Nanocomposite materials based on industrial thermoplastics for metal-polymer systems with high resource

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Abstract: *Methodological approaches to the creation of nanocomposite materials based on thermoplastic matrices of industrial production for metal-polymer systems with high resource are considered. The concept of energy and technological compliance of components is proposed. This concept allows to achieve a synergistic effect when introducing dispersed particles in the nanostate into the thermoplastic matrix due to the formation of a structure with special parameters of characteristics. Examples of practical use of the concept of energetic and technological compliance of components in the creation of nanocomposites for special structures are presented.*
KEYWORDS*: NANOCOMPOSITE MATERIALS, INDUSTRIAL THERMOPLASTICS, THE CONCEPT OF ENERGY AND TECHNOLOGICAL COMPLIANCE OF COMPONENTS, METAL-POLYMER SYSTEMS WITH HIGH SERVICE LIFE*

1. Introduction

The modern development of various branches of economic activity is based on the expanded use of functional materials of a new generation – nanocomposites – in the structures of machines, mechanisms, technological equipment, products, which ensure the achievement of high parameters of operational characteristics by innovative developments [1]. In the brand range of nanocomposite materials, a special place belongs to nanocomposites based on polymer, oligomeric and combined matrices, which, in terms of a number of operational parameters and manufacturability of processing, are the only materials for the production of motor vehicles, agricultural machinery, technological equipment, shut-off and control valves for the heat power industry, the petrochemical complex, functional elements of special techniques used in healthcare.

Studies carried out in various scientific schools have shown that the parameters of the performance characteristics of nanocomposite materials based on high-molecular matrices are largely determined by the intensity of physical and chemical processes at the matrix-modifier interface, which depend on a special state of nanosized particles called the nanostate. The achievement of the nanostate phenomenon by the component of the nanocomposite material has a decisive effect on the structure parameters that characterize the stress-strain, tribological, adhesive and other functional characteristics of products in metal-polymer systems for various purposes. At the same time, there are no systematic studies of methodological approaches to the implementation of the phenomenon of nanostate in materials science and technology of nano-composite materials based on industrial polymers. Therefore, the study of the mechanisms of structure formation of nanocomposite materials based on various matrices obtained by thermo-mechanical combination of thermoplastics is an urgent problem of domestic materials science and technology of nanocomposite materials, which is of great scientific and applied importance.

2. Materials and research methods

Nanodispersed particles of carbon-containing (graphite, UDD, CNT, shungite, carbon fibers), metal-containing (oxides, salts of organic acids) and silicon-containing (mica, tripoli, opal, clay) compounds, as well as products obtained by technological effects on natural and synthetic semi-finished products (UPTFE) 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.

Thermoplastic polymers and oligomers, the most common in materials science and technology of polymer materials, were used as components for the production of combined matrices and composites for various purposes: aliphatic polyamides (PA) – PA6–210/310 low-viscosity, PA6.6-L (Khimvolokno Plant branch of Grodno Azot OJSC), PA66/6 Grilon TSS/4, PA12 Grilamid L20 (EMS–CHEMIE AG, Switzerland), PA11 Rilsan (Arkema, France), polyolefins – polypropylene (PP), high-density polyethylene (LDPE), low-density polyethylene (HDPE) (JSC "Polymir"), polyesters – polyethylene terephthalate (PET), polybutylene terephthalate (PBTF) primary (JSC "Mogilevkhimvolokno") and regenerated (JSC "Belvtorpolimer"), fluorine-containing compounds – polytetrafluoroethylene (PTFE) F4 and F4-M (JSC "Halogen", Russia), fluorine-containing oligomers "Foleox" (Research Institute of Synthetic Rubber named after Academician S.V. Lebedev, Russia), products of thermogas-dynamic synthesis of PTFE (TGDS), produced under the trademark "Forum" (Institute of Chemistry of the Far Eastern Branch of the Russian Academy of Sciences, Russia), positioned as ultrafine polytetrafluoroethylene (UPTFE).

Polymeric primary materials were used in the state of industrial supply in the form of granules, a powder obtained by cryogenic dispersion of granules at a temperature of 87 K.

The structure and properties of nanocomposite materials and products made of them were studied using modern methods of physical and chemical analysis: IR spectroscopy (Specord), EPR spectroscopy (RE 1306, Bruker), X-ray diffraction (Drone 3.0), differential thermal (Q-1500) analysis, optical (MRM-10, MF-2), scanning electron (ISM-50A, Nanolab-7) and atomic force (Nanotope III) microscopy. The energy state of nanoscale modifiers and composite materials was evaluated using EPR spectra and temperature-stimulated current spectra (TST) at the original facility of the Institute of mechanics of metal-polymer systems named after V.A. Bely of the National Academy of Sciences of Belarus (IMMS). Modeling of the technology for forming products and samples by 3D printing was carried out on Stratasys Fortus 450mc, FlashForge Dreamer units at the technological modes recommended by the manufacturer, using filaments from the manufacturer (China) and filaments obtained using the original technology of inoculation with polyamide resin (PR) developed at the educational institution "Belarusian State Technological University" and produced under the ProChemDuo trademark of PromKhimTechnologies LLC (Smolevichi), and nanosized particles of various compositions.

The combination of the components of the composites was carried out using the technologies of extrusion mixing on a twin-screw extruder MRS 67/2 manufactured by Compex, thermomechanical mixing in the material cylinder of the Battenfeld injection molding machine of the TM series (Wittmann Battenfeld GmbH, Germany) and deposition of dispersed particles from the fluidized bed on a solid substrate under the modes regulated by the equipment manufacturers.

3. Results and discussion

Multicomponent functional 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 impact on them in the process of composite formation and material processing. In the interphase 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 specific conditions of formation and operation of the system object, determines the resistance of an element made of a composite or metal-polymer system to the impact of operational factors, that is, the operational life [1].

To characterize *the energy state*, a complex parameter was used, which is the aggregate 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 the prevailing interfacial reactions in the composite or metal-polymer system by forming the energy state of components with certain parameters of electrophysical characteristics.

Based on the concept of energy and technological compliance of components, approaches are proposed for the formation of systems with optimized parameters of structural characteristics at various levels of organization: supramolecular, intermolecular, interphase.

In accordance with the concept of energy and technological compliance (figure), it was determined that *the energy correspondence of components* implies the possibility of achieving an aggregate energy state that corresponds to the activation energy of the prevailing physicochemical process that determines the mechanisms for the formation of the optimal structure of the system at the supramolecular, intermolecular, interfacial levels of organization in composites or metal-polymer systems.

When choosing an adequate technological impact, conditions are created for the transformation of the initial energy state and the achievement of the nanostate directly in the zone of interfacial interaction, which ensures the course of the prevailing physicochemical process of forming the optimal structure of the boundary layer in the "matrix – modifier" or "composite – metal substrate" systems.

The possibility of forming an interfacial (boundary) layer of an optimal structure that provides a given service life of the product and the metal-polymer system determines *the technological compliance of the components of* functional materials or structures, which is understood as the possibility of achieving the specified values of energy parameters *at a certain stage of the formation of the composite, the product and the structural design of the unit*, ensuring the course of the prevailing process of interfacial interaction with a given intensity.

Directions for the implementation of the phenomenon of the nanostate of material objects in materials science and technology of functional nanocomposites based on industrial thermoplastics and regeneration products and metal-polymer systems with increased operational requirements, focused on the state of the domestic technological base of industrial enterprises, related mainly to the IV and V modes are proposed [2–9].

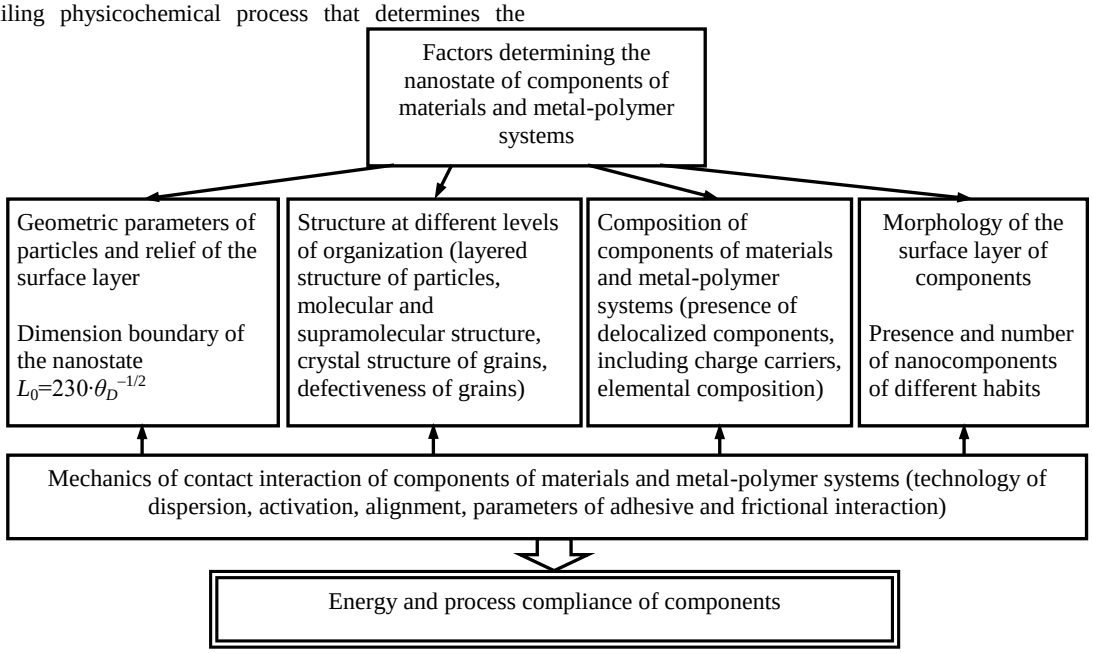

Fig. *Factors that determine the concept of energy and technological compliance*

In the creation of functional nanocomposite materials based on thermoplastic matrices, the principle of multilevel inoculation proposed in the works of Prof. V.A. Struk is implemented, consisting in the directional structuring of the binder by introducing modifiers of various mechanisms of action and dimensions. The introduction of functional components into the composition of the thermoplastic polyamide matrix (PA6) – nanosized particles (UNT, UDAG, KGP S-1, copper) in combination with flame retardants (TG) and reinforcing particles (SV) ensures the achievement of a synergistic effect of increasing the parameters of strength, non-flammability and resistance to long-term effects of thermal-oxidative media.

Among the promising technologies for the manufacture of functional products for various purposes are additive manufacturing technologies based on 3D printing using polyamide filaments. Compositions of nanocomposite materials based on industrial polyamides have been developed for the manufacture of import-substituting filaments based on PA6.6, PA6 and functional modifiers (Table) [8].

***Table** – Parameters of deformation and strength characteristics of samples made of composite material PA6.6 (84%) + PA6 (10%) + PA12 (5%) + Irganox 1010 (1%) obtained using various technologies*

Sample Acquisition Method	Parameter characteristics								
	Tensile strength, MPa	Deformation at rupture, %	Tensile modulus (*V=50mm/min), MPa*	Yield strength (1% offset), MPa	Deformation at yield strength, %	Maximum bending stress, MPa	Modulus of flexural elasticity, MPa	Elongation during bending, mm	Charpy impact strength, kJ/m^2
Injection Molding	79,5	4,0	1289,1	–	–	110,4	2795,3	6,4	4,9
Additive molding in filament stacking:									
– along the tensile force	59,6	3,2	950,2	–	–	78,4	1982,6	5,3	4,6
– across the tensile force	40,9	3,0	752,1	–	–	57,3	1809,4	4,8	3,8

The developed methodological principles for the implementation of the nanostate phenomenon in materials science and the technology of functional composites based on polymer matrices and metal-polymer systems were tested in the targeted structuring of industrially produced thermoplastics for the creation of structural, sealing, tribological products based on primary and regenerated binders.

4. Conclusion

The developed compositions of nanocomposite tribological materials based on aliphatic polyamides of domestic production (branch "Khimvolokno Plant" of JSC "Grodno Azot") are recommended for the application of anti-wear and anti-scuffing coatings of spline joints of cardan shafts manufactured by JSC "Belcard", and the drive gear of self-centering lathe chucks produced by JSC "BelTAPAZ".

Composite materials based on thermoplastic primary and regenerated matrices (HDPE, PP, LDPE, TPU), geomodifiers modified with nanoparticles, carbon-containing and metal-containing compounds (tripoli, UDD, clay, shungite, opal, granite flour) are advisable to use for the manufacture of damping and sealing elements of automotive units (shock absorbers, brake chambers) and functional elements of road vehicles used in specialized fleets (Belcard JSC, Beldormash LLC).

An effective area of use of composites based on regenerated polyolefins is the manufacture of fasteners of the "metal-polymer dowel" type, used in construction technologies for fixing heat, sound insulation and decorative panels made of composites based on glass fibers and foamed thermoplastics (polyurethanes, polystyrene, polyolefins), metal-polymer rollers of belt conveyors (JSC "Belaruskali") and identification and restrictive posts for underground communications (JSC "Belvtorpolimer").

Composite materials based on the thermoplastic blends (PA6, PP, HDPE) and thermoplastic elastomers (TPU, EVA) are advisable to use for the manufacture of products with increased parameters of resistance to abrasive wear and the effects of alternating loads – sealing, sealing, protective and damping elements of automotive units (propeller shafts, brake chambers, automotive shock absorbers) produced at Belcard JSC and Lidselmash OJSC.

The developed designs of nozzles for the hydrovacuum aspiration apparatus made of composite materials with a pronounced bactericidal effect are effective in the prevention and treatment of otorhinolaryngological diseases and are recommended by the Ministry of Health of the Republic of Belarus for use in all specialized medical institutions when organizing their industrial production at a specialized enterprise.

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