on polymer, oligomeric and combined matrices, which, according to a number of performance characteristics, are the non-alternative materials in the production of automotive, special, agricultural machinery and technological equipment for thermal power plants, petrochemical and processing complexes. At the same time, the potential of such matrices produced by the domestic industry in the creation of functional nanocomposites is not fully realized, despite the developed base of their large-tonnage production and the equipping of enterprises with modern technological equipment [1–5].

The mechanism and kinetics of the processes of structure formation of composite materials at different levels of the organization are determined by the activation energy, which depends on the parameters of the energy characteristics of the components under a given technological impact. Studies by domestic and foreign specialists have established the effect of the transition of a material particle upon reaching a certain size range into a state with special parameters of energy characteristics, which is called a nanostate according to the established terminology [6–10]. It is obvious that the achievement of the nanostate by the component will have a significant impact on the structural processes in the composite material at different levels of organization, which determine the parameters of stress-strain, tribological, adhesive and other characteristics of products in metal-polymer systems.

At the same time, despite the experimentally established influence of energy parameters on structuring processes, there are no systematic studies of methodological approaches to the implementation of the nanostate phenomenon in materials science and technology of nanocomposite materials based on industrial polymers.

The purpose of this work was to develop methodological approaches to the implementation of the phenomenon of nanostate at various levels of organization of the structure of nanocomposites for the creation of functional materials based on industrial thermoplastics with high performance parameters.

1. Research methodology

Nanodispersed particles of carbon-containing (graphite, detonation synthesis ultra-dispersed diamonds (UDD), carbon nanotubes (CNT), shungite, carbon fibers (CF)), metal-containing (oxides, salts of organic acids) and silicon-containing (mica, tripoli, opal, clay) compounds obtained by technological effects on natural and synthetic semi-finished products produced at industrial enterprises in Belarus and the Russian Federation were chosen as the main objects of the study. Nanoscale components were obtained by mechanical crushing and heat treatment of dispersed semi-finished products at temperatures of 673–1473 K.

Two main types of thermoplastic materials were used as polymer matrices: the first are with hereditary high melt viscosity (HHMV) due to the chemical structure of the chain and molecular weight: polytetrafluoroethylene (PTFE) and ultra-high molecular weight polyethylene (UHMWPE); the second are materials with acquired high melt viscosity (AHMV): industrial thermoplastic polymers such as polyamide PA6, low density polyethylene (LDPE), ethylene vinyl acetate (EVA) copolymer, polypropylene (PP), thermoplastic polyurethane (TPU), etc., with characteristic parameters of rheological properties that were changed by the introduction of nanoscale modifiers.

The structure and properties of nanocomposite materials and products made of them were studied using modern methods of physical and chemical analysis: IR transmission spectroscopy and attenuated total reflectance (ARP) technique (Specord), spectroscopy of electron paramagnetic resonance (EPR) (РЭ 1306, Bruker), X-ray diffraction (Drone 3.0), differential thermal analysis (Q-1500), optical (MF-2), scanning electron (ISM-50A) and atomic force (Nanotope III) microscopy. The energy state of nanoscale modifiers and composite materials was evaluated using EPR spectra and temperature-stimulated current (TSC) spectra at the original facility of the V.A. Belyi Metal-Polymer Research Institute of National Academy of Sciences of Belarus. The regulation of the nanorelief of the surface layer of polymer samples and fillers was carried out using short-pulse laser and accelerated ionic action with a given power density.

The parameters of the stress-strain characteristics of the developed materials were evaluated on standard samples according to the relevant Russian standards. Tribological characteristics were determined on universal or original friction machines according to the schemes "indenter – disk", "shaft – partial liner". Assessment of the performance of products made of developed nanomaterials in the structures of automotive units for various purposes and technological equipment was carried out on stands and in the process of virtual tests using the SKIF supercomputer and full-scale tests.

2. Results and discussion

Multicomponent materials based on high-molecular matrices are systems, the parameters of characteristics (stress-strain, tribological, adhesive, thermophysical, etc.) are determined by the structure at various levels of organization, formed by physical and physicochemical processes, the mechanisms and kinetics of the flow of which depend on the composition of components and the parameters of technological characteristics. In the interfacial region of the system, a complex of physical and physicochemical reactions takes place simultaneously with a predominance of one or several, for which the most favorable conditions are realized, determined by the value of the activation energy. Such a prevailing reaction, the kinetics of which is in accordance with the conditions of formation and operation of the system, determines the resistance of an element made of a composite or metal-polymer system to the impact of operational factors.

A methodological approach to the formation of composites, based on the establishment of the prevailing physicochemical reaction, made it possible to establish a correlation between the parameters of the structure and energy characteristics of the components (energy state) [11, 12].

To characterize *the energy state*, a complex parameter was used, which is a cumulative result of the transformation of the initial individual parameters of the components (structure, composition, morphology, shape, size) under the influence of technological and operational factors. A characteristic feature of the proposed methodological approach is the possibility of purposeful intensification of prevailing interfacial reactions by forming the energy state of components with certain parameters of electrophysical characteristics.

Using the concepts of condensed matter physics, the conditions for the acquisition of a nanostate by a material object are determined, which can manifest itself when the dimensional parameter L_0 is reached by both a single particle and the components of the surface layer of a particle or substrate of the micro- and macro-range. To analyze various types of interfacial interactions in systems based on the energy factor, the definition of "nanostate" is proposed, which makes it possible to identify the main forms of its manifestation [13–19].

The concept of energy and technological compliance of components has been developed for the formation of systems with optimized parameters of structural characteristics at various levels of the organization.

The energy compliance of components assumes the possibility of achieving an aggregate energy state that corresponds to the activation energy of the prevailing physicochemical process that ensures the formation of an optimal structure at the intermolecular, supramolecular, and interphase levels of organization in composites or metal-polymer systems.

The formation of the interfacial (boundary) layer of the optimal structure indicates the *technological compliance of the components* of functional materials and metal-polymer systems, which is understood as the possibility of their achieving the specified energy parameters at a certain stage of the formation of a composite, product or structure that ensures the flow of the prevailing mechanism of interfacial interaction.

Physical and physicochemical processes are due to the transfer of electrons during the formation of intermolecular, supramolecular, interfacial structures, which determined the choice of the maximum value of the thermostimulated current (TSC) in the temperature range adequate to the technological modes of production, processing of composites and the operation of metal-polymer units as a determining parameter for assessing the energy state of the components of the systems.

The analysis of the parameters of the energy state of dispersed particles of various composition, structure and production technology, which are widely used in materials science of polymer nanocomposites (silicon-containing – clay, mica, talc, tripoli, carbon-containing – UDD, CNT, CF, shungite, colloidal graphite product (CGP), metal-containing – particles of metals and oxides), indicates the nonlinearity of the dependence of the TSC value on temperature, the presence of extremes in the temperature ranges characteristic of each type modifier, and instability $I = f(T)$ when changing dimensional parameters, dispersion modes, intensity of the impact of temperature, mechanical and other energy and technological factors. The characteristic type of TST spectra of particles of products of thermogasdynamic synthesis (ultradispersed polytetrafluoroethylene UPTFE), silicon, shungite with a size of 50–100 μm is shown in Fig. 1 and 2. The nonlinearity of the dependence $I = f(T)$ is also characteristic of other objects of organic and inorganic nature, of different composition, structure, and molecular weight.

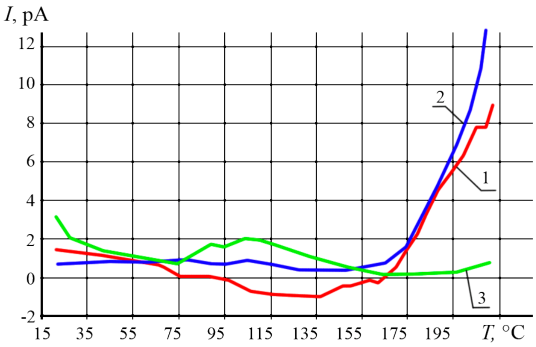


Fig. 1. – Characteristic TSC spectrum of products of thermogas-dynamic synthesis (UPTFE) initial (1) and heat-treated at 373 K (2), 473 K (3)

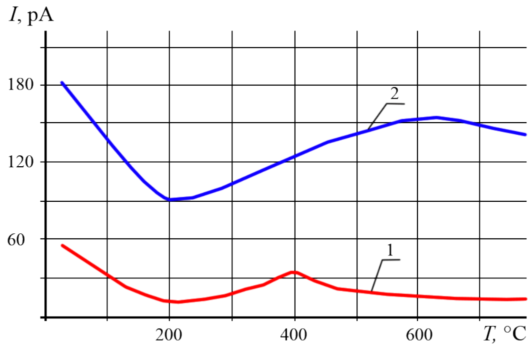


Fig. 2. – Dependence of the value of the maximum thermally stimulated current (TSC) on the temperature for particles of silicium (1), shungite (2). Particle dispersion 50–100 μm

A characteristic feature of dispersed particles of common modifiers of high-molecular matrices is the presence of an uncompensated charge with a long relaxation time, which is confirmed by the data of EPR spectroscopy (Fig. 3).

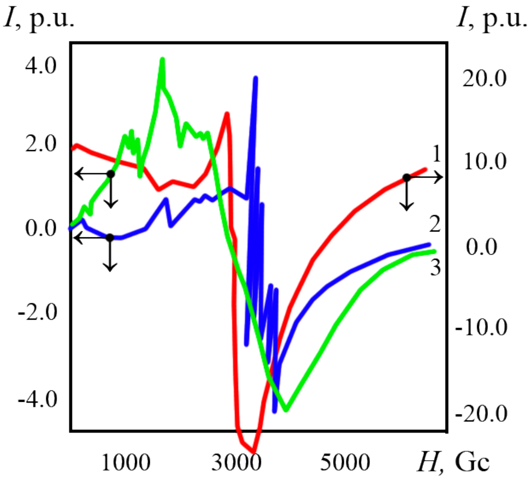


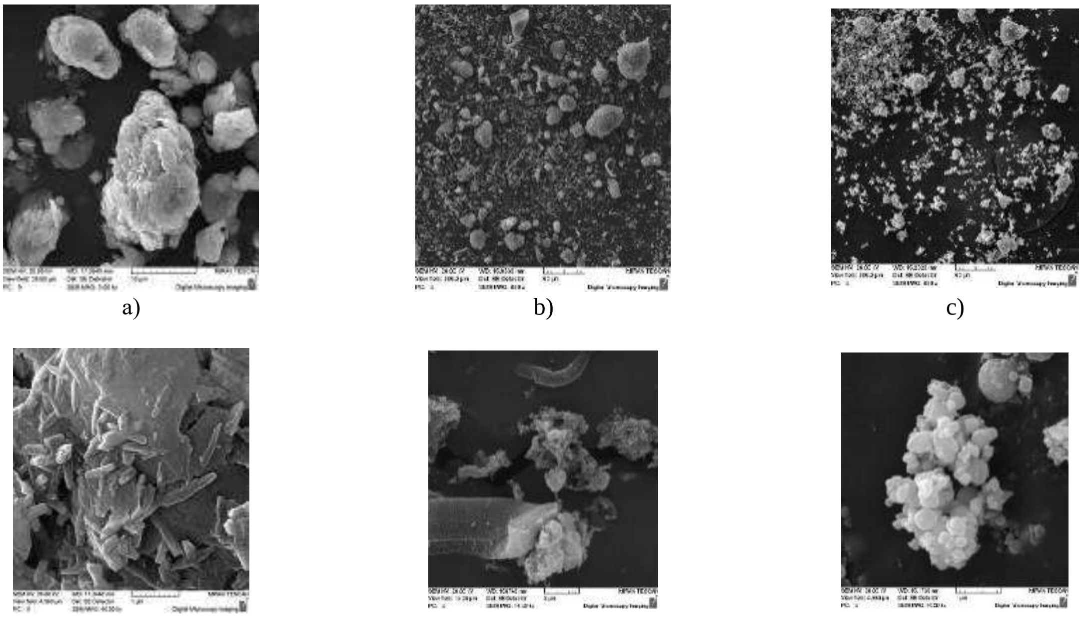
Fig. 3. – EPR spectra of opal (1) and clay minerals of various compositions (2, 3). Sample dispersion is 100–200 μm

Along with special parameters of electrophysical characteristics due to the peculiarities of composition and structure, material particles can be in a nanostate, the concepts of which were proposed by Prof. P. von Weimarn, P. M. Ajan, I. P. Suzdalev, A. I. Gusev, and others, under certain types of technological action that change the size, geometric characteristics, and morphology of the surface layer. The size range of the transition of material objects into the nanostate is individual for particles of different composition and structure and is determined by the analytical expression proposed by V. A. Liopo, according to which the limiting size of $L_0 = 230 \cdot \theta_D^{-1/2}$, where θ_D is Debye temperature. The validity of using this expression to analyze the structure of polymer nanocomposites is confirmed by system studies, the results of which are summarized in monographs [11, 12].

The analysis of the morphological features of dispersed particles widely used in the materials science of polymer composites using the SEM and AFM methods indicates the presence of nanoscale components in objects of the micron range that form the morphology of the surface layer (Fig. 4).

The presence of such components is the most important factor determining the activity of modifiers in the processes of formation of polymer composites at various structural levels (intermolecular, supramolecular, interphase) due to the manifestation of energy parameters characteristic of the nanostate by the surface layer of particles. Therefore, the technologies for activating polymer matrix modifiers should ensure the formation of nanoscale components in quantities sufficient to implement the determining process of the required intensity, by establishing mechanisms for their formation under various types of technological impact on the semi-finished product.

Using the fundamental principles of condensed matter physics based on the barrier model of juvenile surface formation, mechanisms for dispersion of layered minerals such as mica, talc, kaolin with the formation of nanoscale components of lamellar shape are proposed. It has been established that the determining processes of degradation of particles in the micrometer range are dehydration and dehydroxylation, which cause the destruction of the original layered structure and the formation of nanoscale elements of the lamellar form in an active state with a long relaxation time sufficient for implementation in the technology of polymer nanocomposites [1, 2]. It has been experimentally established that the activity of such elements in the processes of interaction with the environment (components of the system) depends on its composition, temperature and time characteristics. To intensify the process of dispersion of layered minerals, it is advisable to use thermal shock at temperatures of 800–1000 K or diffusion saturation of interlayer regions with low-molecular and oligomeric media based on carbon-containing products with low resistance to thermal degradation.



a) b) c)

d) e) f)

Fig. 4. – Characteristic morphology of dispersed clay particles (a, d), carbon nanotubes CNT (b, e), metal oxides (c, f)

Model studies of the dispersion of layered minerals such as mica (muscovite) have shown the possibility of forming nanoparticles with a size of 30–50 nm under the impact thermal effect on the initial semi-finished product at 1073 K for 5–20 min. The formed lamellar particles have high adsorption activity in the processes of interaction with the environment, including polymer matrices in a viscous state, and intensify the intermolecular structuring of the composite.

Dispersion of particles of layered silicates can be implemented directly in the process of obtaining or processing composite materials under thermomechanical action on the components of screws of mixers, extruders or injection molding machines. The formation of an intercalated or exfoliated nanocomposite structure provides a technically significant effect of increasing the parameters of stress-strain and tribological characteristics even with a doping content (0.1–1.0 wt.%) of the modifier.

Thermal action on dispersed particles changes the energy parameters not only of layered silicates (clays, talc), but also of framework and chain (flints, zeolites) and multiphase natural (tripoli, shungite) products (Fig. 1 and 2).

An effective technology for activating dispersed particles is their dispersion under mechanical or mechanochemical action. Not only an increase in the specific surface area, but also the formation of nanoscale components in the surface layer of particles has been experimentally established. Modifiers activated in this way remain active for a technologically significant time (up to a year).

Nanoscale components of the structure of the surface layer can also be formed as a result of the impact of energy flows on the semi-finished product, i.e. ionizing, laser radiation. At the same time, not only the specific surface area of the particle, which provides the mechanical component of interfacial interaction, increases, but also the parameters of the characteristics that determine its nanostate, which affect the supramolecular structure and adsorption capacity of the surface layers of modified substrates (PET, PTFE, PP, HDPE, CF) (Fig. 5).

An energy assessment of the nanostate of polycrystalline particles is carried out to establish the temperature equivalent of geometric parameters. It is shown that for a nanoparticle, due to the increased role of surface energy in comparison with a massive sample, there is a correlation between the size of the particle and its energy state, which can be estimated by the temperature factor.

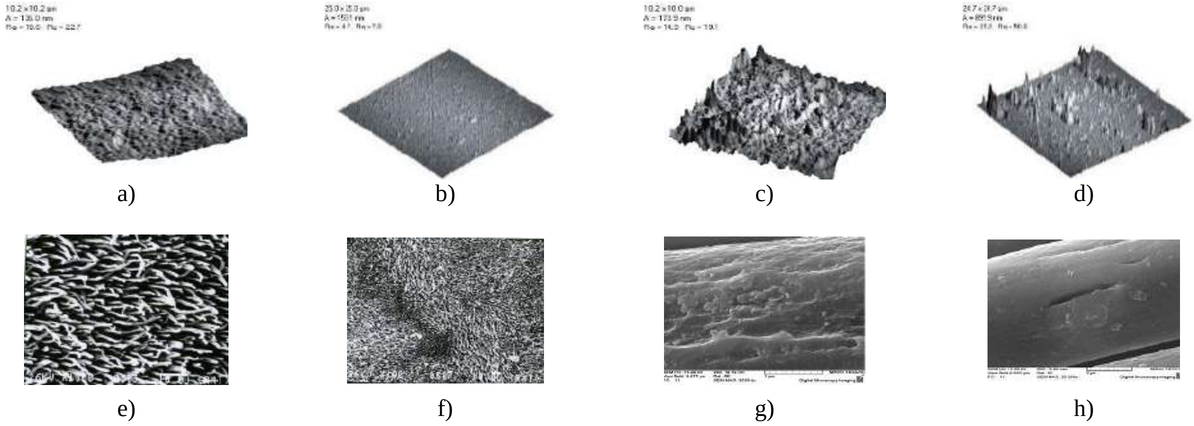


Fig. 5. – Characteristic morphology of the surface layer of the substrate of PTFE (e, f), PET (b, d), HDPE (a, c), carbon fiber (g, h), initial (a, b) and exposed to nitrogen ions at a dose of 1016 ion/cm2 (g, h), pulsed laser radiation with a power density of 2.0 W/cm² (c, d). AFM data (a–d) and SEM (e–h)

With a decrease in the size of the δ particle by 1%, there is an increase in energy parameters by the amount of $\delta t = k(\delta T) \approx 3{,}5{\cdot}10^{-28}$ J [20]. Therefore, the formation of nanoscale particles or nanoscale components in the structure of the surface layer of a macroparticle (substrate) is accompanied by an increase in the parameters of energy characteristics estimated by the maximum value of the thermally stimulated current and the intensity of interfacial processes in the systems.

The conducted set of studies on modeling the processes of formation of the structure of material objects with a pronounced manifestation of the nanostate made it possible to determine effective ways to achieve it in the technological processes of obtaining and processing nanocomposite materials based on matrix polymers of industrial production. The choice of the conceptual direction of the technological embodiment of the phenomenon of the nanostate is determined by a set of materials science, technological, economic, and operational factors. An algorithm for the implementation of the methodological approach has been developed, which allows, on the basis of factors that determine the nanostate of the components of the system for a specific purpose and design, to choose the technology for their implementation at a specific stage of the process, taking into account material, economic, ergonomic, environmental and other aspects.

Methodological principles for the implementation of the phenomenon of nanostate in materials science and technology of functional nanocomposites based on industrial polymer matrices and metal-polymer systems with their application, focused on the state of the domestic technological base of industrial enterprises, related mainly to the IV and V modes, are proposed (Fig. 6).

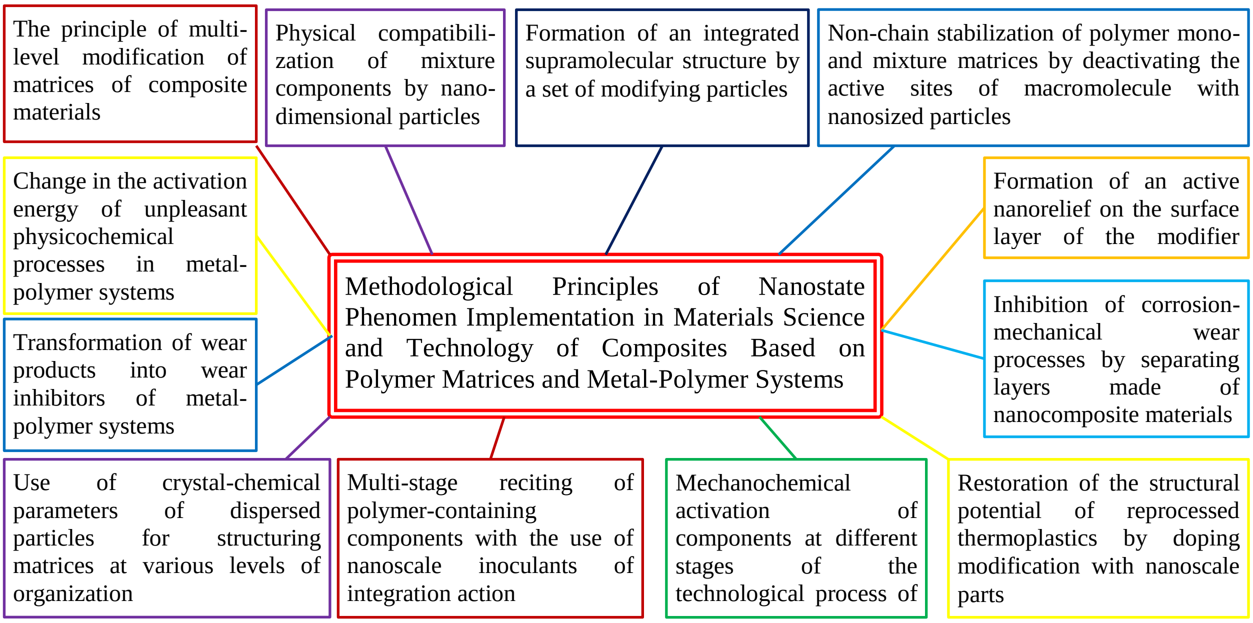


Fig. 6. – Methodological principles of implementation of the nanostate phenomenon in materials science and technology of composites based on polymer matrices and metal-polymer systems [15–19]

The developed principles made it possible to optimize the structure of nanocomposite materials based on polymer, oligomeric and mixed matrices of industrial production intended for the manufacture of structural elements (bearings, seals, fasteners, coatings) of static and dynamic (tribological) metal-polymer systems used in the structures of machines, mechanisms, technological equipment of domestic machine-building, chemical, processing industry, construction industry, which determine the strategy of innovative development of the economy.

The results of experimental testing of the developed methodological approaches to controlling the structural parameters of nanocomposite materials based on industrial thermoplastics are presented in Part 2 of the article.

Conclusion

On the basis of a system analysis of the features of morphological and energy parameters of dispersed components of condensed matter of various compositions, their structure and production technology, methodological approaches to the implementation of the nanostate phenomenon in the formation of the optimal structure of composite materials and metal-polymer systems at different levels of organization have been developed. Scientifically based principles for the creation of nanocomposite materials with high parameters of stress-strain, adhesion and tribological characteristics based on industrial thermoplastics for functional metal-polymer systems and effective technologies for their manufacture and processing into products are proposed, which consist of the following:

1) The concept of energy and technological compliance of the components of functional composite materials and systems has been developed, consisting in the implementation of the parameters of their energy characteristics adequate to the value of the activation energy of the prevailing structural process, which determines the optimal parameters of stress-strain, adhesive and tribological characteristics, under technological effects on the components in the process of obtaining a composite and its processing. The reliability of estimating the parameters of the nanostate of material objects using an analytical expression to determine the limiting size of the transition to the nanostate of a nanoparticle or a component of the morphology of the surface layer according to the Debye temperature θ_D criterion is theoretically and experimentally substantiated. A definition of the nanostate of material objects is proposed, characterizing the relationship between structural, morphological and energy parameters.

2) Methodological principles for the implementation of the nanostate phenomenon in materials science and technology of functional nanocomposites based on industrial thermoplastics of the polyolefin, polyamide, fluoroplastic class have been developed by optimizing the structure at the intermolecular, supramolecular and interfacial levels, ensuring the achievement of a synergistic combination of performance parameters based on:

– established crystal-chemical prerequisites for the selection of natural and synthetic carbon-containing, metal-containing and silicon-containing semi-finished products for the directed formation of active nanosized particles with specified structural, morphological and energy parameters under optimal technological action (mechanic and chemical, thermal, laser);

– implementation of the conditions for the energy compliance of nanomodifiers to the prevailing mechanism for the formation of the optimal structure of polymer, oligomeric and combined matrices at various levels of organization – molecular, supramolecular and interfacial;

– providing conditions for the manifestation of the preferred mechanisms of interfacial physicochemical interactions of components with the formation of boundary layers of optimal structure, which determine the mechanisms of destruction of nanocomposites under the influence of various operational factors.

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Information of the authors

Avdeychik Sergey Valentinovich, PhD (Engineering), associate professor, Doctoral candidate at the Francisk Skorina Gomel State University
e-mail: molder.grodno@gmail.com

Antonov Alexander Sergeevich, PhD (Engineering), associate professor, Yanka Kupala State University of Grodno
e-mail: antonov_as@grsu.by

Struk Vasily Alexandrovich, DSc (Engineering), professor, Yanka Kupala State University of Grodno
e-mail: struk@grsu.by

Prokopchuk Nikolay Romanovich, corresponding members of National Academy of Sciences of Belarus, DSc (Chemistry), professor, honored scientist of the Republic of Belarus, Belarusian State Technological University
e-mail: nrprok@gmail.com

Zhang Ruoyu, Ph.D., professor, Zhejiang International Scientific and Technological Cooperative Base of Biomedical Materials and Technology, Zhejiang Engineering Research Center for Biomedical Materials, Laboratory of Advanced Theranostic Materials and Technology, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences
e-mail: zhangruoy@nimte.ac.cn