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MULTILEVEL MODIFICATION IN MATERIALS SCIENCE AND POLYMER NANOCOMPOSITES TECHNOLOGY

МНОГОУРОВНЕВОЕ МОДИФИЦИРОВАНИЕ В МАТЕРИАЛОВЕДЕНИИ И ТЕХНОЛОГИИ ПОЛИМЕРНЫХ НАНОКОМПОЗИТОВ

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Abstract: *This paper describes directions of realization of the multilevel modification principle in materials science and technology of polymer composite materials based on thermoplastics. It is shown that the introduction of nanoscale particles of different structures and production technologies into the composition of the composite makes it possible to transform the structure at various organization levels, which leads to the achievement of a synergistic effect of increasing the parameters of deformation-strength, tribotechnical characteristics and resistance to the action of thermal-oxidative medium. One of the perspective technologies of the nanomodifiers introduction into the composite material is the diffusion treatment of components and products in precursor solutions. Mixture of composite materials with increased parameters of performance characteristics for use in engineering, chemical and mineral resource industries have been developed.*
***KEYWORDS**: MUTILEVEL MODIFICATION, NANOMODIFIER, NANOCOMPOSITE, POLYMER BLENDS, POLYMER STABILIZATION*

1. Introduction

Review of recent results [1 – 7] in materials science and technology of polymeric functional materials area allows us to assert about the prevalence of the structural factor in the achievement of the set value of stress-strain, tribotechnical adhesion, and other characteristics of products under different operating factors intensity. Traditional methodology of polymer materials creation for the production of components for static (adhesive) and dynamic (tribotechnical) metal-polymer systems with various functionality and operating conditions is based primarily on methods of managing a structural organization that take into account the influence of one or several prevailing factors – thermophysical, deformation, corrosive, destructive, etc. [1, 3 – 12]. The practical realization this methodology is based on managing the structural parameters of composites at one of the levels of their organization (molecular, intermolecular, supramolecular and interphase) by introducing of functional components into the composition of the material or using special methods for modification of products (Fig. 1). A system approach to determining the potentialities of composite materials to adequately counteract the operational factors that cause the destruction or wear of the components of the metal-polymer system indicates the necessity to take into account the combined effect of various physical and chemical, thermal, deformation, corrosion, electrophysical and other processes that determine the mechanisms and kinetics of structural transformations at various organizational levels. The prospective of the system approach has been proved in a number of studies devoted to the development of low-wearing metal-polymer systems by introducing components that form a structure with the function of inhibitors of unfavorable processes under the influence of operational factors [13].

It is obvious that the new generation composite materials should transform the original structure with a high degree of adequacy under the influence of variable operational factors with varying intensity for optimal confrontation and preservation of the specified parameters for safe, efficient and comfortable operation of the metal-polymer system of a certain design and functionality. In this regard, the development of technological methods for practical implementation of the principle of multilevel modification [14] has a special perspective.

2. Research methods

For research we used polymer materials belonging to the class of aliphatic polyamides: PA6, PA6.6 (Branch “Khimvolokno Plant” of Public Joint-Stock Company “Grodno Azot”, Belarus), PA66/6 Grilon TSS/4, PA12 Grilamid L20 (EMS-CHEMIE AG, Switzerland), PA11 Rilsan (Arkema, France). Some experiments were carried out with polyolefins – polypropylene (PP), low-density polyethylene (LDPE) and high-density polyethylene (HDPE).

For control the parameters of the structure and performance characteristics of composite materials we used dispersed (including nano-sized) carbon-containing particles (colloidal graphite preparation C-1, detonation synthesis ultradispersed diamonds (UDD) (Scientific and Production Closed Joint-Stock Company “SINTA”, Belarus), carbon nanotubes (CNTs) (A. V. Luikov Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus)), silicon-containing (clays, tripoli) and metal-containing (copper formate) compounds obtained by original technologies of producers.

The components were combined by extrusion blending technology on a twin screw extruder of compounding line Berstorff Compex MPC 67/2, thermomechanical mixing in the material cylinder of the injection molding machine Battenfeld TM (Wittmann Battenfeld GmbH, Germany) under the conditions specified by the equipment manufacturers.

Diffusion modification of granular or powder semi-processed polymer materials was carried out by exposure in a precursor solution (copper formate) for 1 to 10 hours with drying for removing of the solvent.

Physical and chemical processes at various levels of the structural organization of composite materials were investigated by using modern methods of analysis: IR spectroscopy (Tensor-27), X-ray diffractometry (Dron-3.0), differential thermal analysis (Thermoscan-3), atomic-force (AFM), scanning electron (SEM) and optical microscopy by the instrumentality of devices Mira, Tescan, NT-206, MDS.

The parameters of stress-strain, tribotechnical and adhesion characteristics of composite materials and coatings were evaluated according to standard methods by using specialized equipment – tensile-testing machine Z010 Zwick and tribo-test device FT-2. The results were processed using the software products included in the equipment package. Data processing were carry out by using software of current technique.

3. Results and discussions

In various metal-polymer constructions the composite materials are exposed by prolonged exposure of higher temperatures which intensify the processes of thermal-oxidative degradation leading to the reduction of parameters of stress-strain, tribological, adhesive and other characteristics [1, 3 – 8, 13, 14]. The increase of the polymer and composite materials products resistance to aging under the influence of operational factorsis one of the topical problems of functional materials science [13].

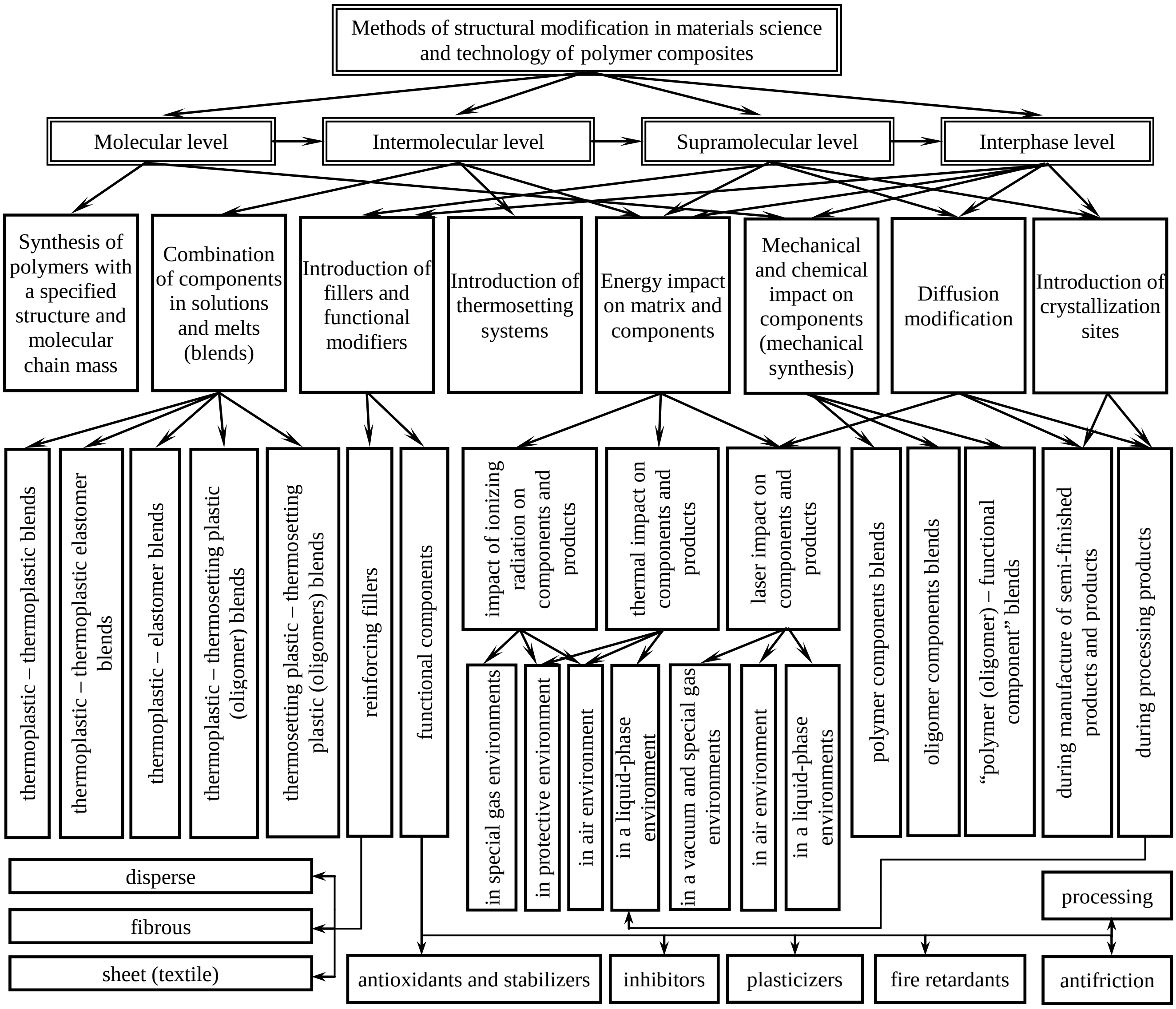

***Figure 1 –** The main directions of structural modification in materials science and technology of polymer composite materials*

An effective direction of the increase of the polymer and composite materials products resistance to thermal-oxidative aging is the realization of the mechanism of non-chain stabilization proposed in the works of Gladyshev G. P. and co-workers [18]. The essence of this mechanism consists in introducing into the composition of components capable of preferentially interacting with active oxygen to form oxide compounds. At the same time, the chain processes of thermal oxidation and destruction of the matrix binder are inhibited. It has a positive effect on the resistance of the products. As such “nonchain” stabilizers, the highly dispersed metal particles with a high sensitivity to oxygen are effective. The approaches proposed in [18] are based on the mechanisms for preventing or reducing the probability of interaction of oxygen atoms (ozone) with the active sites of the macromolecules of the binder and are realized when there are sufficient amounts of modifiers with increased affinity for oxygen in the composite. After the exhaustion of the active modifier, the intensity of the processes of thermal-oxidative degradation and aging increases. It leads to a decrease of the service life of products.

An effective direction of realization of the mechanism of nonchain stabilization in polymer composites based on thermoplastics is the introduction of nanoscale metal particles by thermolysis of metal-containing precursors directly in the melt of the matrix binder during the processing of the composite into a product by injection molding or extrusion [13, 14]. This approach, based on the classical ideas of the influence of supermolecular structure on the kinetics of thermal-oxidative and thermodestruction processes in thermoplastics worked out by prof. Maciulis A. N. [19], was developed in the studies of prof. Struk V. A., prof. Ryskulov A. A. and them colleagues [13, 20, 21]. A special mechanism for the non-chain stabilization of thermoplastic polymers of a class of polyamides, polyacetals, polyolefines and their thermomechanically combined mixtures containing nanoscale metal particles was established. This mechanism consists of a combination of structural factors and phase transformations in metal-polymer composites with a doping content (0.01 – 0.5 wt. %) of a modifier. An important result of the carried out complex studies is the established fact of the change in the energy parameters of the macromolecule of the matrix polymer as a result of the interaction of their active sites with the nanoscale particles of the modifiers (particles of metals and oxides) formed during the thermolysis of the metal precursor.

We made an assumption, that it is possible to realize the mechanism of nonchain stabilization like in metal-polymer systems [21] for composites containing other (including nonmetallic) modifiers with a nanoscale range of the particles.

For research we have chosen aliphatic polyamides and nanosized carbon-containing particles – carbon nanotubes (CNTs), detonation synthesis ultradispersed diamonds (UDD), colloidal graphite preparation C-1 (CGP C-1) in the state of industrial supply.

For evaluation of the effectiveness of nanosized carbon-containing particles action we have used model composites based on aliphatic polyamides PA6, PA6.6, PA11, PA12, containing nanosize copper particles with a content of 0.075 – 0.6 wt. %. The nanoscale metal-containing modifier was obtained by heat treatment of granular or powder semi-finished products diffusively modified in aqueous solutions of a metal precursor (copper formate) for 1 to 10 hours.

A comparative evaluation of the effectiveness of nanodimensional modifiers in original, mixed and composite polyamide matrices was carried out according to the parameters of stress-strain characteristics of standard samples exposed to thermal-oxidative aging at a temperature of 423 ± 5 K (150 ± 5 °C) in air for 200 hours. As a criterion, the tensile strength σ, MPa was chosen. Experimental data are given in Figures 2 and 3.

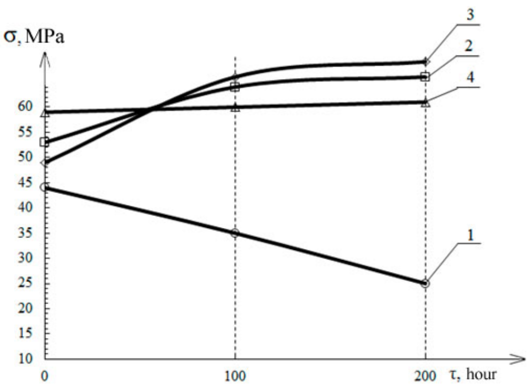

Figure 2 *– The graph of relationship of tensile strength σ to heat treatment time τ at 423 K (150 °C) for PA6 (1), PA6 + copper formate (after 1 hour of diffusion modification) (3), PA6 + copper formate (after 5 hours of diffusion modification) (2), PA6 + copper formate (after 10 hours of diffusion modification) (4)*

As follows from the data presented in Fig. 2, the diffusion treatment of granulated polyamide 6 (PA6) in an aqueous solution of copper formate [$Cu(HCOO)_2$] for 1 – 10 hours leads to a significant change in the resistance of standard samples to thermal-oxidative aging. The original tensile strength parameter of samples from PA6 decreases from 44.67 MPa to 26.66 MPa after 200 hours of thermal oxidation in the air medium (Fig. 2 curve 1). At the same time, the samples modified by nanoparticles of copper not only do not reduce the original tensile strength parameter, but also significantly increase it to 61.95 – 67.22 MPa after thermal oxidation for 100 – 200 hours (Fig. 2 curves 2, 3, 4).

The obtained results confirm the basic positions of the mechanism of action of nanoscale copper particles, described in [13]. It should be noted that the diffusion mechanism of introducing nanoscale particles into the polymer matrix has a special perspective of practical application, because it is characterized by the simplicity and availability of technical operations to achieve a technically significant effect in comparison with other technologies, for example, blending or mixing.

A similar technically significant effect of increasing the resistance to thermal-oxidative aging has been achieved for samples of composite materials based on polyamide PA6 modified by fire-retardant agents (PA6-GF) and a combination of fire-retardant agents with 20 wt. % fiberglass (PA6-FG20-GF). The introduction of nanosized copper particles into the composites in the amount of 0.085 – 0.6 wt. % by diffusion treatment in an aqueous solution of copper formate significantly increases not only the original parameters of stress-strain characteristics, but also their values after 100 hours and 200 hours of thermal oxidation at a temperature of 423 ± 5 K (Fig. 3).

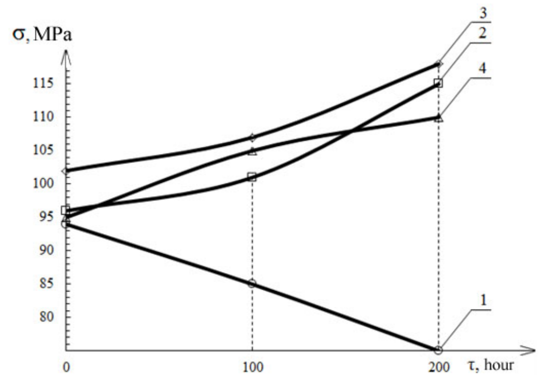

Figure 3 *– The graph of influence of nanoscale copper particles on the resistance of glass-filled polyamide to thermal-oxidative degradation for PA6-FG20-GF (1), PA6-FG20-GF + copper formate (after 1 hour of diffusion modification) (2), PA6-FG20-GF + copper formate (after 5 hours of diffusion modification) (3), PA6-FG20-GF + copper formate (after 10 hours of diffusion modification) (4)*

A significant increase of the tensile strength parameter for composites PA6-GF modified by copper nanoparticles indicates the realization of structural modification mechanisms at various levels, proposed in [13, 14].

For composites containing functional filler (fire-retardant agents and fiberglass) the structuring effect is observed when copper nanoparticles are introduced. This effect is manifested in a decrease of deformation evaluated by the tensile elongation criterion.

The most important factor of increasing the resistance of carbon-containing nanocomposites based on combined aliphatic polyamides to thermal-oxidative aging is the structure formed by close-structure macromolecules at different levels – intermolecular, supramolecular and interphase.

It is known that aliphatic polyamides are partially crystalline polymers with predominantly spherulite type of supramolecular structure [19].

As shown in the studies of prof. Savkin V. G. and co-workers [15] in the realization of the increased parameters of the stress-strain characteristics of polyamides, the dimensions of the spherulites, their structural perfection and the parameters of the spherulite interface are most important.

Due to the close structure of the macromolecules of the matrix polyamide PA6.6 and the modifiers PA6, PA12, the spherulite structure of the blend composite is formed with the participation of pass-through macromolecules. As a result, there is formation of a structure similar to the cross-linked, created by the pass-through macromolecules of the alloying polyamide. Such a structure is able to withstand the action of external loads applied to the sample (product). In addition, the presence of a low-melting component (PA12) in the composite promotes to reduce residual stresses during crystallization and chilling of the matrix polymer (PA6.6).

These factors contribute not only to a significant increase of the parameters of stress-strain characteristics of blend composites, but also to resistance to thermal-oxidative medium. In this case, the tensile strength parameter significantly decreases.

When nanodispersed carbon-containing particles, mainly located in the interspherilite regions, are introduced into the blend composite, the effect of higher resistance to thermal-oxidative degradation increases due to the formation of additional physical bonds of the adsorption type (Fig. 4).

Thus, nanosized carbon-containing particles act as a physical compatibilizer. It is stimulate to the formation of a perfect composite structure at different levels of organization.

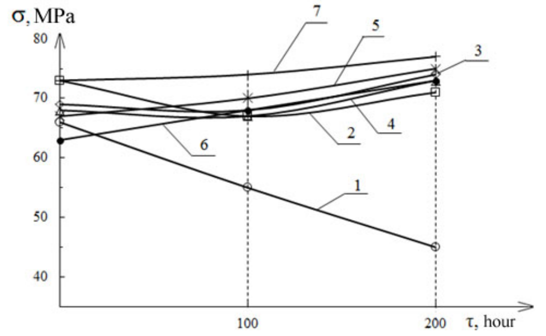

***Figure 4** – The graph of relationship of tensile strength σ to heat treatment time τ at 423 K for polyamide composite materials:*
1 – PA 6.6;
2 – PA6.6 (94 wt. %) + PA6 (5 wt. %) + PA12 (1 wt. %);
3-PA6.6 (90 wt. %) + PA6 (5 wt. %) + PA12 (5 wt. %);
4-PA6.6 (85 wt. %) + PA6 (10 wt. %) + PA12 (5 wt. %);
5-PA6.6 (84.5 wt. %) + PA6 (10 wt. %) + PA12 (5 wt. %) + CGP C-1 (0.5 wt. %);
6-PA6.6 (84.5 wt. %) + PA6 (10 wt. %) + PA12 (5 wt. %) + CNT (0.5 wt. %);
7 - PA6.6 (84.5 wt. %) + PA6 (10 wt. %) + PA12 (5 wt. %) + UDD (0.5 wt. %)

Thus, the modification of blend composites based on aliphatic polyamides with nanoscale particles with different structure and production technology makes it possible to realize the synergistic effect of increasing the parameters of stress-strain, adhesion, tribotechnical characteristics and resistance to the action of thermal-oxidative operating media. The mechanism of synergistic effect realization is due to the interaction of active sites of nanosized particles with the sites of polymeric macromolecules with the formation of adsorption type bonds [14]. The formation of such bonds changes the intensity of intermolecular interaction in composites based on mono- and blend matrices. It is manifested in the transformation of the structure of the composite at the intermolecular, supramolecular and interphase levels. Due to the multilevel structural modification, the resistance to influence of operational factors (including to the processes of tribochemical interaction in metal-polymer systems and high temperatures in the air environment) is increases.

The effect of the antioxidant effect of nanoscale carbon-containing particles of different structures and synthesis technology is mainly due to the adsorption interaction of active sites with the formation of physical bonds. This hypothesis is confirmed by the facts of changes not only parameters of thermophysical characteristics during introducing doping amounts of the modifier (0.01 – 1.0 wt. %), but also of rheological and stress-strain properties. At the doping content of a nanosized modifier the amount of carbon-chain compounds that can perform the function of the antioxidant of polymer matrix, as noted in [22], is insignificant and can not have any significant effect on the kinetics of thermo-oxidative processes during long exposure times in an oxidizing environment. Therefore, the prevailing role in the demonstration of the antioxidant effect belong to reduce the sensitivity to oxygen by macromolecular due to a decrease their activity determined by the formation of physical spatial bonds. Thus and so, this effect is relevant for different nanosize particles, which do not belong to antioxidants in the common sense of the term. It is confirmed by the smooth behavior of experimental curves $\sigma = f(\tau)$ for the nanocomposites at the time of thermal oxidation up to 1000 hours as opposed to the analogous experimental curves typical for composites containing antioxidants (these curves characterized by a spasmodic change in the parameter σ after the consumption of the antioxidant) [19].

A special perspective in the realization of the principle of multilevel modification in composite materials based on thermoplastic blends is the technology of introducing nanoscale particles by diffusion of solutions of various compounds.

In the case of diffusion modification of composite products based on blend matrices or reinforced by fragments of carbon, glass and other fibers, the effect of structural modification of the most defective structureless layer is realized. This layer largely determines the performance parameters of metal-polymer systems, primarily adhesion and tribotechnical characteristics. A sufficiently large thickness of the diffusion-modified layer [19] makes it possible to realize the gradient structure of the product. The near-surface layer of this product is a nanocomposite material with a high degree of structuring. It due to the formation of a spatial grid of adsorption physical bonds determined by the localization of nanoparticles in intermolecular regions and structural defects. The nanostructured layer is located on a composite base formed by a matrix binder and functional components with various functionality. During the introducing of reinforcing fibers into a composite, their functions are realized increasingly due to the formation of a nanostructured near-surface layer and a decrease of the probability of formation and development of microcracks under the action of mechanical, thermal, thermomechanical stresses arising under the operational factors.

The combination of various techniques of introducing nanoscale particles into the composite material, for example, diffusion treatment of the granules of the components (filled and unfilled) and the product obtained from these granules, makes it possible to form a composite structure with optimal organization at various levels. Such a structure forms prerequisites for the realization of synergistic effects in various mechanisms of their demonstration. For example, as shown before, in the blends based on thermoplastic components or composite materials containing functional components, along with the achievement of increased parameters of stress-strain, adhesion and tribotechnical characteristics, we have a technically significant effect of increasing the resistance to thermal-oxidative aging. This effect, in some cases, determines the parameters of the service life and reliability of the metal-polymer system. It should be emphasized that the effect of increasing the resistance to the action of thermal-oxidative medium is manifested not only in the diffusion introduction of antioxidants [19], but also in the diffusion introduction of nanoscale particles with different nature and structure.

4. Conclusions

The methodology of realization the principle of multilevel modification for the creation of metal-polymer systems components with high parameters of performance characteristics is considered. It is shown that, for composites based on polyamides containing functional components (reinforcing fibers, flame retardants), it is advisable to introduce nanosize particles by preliminary diffusion treatment of granulated semi-finished products in aqueous solutions of thermally decomposing precursors. On application of this technology, a synergistic effect of increasing the parameters of combustion resistance and the resistance of materials to the action of thermo-oxidative medium is realized. At the same time, high values of parameters of stress-strain characteristics are maintained.

For composites obtained by thermomechanical combination of aliphatic polyamides with different structure and molecular chain mass, it is effective to introduce the nanosized carbonaceous particles (colloidal graphite preparation C-1, carbon nanotubes, UDD), which contribute to the formation of a structure providing high parameters of performance characteristics (adhesion, tribotechnical, stress-strain) with simultaneous increase of resistance to thermal-oxidative aging. Additional modification of semi-finished products (granules or powders) by copper formate with using the diffusion treatment contributes to the increase of the parameters of the performance characteristics.

A mechanism for realizing the principle of multilevel modification in filled and blend composites is proposed. This mechanism consists in the formation of an optimal structure at different levels of organization – intermolecular, supramolecular and interphase, due to the formation of a spatial grid of adsorption physical bonds between nanoparticles and active sites of polymeric macromolecules. The presence of such bonds in combination with the functional action of the components introduced into the composite creates the prerequisites for the realization of the synergistic effect of increasing the values of the performance parameters.

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