ENERGY ASPECTS OF STRUCTURE FORMATION OF NANOCOMPOSITES BASED ON THERMOPLASTIC

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Abstract: Using methods of spectroscopy of thermally stimulated currents (TSC spectroscopy), atomic force microscopy (AFM) and scanning electron microscopy (SEM) analysis was done of the energy state of dispersed particles of different composition and structure - mineral (tripoli, shungit, clay, mica, silica) and synthetic (ultra dispersed polytetrafluoroethylene, nanodiamonds, silicate glass, metal oxides). There was established the effect of occurrence of the special energy state of dispersed particles, due to the presence of nanoscale components of the structure. There were studied parameters of the energy characteristics of the modifier (value and density of the residual charge, activation energy of the relaxation, time of charge relaxation et al.) depending on the action of technological factors - temperature, mechanical stress, energy flows. The optimal ranges of occurrence of effective modifying action in macromolecular matrices of various types - polymeric, oligomeric, combined. There were proposed technological principles formation of mechanical engineering nanocomposite materials with improved parameters of deformation and strength and tribological characteristics.

KEYWORDS: ENERGY STATE, DISPERSED PARTICLE, TECHNOLOGICAL IMPACT, MODIFYING EFFECT, NANOCOMPOSITE MATERIAL.

1. Introduction

In a wide range of engineering materials occupy a special place composite materials for various purposes, which are obtained by modifying the matrix polymer, oligomeric and combined components of the target on the basis of silicon, carbon, metal-containing compounds with a given dispersion and form [1-22]. Acting in materials science of polymer composites based on commercially available thermoplastics paradigm based on three main approaches of structure parameters management:

a. on the supramolecular level by introducing binding matrix modifiers providing the prevailing mechanism of formation of the supramolecular structure of the given type and geometric parameters, or the use of special types of thermal processing on products, semi-finished or functional structures [8, 12];

b. on the interfacial level by introducing reinforcing components mainly fiber-like fragments of a predetermined length of fragments into the polymer, oligomeric and combined matrices [1-7, 10-22];

c. on the intermolecular level by forming a three-dimensional crosslinked structure under the action of high-energy radiation. [19]

Without considering the features of mechanism of modifying action of the dispersed particles of different composition, structure and dispersion, we note the common criteria for their informed choice: 1) prevalence, availability and cost of raw semi-finished; 2) adaptability to the dispersion process in obtaining a stable output optimal size fraction; 3) processability of combination of dispersed particles with a matrix binder; 4) required activity in the modifying processes on the molecular, supramolecular and intermolecular levels; 5) technological time of active state relaxation; 6) ecological compatibility and safety of application in traditional technology of composite materials; 7) ability to secure recycling of technologically justified waste products and amortized articles made of composite materials.

The implementation of the entire set of selected criteria in a specific composition modifier for a particular type of composite material, is generally difficult to achieve the solution of which depends on many factors, primarily on the established methodological approaches in a regional or national industry caused by the material, human, technological, organizational maintenance of existing facilities.

However, in all cases the use of high-matrix modifiers, generalizing (basic) criteria of their choice is given the effectiveness of action necessitates technically significant effect of improving the parameters of strength, tribological, thermal, adhesive and others service characteristics with minimal economic costs, taking into account the material and energy intensity and staffing processes of production and consumption target.

The obvious is the condition for the implementation of this criterion, suggesting the achievement of optimal structural state at a given level of organization of the composite material at a particular combination of matrix binder, a kind of modifier and combining and processing technologies.

An analysis of the literature devoted to materials science and technology of composite materials based on high molecular matrices [1-22], indicates a lack of unified methodological approaches to the selection of functional modifiers to create a composite of a particular functional purpose.

As a rule, is implemented the traditional labor-intensive approach based on the use of results of experimental studies to determine the mechanisms of modifying action of various components of the composition, structure, and technology for dispersion. The practical implementation of this approach is not only costly, but also tends to not achieving an optimal technical effect. Moreover, in some cases are formed the conditions of manifestation of "structural paradox", the essence of which is inadequate change the service characteristics of composite materials, even when using high-efficiency, including high strength and heat resistance, components. An example of such a manifestation of the structural paradox is given in [23].

The obvious is the need to develop criteria for informed choice of components to create functional materials that take into account the most common features, common to all types of condensed matter, which form the physical paradigm of modern materials.

The objective of this work was to analyze the possibility of evaluating the effectiveness of modifiers in high-molecular matrix on the criteria of energy state.

2. Methods of research

As binders for composites using thermoplastic polymers - polyamide 6 (PA 6) and polyamide 11 (PA 11), high density polyethylene (HDPE), polypropylene (PP), polytetrafluoroethylene (PTFE) in the state of industrial supply (JSC "Grodno Azot" JSC "Polymin", JSC "HimvoloknoMogilev"). Some experiments were carried out with the regenerated thermoplastic (HDPE, PP, LDPE)
obtained at JSC "Beltorpolimier" in accordance with the existing standard documentation.

In order to control the parameters of the energy state and dispersion components were used technological methods based on mechanical dispersion, mechanochemical combination, the impact of energy flows in the heat treatment, exposure to corona discharge, microwave, laser beam, using original cryogenic plants dispersion, rolling shear (Yanka Kupala State University of Grodno), the installation of the planetary mixing AGO-2 (Institute of Solid State Chemistry and Mechanochemistry of the SB RAS) systems for the treatment of microwave radiation, laser QUANTUM-15, high-shredder - dismembrator, installations for the electrostatic application of coatings (JSC"Grodno Mechanical Plant", JSC "Belcard", JSC "Lakokraska"). Select the type of energy and the impact of the conditions for the activation process was driven by the composition, structure and chemical and dimensional parameters of components, the functionality of the coatings or products.

To obtain composite materials used highly dispersed, including nanoscale particles of carbonaceous (UDD, UDAG, nanotubes, colloidal graphite), siliconic (mica, clay, flint, shungite tripoli), fluorine (UPTFE) and metal-containing (oxides of Fe, Cu, Zn) compounds obtained by the original technology of manufacturer (JSC "Sinta", SSI "Lykov Institute of Heat and Mass Transfer", Institute of Chemistry FEB RAS), or as a result of specific technological effects on the semi-finished product (mechanochemical dispersion, sublimation).

Physical and chemical processes at the interface "matrix-filler" "coating-substrate" in the preparation and processing of composites and coatings use of the products were evaluated using the methods of IR-spectroscopy (Tensor-27), X-ray diffraction (DRON 2.0, DRON 3.0), DTA (Thermoscan-2) by conventional means. The morphological parameters of the particles and substrates subjected to different types of energy impact, examined using an atomic force (NT-206), scanning electron (Mira, Tescan), optical (MDS) microscopes. Energy state of dispersed particles, samples of composites, coatings and substrates investigated by thermally stimulated currents (TSC-analysis) on the original installation (ODE "MICROTESTMACHINES").

3. Results and discussion

An analysis of the literature devoted to materials science and technology of polymeric composites [1-23] suggest that the use of modifiers that are in the nanometer range, the so-called nano-sized particles of different composition, structure and technology of. In the presence of a large number of studies on the mechanisms of modifying action of the nanoparticles in the polymer, oligomer and combined matrices, it is necessary to emphasize the ambiguity of the results and the lack of a unified view of determining the dimensions and the concentration range of the optimal effective action of dispersed particles in the matrix binders, differing in molecular weight, chemical structure macromolecules, structural features of the organization under the influence of technological factors - temperature, pressure, exposure time and others. The most effective multi-purpose modifiers appeared natural compounds of silicon - zeolites [21, 22], fine products of detonation [14, 18], termogas dynamic and plasma [20, 23] synthesis - nanoceramics Silions, nanodiamonds (UDD), diamond-charge (UDAG) nanoceramics, fullerences, nanotubes, thermally split graphite, mica, clay, as well as nano-sized particles of metals and oxides obtained by thermolysis of metal precursors in molten thermoplastics [25 ]. This set a number features of modifying action of nanoparticles of different composition, structure and technology which determine the efficiency of use. These features can be systematized by characteristic criterions:

1) increasing the degree of dispersion nonlinear effect on the energy state of the particles, and efficiency of their modifying action [24];
2) increase the degree of dispersion of the particles increases the tendency to the formation of cluster structures of different structures [21];
3) the activity of modifying action nonlinear depends not only on the composition, structure and technology of fine particles, but also on external, including technological, factors acting on components during their production, storage, manufacturing and processing of composite materials [24];
4) an increase in the degree of dispersion of the particles determines the non-linearity of the economic costs of their production, storage and practical use;
5) dispersed modifiers particles of high-molecular matrix are usually necessitated the development of special technologies and equipment for their practical application [15, 20, 22];
6) superfine (including nano-sized) particles have a negative impact on the environment and require special measures to comply with the conditions for their safe production and use [26];
7) long-term (long-acting) effects of superfine (including nanocrazed) particles on the mechanisms and kinetics of physical and chemical (including biochemical) processes studied not fully [24, 26];
8) the effectiveness of modifying action of superfine (including nano-sized) particles in some cases inadequate to prognosis due to technological constraints of the optimal (settlement) conditions of interfacial interactions at various levels of the structural organization of the composite material [14-24].

Distinctive features of the practical application of nanoscale modifiers indicate the need for systematic analysis of the mechanism of their action, which will determine the most characteristic features of their effective action and conditions for their manifestation in practical technology of polymer nanocomposites.

In order to establish these common characteristic features studied the morphology of the dispersed particles of different composition, structure and technology which have found wide application in practical materials science. SEM and AFM methods found that, regardless of individual characteristics of the dispersed particles are characterized by their tendency to agglomerate and form cluster structures of different structure and the presence of micro-particles in the range of components that belong to the nanoscale. Such nanoscale components have a plate (Figure 1b, 2b, 3b), spherical (Figure 1d, 2f, 3d, e, f), needle (whisker) (Figure 1f, h) habitus.

The presence of such nanoscale components in the structure of the dispersed particles causes the expression of characteristic energy state of the surface layer, which causes a structuring of the surrounding macromolecular binder to form a quasi-crystalline structure [14, 15, 24]. Experimental confirmation of a particular energy state of the surface layer of dispersed particles is the spectroscopic data of thermally stimulated currents (TSC) (Figure 4). Regardless of the individual characteristics of dispersed particles (composition, structure, dispersion, obtaining technology), there are characteristic features of the particles of different nature. In other words, all the dispersed particles, irrespective of their individual composition, structure and preparation technology, a certain contribution to the mechanisms and kinetics of the formation of the boundary layer in the composite material making energy state due to the presence of nanoscale fragments in the surface layer of the particle. This contribution depends not only on the individual characteristics of the particles - the composition, structure, technology of obtaining, but also on the technological parameters of processing. For example, heat treatment of the dispersed particles of natural modifiers flint and shungite in the temperature range 100-200 °C is ambiguous effect on their energy state, as measured by the value of the maximum value of TSC (Figure 5). The observed effects of increasing and decreasing the value of the parameter I, depending on the treatment temperature due to the occurrence of physical and chemical processes that change the original structure of the particles - dehydration, dehydroxilation, oxidation, thermal oxidative degradation et al. [2, 14-18].

The characteristic features of the structure of the investigated particles cause multiple destinations their activity management through the use of technological operations specified destination. For example, the layered minerals such as clay, mica is effective
pre-treatment of the components, the ability to penetrate into the interlayer space and destroy the original structure of the particles to form nanoscale platelets [16]. As a result, the impact of processing technology factors intercalated composite with filler particles occurs percolation macromolecular binder in the interlayer space to form a reinforced nanostructure with high parameters of strength characteristics [15, 16].

When used as a modifier precursors of metal salt formic acid (formate) type, it is necessary to take into account the morphology of the precursor particles, which contribute to the formation during thermolysis not single particles of metals (Cu, Fe, Ni, Co), and their cluster formations providing nexus the structure of a nanocomposite [2, 14].

A particular importance in nanocomposites creating have a high energy state and morphology of the surface layer of high-strength reinforcing fillers - fragments of a fiber given composition and size [4, 27, 28].

When using carbon fiber (CF), despite the presence of characteristic nanorelief (Figure 3 d), fails to provide the required level of interfacial interaction in composites based on thermoplastic matrices and crosslinking. Therefore, in some cases, the introduction into the polymer matrix (e.g., PTFE), high-strength carbon filler (CF) leads to the appearance of the structural paradox [21, 23, 28]. An effective way to increase the efficiency of
modifying action of carbon nanofibers is a modification of the surface layer with the use of fluorine-containing compounds, such as PTFE particles. Mechanochemical treatment of CF by UPTFE promotes the formation of a specific structure of the boundary layer (Figure 3b), which increases the compatibility of the filler with a PTFE matrix [28].

![Image](image1.png)

Figure 3 - The characteristic morphology of source carbon fiber (a, b, c), and treated with ultrafine particles of polytetrafluoroethylene (d), ultrafine particles UPTFE (e), ultrafine diamond (f)

![Image](image2.png)

Figure 4 - The spectra of thermally stimulated currents of dispersed particles of flint (1), shungite (2), tripoli (3), carbon nanotubes (4)

![Image](image3.png)

Figure 5 - The dependence of the maximum current $I_{max}$ by thermally treating temperature of dispersed particles

Specific nanorelief reinforcing particles may be formed and by introducing into the polymer matrix of pore formers. For example, the structure of polysulfone fibers with porogen fragments comprises nano- and micro-sized range, which promote infiltration of the matrix binder and increase the proportion of the mechanical component adhesive interaction at the interface [4, 9, 12].

Thus, driving technological factors in the preparation of the dispersed particles and the direction of the modification, realization of special morphology and the energy state of the surface layer defining the mechanisms and kinetics of interfacial processes in composite materials for various applications. Obviously, the choice of technology activation of dispersed particles of modifiers is a multifactorial problem, including not only the materials science, but also economic and environmental aspects.

Of particular interest are technologies that combine several mechanisms for modifying the surface layer of the dispersed particles, ensuring the simultaneous effects of both mechanical (thanks to effect of flowing in the micro-nano-relief of the surface layer) and adsorption (due to the intensification of physical and chemical processes of interfacial interactions) and structured (by forming special structure of the boundary layer) factors on the mechanism and kinetics of interfacial processes in composite materials. However, these factors can occur at different stages of the process - the preparation of components, mixing them, during processing of the composite article while modifying special treatment products to impart the specific parameters of service characteristics.
For a reasonable choice of composition, size modifying particles with sizes microrange values, it is necessary not only to evaluate the energy activity in the parameter maximum thermally stimulated current (TSC) in a certain temperature range, the corresponding technological modes of production and processing of the composite, but to optimize the process conditions create a surface nanorelief layer, which will generate a boundary layer with mechanical and adsorptive implemented components adhesion strength. Estimates of the dimension of the parameter surface morphology \( L_0 \) providing the necessary action modifying particles, it is advisable to carry out using the expression \( L_0 = 230 \cdot \theta_D^{-1/2} \)
, where \( \theta_D \) - the Debye temperature of the sample material for the semi-finished product, which is obtained from modifying particles. Experimental studies carried out with the various components of the composition, structure and technology of show the adequacy of the size parameter \( L_0 \) obtained using the proposed analytical expression, literature data [23-26].

Among the promising areas of particular target modification components is their mechanochemical activation under specified conditions the energy impact [1, 2, 19-34]. Due to mechanical stress certain intensity is ensured not only the formation of the active sites of the surface layers of the matrix and modifying components, and their interaction with the formation of the boundary layer of the combined product of optimal structure.

The research allowed to offer effective approaches to optimal selection of dispersed particles of high-matrix modifiers:

1. It is advisable to use fine particles of micron range mainly developed morphology of the surface layer formed nanoscale components of different composition and structure;
2. The ratio of geometrical parameters of the components of the surface layer and the amount of fine particles must be determined using physical criteria characterizing nanostate selected material objects (matrix modifier);
3. In order to ensure effective action modifying fine particles need to give particular energy state due to the combined effect of the structural and chemical, dimensional and technological factors. Choosing the prevailing factor determined by a combination of operational, energy, economic and environmental parameters that determine the effectiveness and appropriateness of industrial application in accordance with the terms of reference;
4. When choosing a method of activation of superfine particles provides an optimum modification, it is necessary to establish the prevailing mechanism of formation of the transition (boundary) layer of a given structure and parameters of strength and adhesion characteristics and unconditional implementation of the principle of "reasonable sufficiency" in relation to a particular combination of material science, environmental and economic factors;
5. The greatest prospects to create functional composite materials and their production tonnage based on macromolecular matrices have dispersed particles derived from natural compounds laminate, the frame, the chain-like fibrous structure and natural, synthetic and semi-finished artificial using conventional and special technologies for the formation of the morphology surface layer with nanoscale components with an optimum level of energy activity;
6. For composites based on high viscosity and high melting matrix preferably using technology joint mechano-chemical activation of components and multi-level modification using particles of different composition, structure and dispersion.

Practical testing of the proposed methodological approach was implemented to create composite materials based on thermoplastic matrices and greases for heavy-duty friction units of machines and technological equipment used at the enterprises of mechanical engineering, building industry, chemical and mining industries.

For the development of composite materials for the application of tribological coatings used primary and recycled thermoplastic polymer matrix produced tonnage, including domestic manufacturers - PA 6, HDPE, PP. Modifying the matrix polymers functional components (tripoli, flint, kaolinite, UPTFE, HDPE) was performed by mechanochemical activation (MA), followed by grinding at cryogenic temperatures (-198 °C). The coatings are produced by fluidized bed. Comparative studies have shown that compounds designed not only inferior to similar imported PA 11 («Rilsan», France), but also significantly superior in its durability. This developed on the basis of the domestic polyamide 6 (JSC "Grodno Azot") compositions of composite materials have a value of 3 - 5 times lower than the imported counterpart. Composition of mechanically activated composites components have been successfully tested in the construction of drivesharts trucks, lathe chucks, produced by JSC "Belcard" and JSC "BelTAPAZ." Compositions and technology of multilayer coatings on the basis of solid and highly rigid substrate formed by deposition from the gas phase active. In order to optimize the parameters of strength characteristics of the sub-layers of diamond-like carbon (APT) and the titanium compound (TiCN, TiAIN) proposed treatment of microwave radiation (microwave) with a wavelength \( \lambda = 12.25 \) cm, the frequency of 2450 MHz. On the sub-layers with high hardness settings applied by dipping and rubbing (rotaprintny method) layers of fluorinated oligomers ("Foleoks") and polymer-oligomeric products termagodzhanicheskikh synthesis (UPTFE). Composite multi-layer coatings with activated substrates based on APT, TiCN, TiAIN effective for use as an anti-antirazgarnyh and in the construction of the friction units of precision tooling (lathe chucks) and molds for the manufacture of non-ferrous metals produced at UP "Tvesslit". The compositions of multilayer composite coatings based on titanium compounds (TiN, TiCN, TiAIN) and fluorinated oligomers for use on metal working tools (drills, taps, milling cutters, broaches, etc.), Used in the manufacture of automotive components, lathe chucks and mining equipment at JSC "Belcard", JSC "BelTAPAZ", JSC "SIPR with OP".

Activity dispersed particles subjected to energy shocks, manifested in the developed morphology of the surface layer and the presence of uncompensated charge with a long relaxation time, allowed to develop effective formulations of lubricants and greases for heavy-duty friction units on the basis of industrial products.

With the introduction of fine particles, activated by thermal, laser or mechanochemical action, in the lubricating composition of the charge formed clusters that improve the load-carrying capacity and thermal stability of the separating layer in the area of frictional contact. The compositions of lubricating oils, hydraulic fluids and greases for use in the construction of automotive components (brake chambers, drive shafts), and lathe chucks for metalworking equipment. Introduction to the base composition of nanoscale products obtained laser or thermal ablation of PTFE in combination with activated silicate-containing particles (SiO2, flint) to stabilize the viscosity of the damping fluid based on mineral oil in the temperature range 25 - 80 °C, increases resistance to galling lathe chucks drive unit 1.5 - 2.0 times and resource needle bearing crosses the propshaft trucks MAZ, BelAZ, KAMAZ. The compositions have been testing at the leading enterprises of the Grodn region (JSC "Belcard", JSC "BelTAPAZ") and recommended for implementation.

4. Conclusion

The features of the selection modifiers disperse macromolecular matrix composite materials to create the specified functionality. The role of the energy state due to the peculiarities of the composition, crystal-chemical structure and morphology of the surface layer of dispersed particles used as a modifier to achieve the desired technical effect is significant.

Methodological approaches to the process of selecting the components and functional materials and methods of activation, based on the provision of prevailing flow mechanism of interfacial interactions and the formation of the optimal structure of the boundary layer.

We consider the practical application of methodological approaches designed to create composite materials for the manufacture of products used in engineering, construction industry and mining.
5. Literature

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