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THE NANO-STATE FACTOR IN THE MATERIALS SCIENCE OF POLYMER NANOCOMPOSITE MATERIALS

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Abstract

Based on a systematic approach to studying the influence of structural features and energy states of nanoscale particles in condensed media, this work proposes mechanisms of physicochemical processes in polymer matrices that determine structural parameters at molecular, supramolecular, and interphase levels. The study explores how the unique energy states, or "nano-states," of nanoscale particles play a crucial role in the behavior of polymer matrices, particularly in terms of their structural organization and functionality. Methodological frameworks for developing advanced nanocomposite engineering materials with enhanced stress-strain, tribological, adhesive, and protective properties are presented. These materials utilize industrial thermoplastics, including polyolefins, polyamides, polyacetals, and polytetrafluoroethylene, along with their corresponding processing and technologies. A thorough analysis is conducted to understand the key factors that contribute to the formation of an optimal nanocomposite structure, focusing on the interactions between components at various levels of structural organization. The work also introduces a principle of energy and technological compliance between the components of the composite, ensuring the successful integration of nanoparticles within the matrix. This principle guarantees the achievement of a well-ordered material structure that enhances the stress-strain, tribological, adhesive, and other functional performance characteristics of the final product. The findings aim to offer significant insights into the development of high-performance nanocomposites tailored for diverse industrial applications

Keywords: *nanocomposite materials based on high-molecular matrices, energy state of components, principle of energy and technological compliance of components, mechanisms of modifying action of nanoparticles, methodology for obtaining nanocomposites*

Introduction

A key factor driving the progress of mechanical engineering and its alignment with the demands of innovation-driven societies is the development of functional materials based on metallic, polymeric, ceramic, and hybrid matrices. These materials exhibit tailored combinations of performance characteristics, enabling the creation of advanced transportation systems, specialized machinery, process equipment, tools, and fixtures. Such innovations adhere to the principles of energy efficiency, resource conservation, operational effectiveness, safety, environmental sustainability, and user comfort across all lifecycle stages, as mandated by the core tenets of sustainable development strategies.

A groundbreaking advancement in functional materials science lies in harnessing the *nano-state phenomenon* at various structural levels. This approach unlocks synergistic enhancements in composites' electrophysical, stress-strain, tribological, thermophysical, adhesive, and protective properties through the integration of nanoscale components with diverse compositions, structures, and synthesis methods. However, the lack of cost-effective nanoscale particle production technologies compatible with large-scale composite manufacturing continues to hinder industrial adoption in high-potential sectors. Consequently, nanocomposites remain predominantly limited to electronics, micro- and nanodevice engineering [1–8].

The implementation of the National Strategy for Sustainable Development of the Republic of Belarus for the period till 2035 (NSUR-2035) and the Socio-economic development strategy for 2022-2026 of the Republic of Azerbaijan necessitates the widespread adoption of next-generation functional materials to create import-substituting, competitive products with superior performance characteristics [9, 10]. Priority sectors include mechanical engineering, energy, chemical processing, manufacturing, and construction – industries central to economic and social advancement.

Despite significant breakthroughs in nanocomposite materials science, industrial production and sectoral application face substantial challenges. These stem from the absence of unified, scientifically grounded methodologies for:

- theoretical frameworks guiding the design of functional nanomaterials;
- targeted selection of components and synthesis/processing methods;
- scalable manufacturing tailored to specific applications.

Polymer-, oligomer-, and hybrid-matrix nanocomposites occupy a unique position in modern engineering materials. Their unparalleled functional properties make them indispensable for automotive, agricultural, and specialized machinery, as well as process equipment and pipeline systems in energy, petrochemical, and refining industries. Nevertheless, analysis of scientific literature, patents, and market data highlights an urgent need for theoretical foundations to enable large-scale production of high-molecular-weight matrix nanocomposites. Such advancements are critical to meet industrial demand for cost-effective, high-performance materials.

Prior studies by domestic and international research groups have partially addressed structural-morphological, energetic, and electrophysical properties of nanoscale components (e.g., dispersed particles, thin films) [1-8]. However, translating phenomenological models of the nano-state phenomenon into functional nanocomposite technologies requires a systematic approach. This must account for the influence of structural features, morphology, and energy states of highly dispersed (including nanoscale) components on the molecular, supramolecular, and phase-level organization of high-molecular-weight matrices [11].

Recent studies have highlighted the significant potential of nanocomposites in improving the mechanical and thermal properties of materials used in various industries, including automotive and energy sectors [12-15]. Additionally, the need for sustainable and scalable production methods for nanocomposites is increasingly recognized to minimize environmental impacts while meeting industrial demands [16-18].

Objective of this study: To analyze the role of the *nano-state factor* in the materials science and processing technologies of polymer nanocomposites.

Experimental Part

2.1. Sample Preparation

The study focused on nanodispersed particles of carbon-based (graphite, detonation nanodiamonds (DND), ultra-dispersed diamond-graphite (UDDG) or detonation synthesis charge for ballistic powders, carbon nanotubes (CNTs), shungite, carbon fibers (CF)), metal-containing (oxides, organic acid salts), and silicon-containing (mica, tripoli, opal, clays) compounds. These were synthesized via industrial processing of natural and synthetic precursors sourced from manufacturing facilities in Belarus and the Russian Federation. Nanoscale components were produced through mechanical grinding and thermal treatment of dispersed precursors at temperatures ranging from 673 to 1473 K.

Two primary classes of thermoplastic polymers were selected as matrices:

1. **Inherently High-Viscosity (IHV) Polymers**:
   - polytetrafluoroethylene (PTFE) and ultra-high molecular weight polyethylene (UHMWPE), characterized by melt viscosity dictated by their chemical chain structure and molecular weight.
2. **Acquired High-Viscosity (AHV) Polymers**:
   - industrial thermoplastics, including polyamide (PA6), high-density polyethylene (HDPE), polypropylene (PP), ethylene vinyl acetate (EVA) copolymer, thermoplastic polyurethane (TPU), and others, with rheological properties modified via nanoscale additives.

Polymers were used as industrially supplied granules or powders. Powdered forms were obtained through cryogenic grinding of granules at 87 K.

2.2. Characterization Techniques

The structure and properties of nanocomposites and derived components were analyzed using the following methods:

- Fourier transform infrared spectroscopy (FTIR) with transmission and multiple attenuated total reflection (ATR) modes;
- Electron paramagnetic resonance (EPR);
- X-ray diffraction;
- Differential thermal analysis (DTA);
- Optical microscopy;

- Scanning electron microscopy (SEM);
- Atomic force microscopy (AFM).

The energy state of nanoscale modifiers and composites was evaluated using EPR spectra and thermally stimulated current (TSC) spectra, measured on a custom experimental setup at the V. A. Belyi Institute of Mechanics of Metal-Polymer Systems (NAS of Belarus). Dielectric properties post-energy treatment (laser, ion beam, thermal) were determined via standardized protocols. Surface nanotexturing of polymer samples and fillers was achieved through pulsed laser ablation and ion beam irradiation with controlled power density.

Stress-strain properties were assessed using standardized specimens per relevant GOST protocols. Tribological performance was evaluated on universal and custom tribometers (UMT, MI-2, SMTS-2M) under "indenter-disc" and "shaft-partial bushing" contact configurations. Functional validation of nanocomposite components (e.g., automotive assemblies, industrial tooling) was conducted through bench testing, virtual simulations, field trials under operational conditions.

Results and Discussions

Drawing upon modern principles of materials science, condensed matter physics, and quantum physics - as advanced in the seminal works of V.A. Belyi, V.V. Korshak, A.I. Gusev, A.D. Pomogailo, N. Ashcroft, C. Kittel, V.A. Kargin, and collaborators [1–8] - this study examines key factors governing the formation of composite systems. Particular emphasis is placed on energy-related parameters that dictate the mechanisms and kinetics of interfacial interactions (Fig. 1).

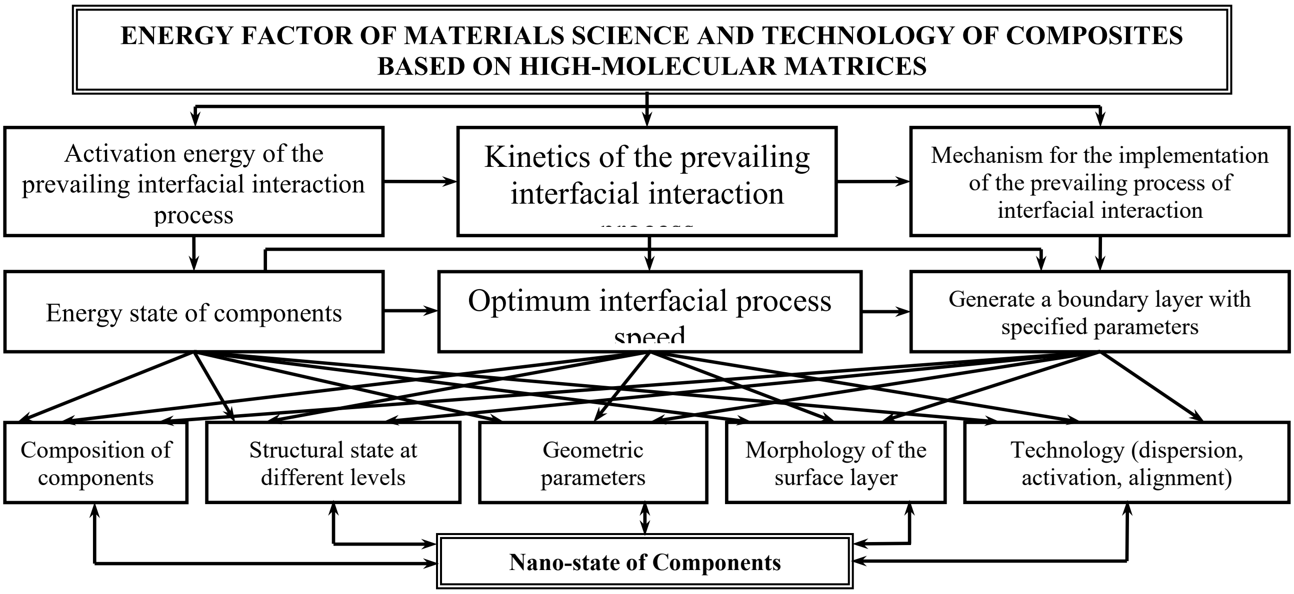

Fig. 1. Energy factor of materials science and technology of composites based on high-molecular matrices

To form the optimal boundary layer structure in a composite material, which determines the parameters of key performance characteristics, it is necessary to ensure the required intensity of the predominant process. This process can occur once the components reach the activation energy value. The activation energy of the process is determined by the electrophysical parameters of the composites, which are acquired under specific technological conditions—such as temperature, pressure, shear rate, and others. Therefore, by controlling the electrophysical parameters of micron-range system components through variations in composition, precursor structure, size, surface layer morphology, and preparation methods (dispersion, activation, and blending technologies), it is possible to achieve the most favorable energetic state, analogous to the state of nanometer-scale particles – the nano-state (Fig. 1). Achieving the conditions for realizing the nano-state in components of micron-scale dimensions (1–100 μm), which are most common in materials science and composite technologies based on high-molecular-weight matrices, enables the utilization of nanoscale particle advantages in interfacial interaction mechanisms while retaining traditional production and processing methods. The practical challenge in developing composite materials with enhanced performance characteristics lies in determining the conditions for achieving the nano-state of dispersed particles and establishing evaluation criteria based on selected parameters that define the energetic properties of the components (Fig. 1). Using optical microscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM), morphological features of dispersed particles with diverse compositions, production technologies, and crystal-chemical structures – widely used in polymer composite materials science – were analyzed. These include metallurgical oxide compounds, mechanically crushed silicate glass products, carbon-containing fibers (CF), detonation-synthesized products (DND), carbon nanotubes (CNTs), and silicon-containing natural particles such as mica, tripoli, clays, shungite, and talc (Fig. 2).

It was established that, regardless of the technological history or crystal-chemical structure of the precursor, dispersed particles form cluster structures composed of individual particles with nanoscale parameters. The morphology of individual particles is characterized by nanoscale elements of spherical, plate-like, or whisker-like shapes, forming a nanoscale surface relief. This relief promotes boundary layer formation during interfacial interactions in the creation of nanocomposite materials. The presence of such nanoscale relief causes the dispersed particles to exhibit a unique energetic state, which, according to the classical definition by P. von Weimarn [1], corresponds to a colloidal or nanostructured state. Building on modern condensed matter physics principles, the term "nano-state" is defined as a form of existence for condensed matter particles. This state reflects their activity in interfacial interactions due to uncompensated and delocalized charge carriers of varying origins, as well as structural components with variable localization and mobility, formed under external directed technological factors (thermal, mechanical, wave-based, etc.). Thus, the specific nanoscale surface relief – determined by composition, crystal-chemical, and technological factors – governs the energetic state and is the dominant factor in selecting precursors and technologies for producing dispersed particles with optimal dimensional parameters.

Notably, the modifier particles can remain in the micron size range while still delivering the desired modifying effect due to their nanoscale surface relief with distinct structural features. This approach enables the practical production of nanocomposite materials with enhanced stress-strain, tribological, and other properties using polymer matrices. It also allows the use of accessible precursors, such as silicon- and carbon-containing minerals, combined with high-throughput dispersion technologies. This strategy significantly expands the range of modifiers available for creating functional nanocomposites based on high-molecular-weight matrices (polymeric, oligomeric, or blended), while maintaining cost-effective and scalable manufacturing processes.

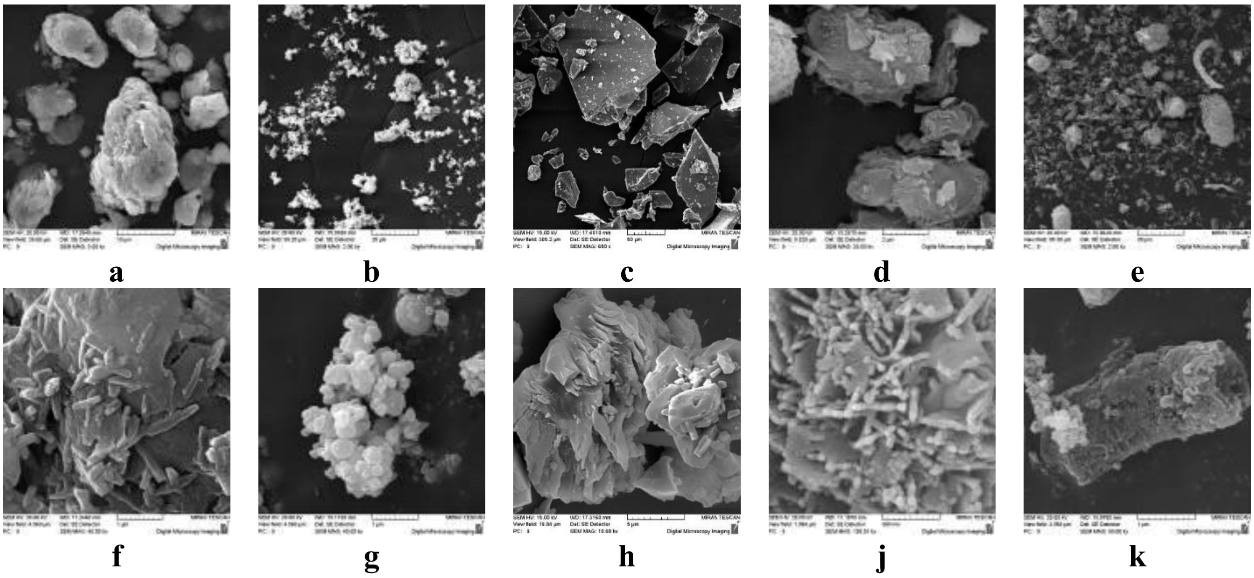

Fig 2. Characteristic morphology of dispersed particles of clay minerals (a, f), oxide compounds (b, g), silicate glasses (c, h), tripoli (d, j), carbon nanotubes (e, k)

Based on the analysis of classical theories regarding the mechanisms of forming boundary layers with optimal structure in polymer composites – which determine the stress-strain, tribological, thermophysical, and other performance characteristics of composites and their products—it has been established that the primary factors influencing their formation mechanism and kinetics are ***mechanical*** and ***energetic***.

The ***mechanical factor*** drives the formation of adhesive bonds between the polymer matrix and the modifier through the entrapment of molten polymer fragments, infiltrated under processing pressure, within the nanocavities of the particle's surface relief. The ***energetic factor*** facilitates adsorption and orientation processes at the matrix–filler interface, leading to the formation of an ordered (quasi-crystalline) nanophase boundary layer structure. This structure exhibits enhanced strength characteristics due to the orienting influence of the modifier's or substrate's energetic parameters on the peripheral macromolecules of the polymer matrix. When the components attain energy parameters equal to the activation energy, chemisorption processes may occur, resulting in a boundary layer composed of interaction products. The combined action of both factors enables a ***synergistic effect***, allowing dispersed modifiers in the nano-state to influence nanocomposite structure at molecular, supramolecular, and interfacial levels. This leads to simultaneous improvements in stress-strain, tribological, protective, and other functional properties.

Using the expression developed by Professor V.A. Liopo and Associate Professor S.V. Avdeychik for evaluating the dimensional boundary of the nano-state in condensed matter particles, $L_0 = 230 \cdot \theta_D^{-1/2}$ [19] the dimensional range of single-element and multi-element substances – metals, non-metals, halides, and other compounds used for modifying polymer matrices - was assessed.

The obtained results show good correlation with literature sources and allow for the identification of the most effective technologies for producing nanoscale modifiers for use in the materials science of polymer nanocomposites.

Analysis of the nano-state characteristics of condensed matter particles using quantum theory demonstrated that for each substance, there exists an energy parameter E_0 that delineates the processes. At $E > E_0$, size effects are negligible, and the bulk approximation is valid for describing the properties of the substance; at $E < E_0$, size effects must be taken into account.

Thus, for the technology of nanocomposite materials based on high-molecular-weight matrices, the determining criterion for selecting a dispersed modifier is its energy state, which is determined by sufficient geometric dimensions of the surface layer formed by nanocomponents of any habitus (Fig. 3) and the presence of an uncompensated charge.

A dispersed particle with a maximum transverse dimension (diameter) $L(D)$ and a core central part size $L_{core}(D_{core})$ has a surface layer L_{surf} formed by nanocomponents with size L_c, which is in a nano-state and determines its activity in interfacial interaction processes – the activity of the modifying effect (Fig. 4).

In accordance with the developed categories of “energy state” and “nano-state”, as well as the proposed structural model of a dispersed particle, classes of modifiers were selected for creating functional materials based on large-tonnage polymer matrices. The intensity of thermally stimulated currents (TSC) flowing through the particle in specific temperature ranges was used as a parameter characterizing the activity of the modifying effect. The feasibility of using this parameter and the dependence $I = f(T)$ has been confirmed in the works of Professor M.P. Tongonogov, L.S. Pinchuk, A.A. Okhlopkova, and their colleagues.

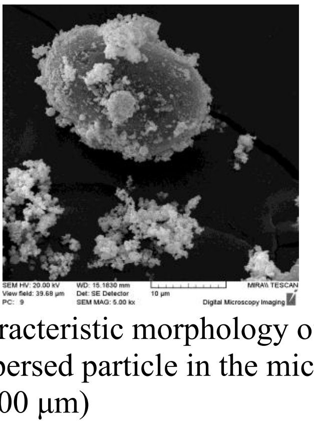

Fig. 3. Characteristic morphology of a dispersed particle in the micron range (~100 µm)

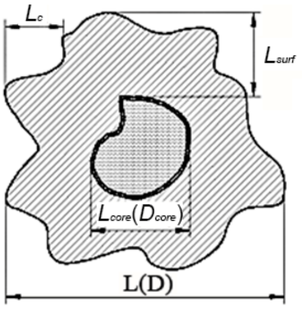

Fig. 4. Structure of a dispersed particle in the micron range

An assessment was conducted on the influence of the size factor on the energy characteristics of dispersed particles containing carbon and silicon components, which are widely used as functional modifiers for polymer and oligomer matrices in the development of nanocomposites with enhanced service performance parameters.

An analysis was carried out on the crystallochemical mechanisms of forming nanoscale particles in an active state under thermal or mechanical treatment of semi-finished products derived from natural silicates with layered, framework, and chain structures (micas, clay minerals, natural opals, tripoli). Among the most common geosilicates are layered silicates, which include various modifications of micas and clay minerals. A common feature of this type of mineral is the presence of a specific crystal lattice with perfect cleavage, consisting of layers of silicon-oxygen tetrahedra (SiO_2) connected by a layer of metal-oxygen octahedra and interlayer cations.

When the block of layered minerals is disrupted, interlayer cations such as Na^+ and K^+ migrate to one of the juvenile surfaces, forming areas with localized charges, known as a “charge mosaic”. This structure of juvenile surfaces in layered silicates, with charge regions whose area significantly exceeds the size of the cations, facilitates intense interaction processes with the environment surrounding the nanophase particle. The presence of active centers on juvenile surfaces, formed by the bases of SiO_2 tetrahedra, alters the course of adsorption processes on the particle surfaces and influences the structural ordering of polymer and oligomer macromolecules in contact with them. Thus, the specific crystallochemical structure of layered silicates creates the prerequisites for the formation of active nanoscale dispersed particles, which exert a modifying influence on polymer matrices.

The conducted research has shown that the unique energy state ('nano-state') of a dispersed modifier particle is determined by the morphology of its surface layer, formed by nanocomponents of various habits (size criterion), and the presence of an uncompensated charge in the surface layer caused by external factors (charge criterion) that lead to the disruption or transformation of the original structure. The contribution of each criterion to the particle's activity is determined by the conditions of composite material formation—technological factors (Fig. 5). A characteristic feature of the studied low-dimensional particles of varying composition, structure, and technological history is the dependence of their energy state, characterized by the magnitude of thermally stimulated currents (TSC), on temperature. Therefore, when selecting a modifier to produce a nanocomposite material with specified functional parameters (tribological, stress-strain, adhesive), it is necessary to consider not only the temperature range of its maximum activity but also the alignment of the energy and size criteria with the component integration technology.

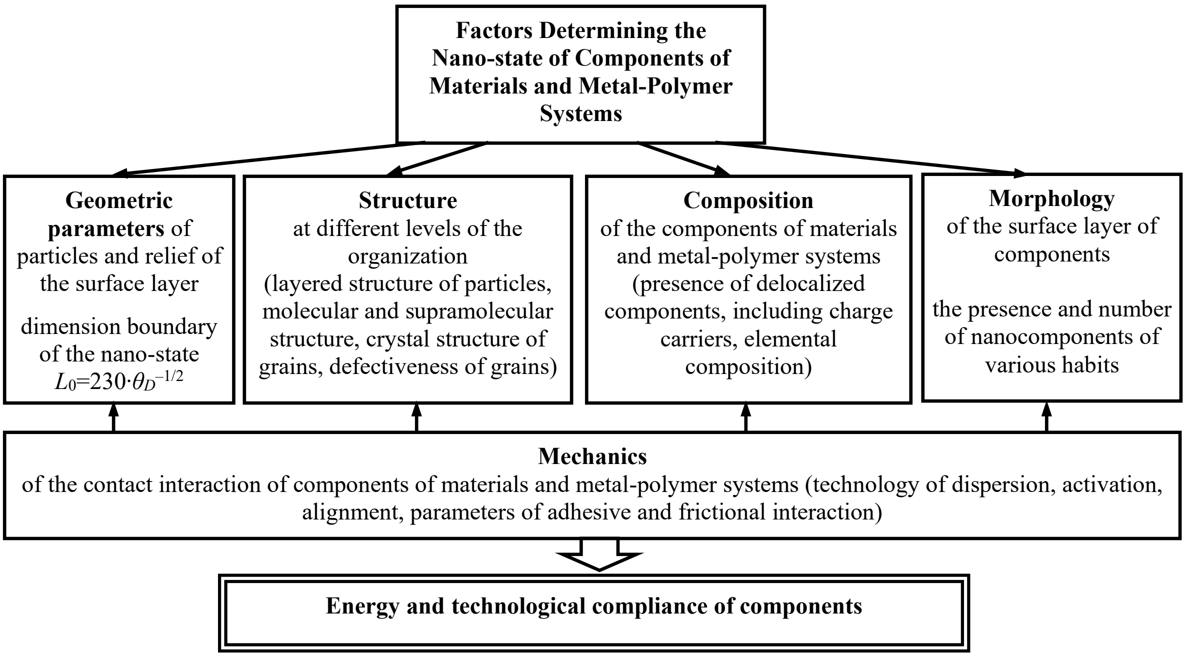

Fig. 5. Nano-state factors of composite materials based on high-molecular matrices

A principle of energy and technological compliance of components in composite materials has been proposed. This principle ensures optimal activity of interfacial interactions, leading to the formation of a structure at various organizational levels that achieves the desired parameters for stress-strain, tribological, thermophysical, and other characteristics. The practical implementation of this established principle of energy and technological compatibility in nanocomposite materials based on polymer matrices enables the achievement of technically significant effects, both at doping levels of nanomodifier content (0.001–1.000 wt. %) and at filler concentrations of 20–40 wt. %.

The mechanism of the modifying effect of highly dispersed and nanoscale particles in polymer and oligomer matrices of various structures has been investigated. Based on the developed model, which assumes the formation of a layer of macromolecules adsorbed under the influence of active centers on spherical nanoparticles, an analytical expression has been derived to calculate the concentration of the modifier sufficient to transition the entire matrix into an ordered state. The matrix will remain in a modified state if the nanoparticle influences the macromolecules of the matrix within a boundary layer of thickness *L*:

$$L = r\left[1+\frac{\rho_f}{\rho_m}\right]\left(\frac{1}{C_f-1}\right)^{1/3}, \qquad (1)$$

where r is the particle size; ρ_f and ρ_m are the specific weights of the filler and polymer matrix, respectively; and C_f is the concentration of the nanofiller.

Even at minimal (doping) nanofiller content (0.001–1.000 wt. %), the ratio $1/C_f \gg 1$ ensures that the modifying action of the particle's energy field propagates across at least 2–3 layers of adjacent macromolecules. This results in a significant technical improvement in the stress-strain, adhesion, and tribological properties of nanocomposite materials based on thermoplastic matrices.

It has been established that the efficacy of nanoscale particles (NPs) and dispersed particles exhibiting the nano-state is influenced not only by their size, composition, and structure but also by their shape. When using particles of layered (plate-like), whisker-like, or spherical shapes, the degree of matrix modification M – defined as the ratio of the total modified volume to the composite's overall volume – varies. Accounting for the differing energetic states of NPs with varying shapes, the following relationship was derived for the modification degree by plate-like (M_{pl}), whisker-like (M_w), and spherical (M_s) particles at equal concentrations:

$$M_{pl} : M_w : M_s = 1 : 0.4 : 0.8 \qquad (2)$$

This expression indicates that layered modifiers, such as natural silicates (clays, micas), are the most effective for creating lightly filled nanocomposites based on polymer matrices.

Experimental and theoretical studies assume that the structure, composition, and habit of NPs introduced into the polymer matrix remain unchanged. However, certain classes of NPs (metallic, oxide, metal-containing) can undergo transformations due to physicochemical processes in the composite's boundary layers under operational factors (thermal, mechanical, mechanochemical, etc.), forming products with altered composition and structure. Therefore, selecting NPs for targeted modification of polymeric or oligomeric matrices requires a systematic analysis of structural-phase transformations, incorporating energetic and physicochemical aspects of metal-polymer system formation and function. Through systematic analysis of the prerequisites for achieving the nano-state in dispersed particles of varying composition, structure, and production methods, principles for optimal component selection have been developed. These principles enable the creation of materials with enhanced performance characteristics using industrially produced polymers (Fig. 6).

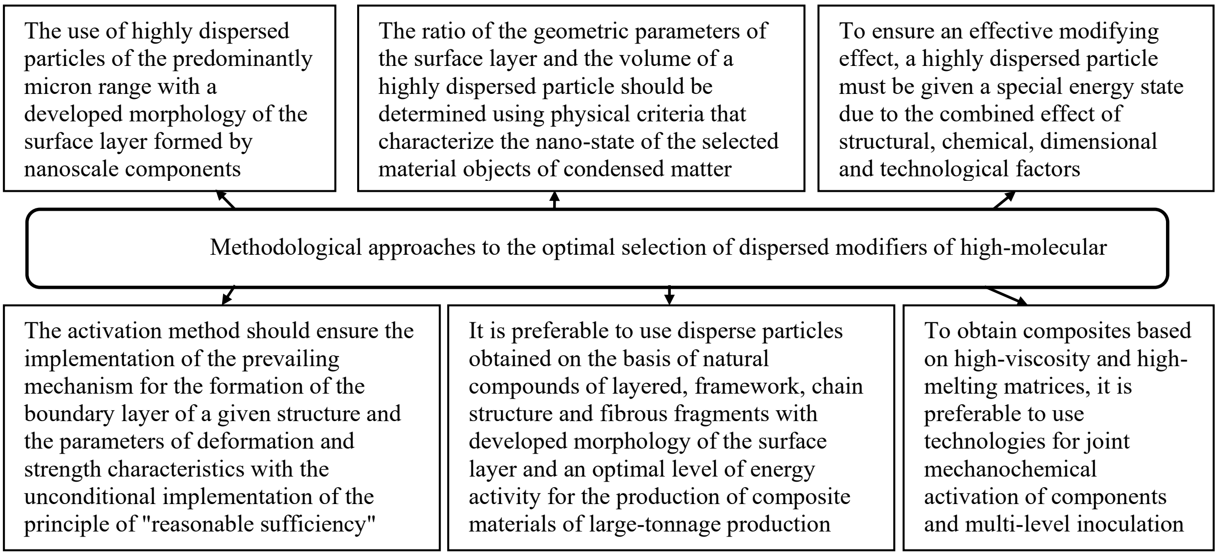

Fig. 6. Principles of optimal selection of dispersed modifiers of high-molecular matrices taking into account the energy factor

A systematic approach to analyzing the features of the modifying effect of nanoscale objects with varying composition, structure, and production technologies has led to the development of scientific principles for creating functional engineering nanocomposite materials. These materials are based on industrially produced thermoplastics such as polyolefins, polyamides, polyacetals, and fluoroplastics, along with processing technologies that enable the production of products with high-performance parameters [13-16].

Conclusion

Based on a systematic approach to studying the influence of structural features and energy states of nanoscale particles in condensed matter, mechanisms of physicochemical processes in polymer matrices have been proposed. These mechanisms determine the parameters of their structure at the molecular, supramolecular, and interfacial levels.

Methodological principles for producing nanocomposite materials based on industrial thermoplastics have been developed, consisting of:

– utilizing crystallochemical prerequisites for selecting natural and synthetic carbon-containing, metal-containing, and silicon-containing semi-finished products to purposefully form active nanoscale particles with specified structural, morphological, and energy parameters under optimal technological treatments (mechanochemical, thermal, laser);

– implementing conditions of energy and technological compatibility of nanomodifiers with the prevailing mechanism for forming the optimal structure of polymer, oligomer, and combined matrices at various organizational levels – molecular, supramolecular, and interfacial;

– ensuring conditions for the manifestation of preferred mechanisms of interfacial physicochemical interactions among components, leading to the formation of boundary layers with optimal structures that determine the failure mechanisms of nanocomposites under the influence of various operational factors.

Compositions of nanocomposite materials with enhanced stress-strain, tribological, adhesive, and protective characteristics have been developed based on industrially produced thermoplastics (polyolefins, polyamides, polyacetals, polytetrafluoroethylene) and their manufacturing and processing technologies into products used in automotive and tractor engineering, construction, thermal power engineering, mining, and chemical industries [13–16].

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