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NANOCOMPOSITE MATERIALS BASED ON THERMOPLASTIC BLENDS FOR THE TECHNOLOGICAL EQUIPMENT WITH A LONG SERVICE LIFE

НАНОКОМПОЗИЦИОННЫЕ МАТЕРИАЛЫ НА ОСНОВЕ СМЕСЕЙ ТЕРМОПЛАСТОВ ДЛЯ КОНСТРУКЦИЙ ТЕХНОЛОГИЧЕСКОГО ОБОРУДОВАНИЯ ПОВЫШЕННОГО РЕСУРСА

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Abstract: *The composite materials based on polymer and oligomer blends with different thermodynamic compatibility have been developed. It is shown that for polymer and oligomer blends of products formed as result of the thermogasdynamic synthesis of fluorine-containing compounds, the ability of oligomeric matrix to multiply deformation and alternating transfer is the most important. In polymer-polymer systems formed in a melt by various technologies the most important factor is the structure of the boundary layers determining the parameters of the stress-strain and tribological characteristics of the composites. The effect of physical compatibilization during the introduction of nanoscale metal-containing and carbon-containing particles into the blend compositions has been established. This effect promotes the thermodynamic compatibility and resistance to the action of thermal-oxidative medium on composites.*
***KEYWORDS**: NANOCOMPOSITE MATERIALS, BLENDS, COMBINATION, STRUCTURE*

1. Introduction

In the nomenclature of functional polymer composite materials the important place have polymer and oligomer blends. The combination of a binding agent (matrix) with a polymer or oligomer modifier leads to required performance parameters achievement that can provide a given resource of products in specific application conditions [1 – 4]. The most significant problem of achieving stable parameters of the structural characteristics of polymer blends determining the load-speed and temperature range of application of products in static and dynamic designs of units and aggregates with various functionalities is overcoming the thermodynamic incompatibility of polymer and oligomer components. The thermodynamic incompatibility is due to the features of the composition, structure of the macromolecule, difference in the rheological, thermophysical and other characteristics.

In this regard, it is reasonable to investigate scientific approaches to formation of polymer blends with given performance characteristics by means of increasing thermodynamic compatibility using the nanostate phenomenon. Therefore, physicochemical and structural transformations during combination of polymer and oligomer components with close molecular structure and using nanoscale functional modifiers with various formula and structure have significant scientific and practical interest.

2. Research methods

The interphase processes in systems obtained by combining thermoplastic polymer and oligomer components under various technology impact, physicochemical and tribochemical transformations during the processing of composites and the using of products from them in metal-polymer constructions with various functionality are considered.

As components of the blend composite materials we used the most common in materials science and technology of polymer materials thermoplastic polymers and oligomers: aliphatic polyamides – PA6, PA6.6, (Grodno Chimvolokno JSC, Belarus) PA66/6 Grilon TSS/4, PA12 Grilamid L20 (EMS-CHEMIE AG, Switzerland), PA11 Rilsan (Arkema, France), polyolefins – polypropylene (PP), low-density polyethylene (LDPE), high-density polyethylene (HDPE) produced by Polymir JSC, Belarus, polyesters – polyethylene terephthalate (PET), polybutylene terephthalate (PBT) primary (Mogilev Chimvolokno JSC, Belarus) and regenerated (Belvtorpolymer JSC, Belarus), polyacetals – copolymer of formaldehyde with dioxolane (POM copolymer), fluorine-containing compounds – polytetrafluoroethylene F-4 and F-4M (Galogen JSC, Russia), fluorinated oligomers "Foleoks" (Federal State Unitary Enterprise "Institute of synthetic rubber", Russia), products of thermogas dynamic synthesis of PTFE under the brand name "Forum" (Institute of chemistry Far East Branch of the Russian Academy of Science, Russia).

For the control of structure and operating characteristics parameters of the composites and products thereof we used the dispersed, including nano-sized particles of carbonaceous – colloidal graphite preparation C-1 (CGP C-1), ultradispersed diamond (UDD), carbon nanotubes (CNT) produced by CJSC "Sinta" and the A. V. Luikov Heat and Mass Transfer Institute of National Academy of Science of Belarus, silicon (clay, tripoli) and metal (copper formate) compounds produced by original technology of manufacturers.

The combination of the components was carried out by extrusion technology using a twin-screw extruder, thermomechanical mixing in the material cylinder of injection molding machine Battenfeld HM series (WittmannBattenfeld GmbH, Germany) and the deposition of particulate matter in fluidized layer on a solid substrate.

The physical and chemical processes at the interface in the blend composites and metal-polymer systems were investigated using modern methods of analyses: IR spectroscopy (Tensor-27), X-ray diffraction (Dron 3.0), differential thermal analysis DTA (Thermoscan 2), atomic force analysis (AFM), scanning electron (SEM) and optical (OM) microscopy using with original equipments (SEM microscope Mira, Tescan, AFM microscope NT-206, metallographic inverted microscope MDS). Energy state of the components was investigated by thermally stimulated currents spectroscopy (TSC-analysis).

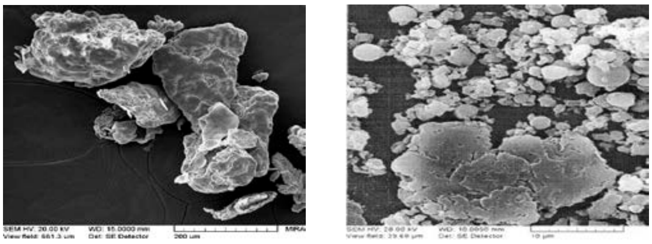
The parameters of stress-strain, tribological, adhesion characteristics of composite materials and coatings was determined by standard techniques on the specialized equipment – tensile-testing machine Z010 Zwick, tribometer FT-2. The rheological parameters of components and blends were examined by melting flow rate meter IIRT-119.

3. Results and discussions

A complex analysis of the composition and structure of the products of the thermogasdynamic synthesis of fluorine-containing compounds, which are produced under the trademark "Forum", have been conducted [5].

Morphological analysis of industrial powder products PTFE F-4 (F-4M) and UPTFE (Forum), conducted by SEM (Fig. 1), indicates the characteristic areas that assume a different structure of particles obtained by thermogasdynamic synthesis (TGD-synthesis).

The developed morphology of PTFE particles is due to the features of synthesis from the gaseous monomers (tetrafluoroethylene) in the presence of polymerization catalysts at certain temperatures and pressures in the reaction volume. The pronounced spherical shape of the particles of UPTFE and their high plastic deformability indicate their polyfraction structure. We made an assumption that the UPTFE have polyfraction structure including oligomer (low-melting) fractions with a melting temperature of 333 – 730 K. The polyfraction structure is due to processes of ablation.



a b

Figure 1. – The characteristic morphology of industrial PTFE (F-4) (a) and UPTFE (Forum) particles (b). SEM method

The carried out researches of features of UPTFE structure allowed to offer a model composite system consisting of a set of oligomer fractions and nanoscale polymer particles with different habit – whisker, lamellar, spherical. The adequacy of the proposed model is confirmed by studies of re-deformation and alternating transfer processes during the relative axial displacement of substrates from inert materials (silicate glass). The presence in the UPTFE of oligomer fraction acting as a matrix ensures its fixing and repeated deformation in the microroughness of the substrate and the plasticizing effect of surface layers of the industrial PTFE (F-4 and F-4M) dispersed particles. During the processing such particles by the products of sublimation of UPTFE at temperatures of 473 – 573 K for 0.1 – 0.5 hours or during mixing with UPTFE under mechanochemical activation are formed the facilities for improving of the components compatibility and monolithization at a temperature of 623 – 643 K with the formation of a low-defect structure. The presence of oligomer and polymer components in the modifier promotes the effect of increasing the strength parameters by 1.1 – 1.2 times and the wear resistance by 1.3 – 1.5 times for the industrial polytetrafluoroethylene F-4 and F-4M [5].

Taking into account the variety of the functionality and design of the technological equipment components, shut-off and control valves and automotive components were considered the features of combining components with different potentials to interfacial interaction: aliphatic polyamide blends (PA6, PA6.6, PA66/6, PA11, PA12), polyamide and polyester blends (PET, PBT), primary and regenerated polyolefins and thermoplastic elastomers, fluorine-containing compounds (UPTFE).

During the thermomechanical combination of polyesters (PET and PBT) and polyamides in the material cylinder of the injection molding machine the heterophase structures with pronounced phase separation are generate due to differences in molecular structure, rheological and thermophysical characteristics. It was found that the introduction into the composite PET (5 – 10 wt. %) and PA6 of 5 – 20 wt. % dispersed particles of layered silicates (mica, talc) contributes to an increase wear resistance by 1.3 to 1.5 times and adhesion strength by 1.2 to 2.4 times of the coatings [6].

The features of the structure and performance characteristics of polymer blends based on components with high thermodynamic compatibility – aliphatic polyamides and polyolefins are investigated [7].

The introduction to the matrix polyamide (PA6, PA6.6, PA66/6) of modifiers (PA12, PA6) allows to realize the advantages of each component of the blends for the attainment of the technically significant effect of increasing the strain-stress characteristics (Table 1). An important feature of polymer blends based on aliphatic polyamides is the high homogeneity of the structure caused by the formation of interphase layers from close-structure macromolecules (Fig. 2).

In contrast to blends with different molecular structure of components (PA6 – PET, PA6 – PBT, PA6 – POM copolymer) the blends of aliphatic polyamides (PA6, PA6.6, PA66/6, PA12) do not have a pronounced interface.

During the introduction to composite material of the nano-sized particles (UDD, CNT, CGP C-1) the values of the Young's modulus (E) parameters are increase from 2207.6 – 2647 MPa to 2797.8 – 2984.7 MPa and tensile strength (σ) from 51.9 – 107.3 MPa to 109.7 – 115.1 MPa. Thermo-mechanically combined polyamides is reasonable to use as binding of structural and tribotechnical materials.

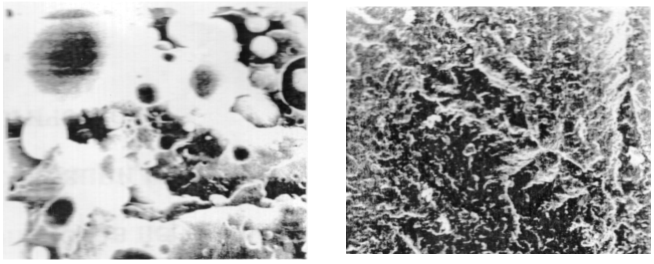


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Figure 2 – The characteristic morphology of the composite materials: PA6 – POM copolymer (a) and PA6.6 + PA6 (b). Samples are obtained in a liquid nitrogen. Content of components is 50 : 50 wt.%

During combining of polyolefins (PP, HDPE, LDPE) the composites with high phase homogeneity and controlled rheological characteristics are formed. The effect is also to be achieved by using the regenerated components. This effect makes it possible to obtain materials for products with various functionality.

The tribotechnical and protective characteristics of rotaprint coatings based on a fluorine-containing polymer-oligomer blends with a thickness of 5 – 10 μm formed on the components of metal-polymer systems are investigated. It has been established that the presence of an oligomer component in the UPTFE composite coating provides the necessary level of adhesion and the ability to re-deform. These characteristics reduce the intensity of corrosion-mechanical wear. In the friction zone the separating layer with the properties of alternating transport is formed. This layer outperforms and has better anti-wear action than the thin films of fluorine-containing oligomers "Foleoks", metal phosphates and titanium nitride layers.

The effectiveness of the anti-wear action of rotaprint coatings of UPTFE is improved by modifying the composition of 0.01 – 0.1 wt. % nano-sized particles of carbon-containing components that have the function of reinforcement additive. Polymer-oligomer composites based on UPTFE are effective when used as rotaprint coatings for splined joints of cardan shafts and sealing units of shut-off and control valves.

The composite materials based on blends of aliphatic polyamides (PA6, PA6.6, PA12) and (PA6, PA11) have been developed. They are used as structural and tribotechnical materials for friction units of automotive components and technological equipment. The modifying of matrix thermoplastics (PA6.6, PA6) by the thermodynamic compatible components (PA11, PA12) in combination with nanoscale particles provides an increase of strain-stress characteristics. At the same time, the variation of the modifying polyamide content makes it is possible to control the parameters of rheological characteristics and hydrophobicity. An important performance property of the developed construction materials based on polyamide blends is high resistance to the action of thermal-oxidative environment. This property is caused by the action of nanosized particles as a non-chain stabilizer [8].

The developed composite materials based on the regenerated polyolefins (PP, HDPE, LDPE) produced by JSC "Belvtorpolimer" are not inferior to the primary materials (produced by Stavrolen, Ltd) at the parameters of strain-stress characteristics and have higher impact toughness and frost resistance (243 – 233 K).

***Table 1** – Parameters of strain-stress characteristics of composite materials based on aliphatic polyamides*

Materials	E, MPa	σ, MPa	ε, %
PA6	2318,1	65,19	3,8
PA6.6	2647,1	77,70	4,0
PA66/6	2207,6	69,36	4,3
PA12	1226,1	56,35	250
PA6.6(94 wt.%)+PA6(5 wt.%)+PA12(1 wt.%)	2571,1	77,71	4,3
PA6.6(90 wt.%)+PA6(5 wt.%)+PA12(5 wt.%)	2525,2	75,58	5,9
PA6.6(84,5 wt.%)+PA6(10 wt.%)+PA12(5 wt.%)+CGP C-1(0,5 wt.%)	2984,7	78,84	3,9
PA6.6(84,5 wt.%)+PA6(10 wt.%)+PA12(5 wt.%)+CNT(0,5 wt.%)	2797,8	54,19	2,1
PA6.6(84,5 wt.%)+PA6(10 wt.%)+PA12(5 wt.%)+UDD(0,5 wt.%)	2850,5	77,80	3,8

4. Conclusions

The structure and performance characteristics of composite materials based on blends of thermoplastic polymer and oligomer components obtained by various technologies have been studied. The composite materials based on blends of aliphatic polyamides (PA6, PA6.6, PA66/6, PA12, PA11), polyolefins (PP, HDPE, LDPE) and fluorine-containing compounds (UPTFE, PTFE) with high parameters of strain-stress, adhesion, tribotechnical characteristics for the manufacture of products and coatings for technological equipment, automotive components, shut-off and control valves.

The structure and composition features of thermal treatment products of block polytetrafluoroethylene (PTFE) in a protective environment at the temperature range 623 – 673 K have been studied. The presence of oligomer and polymer components in the heat treatment products (UPTFE) forming a polyfraction blend of ablation products and recombination of gaseous fractions of the thermal degradation of the block semifinished product of UPTFE was established by the DTA, IR spectroscopy, AFM and SEM methods. Polymer-oligomer blends of heat-treated products of polytetrafluoroethylene have the ability to repeatedly re-deform without destroying and subliming oligomer fractions. These blends can be used as components for tribotechnical materials and coatings and processing additives for processing of polymer blendes based on thermoplastic primary and regenerated (PA6, PA6.6, PET, PBT, PP, HDPE) matrices.

The features of the structure and parameters of strain-stress and tribological characteristics of the composite materials obtained by technologies of thermomechanical combining in a twin screw extruder, processing in injection molding machine with a screw plasticator and deposition of powdered fractions by the heat treatment at the melting temperatures of granular and powdered thermoplastic components with close structure of the molecular chain – polyamides (PA6, PA6.6, PA66/6, PA12, PA11) and polyolefins (PP, HDPE, LDPE). Using IR spectroscopy, DTA, ACM and SEM methods it was found that in polymer-homologue blends which have a different thermophysical and rheological characteristics in comparison to blends of thermodynamically incompatible polymers (PA6 – PET, PA6 – PBT, PA6 – HDPE) is formed heterophase structure with high homogeneity and strength due to the formation of transition layer with a few defects as a result of the mutual diffusion of macromolecules. Under the modifying of polymer blends by nanoscale particles of carbon and silicon containing compounds (UDD, CGP C-1, CNT) in an amount of 0.001 – 1.0 wt. % the formation of boundary layers is intensified due to the formation of physical adsorption bonds between the macromolecules of the combined components.

The structural and tribotechnical materials based on blends of primary and regenerated thermoplastics of the polyamide (PA6, PA6.6, PA66/6, PA12), polyesters (PET, PBT) and polyolefins (PP, HDPE, LDPE) containing nanosized particles of carbon (CGP C-1, UDD, CNT), silicon (clay, talc, mica), metal-containing (copper) modifiers at doping (0.001 – 1.0 wt. %) concentrations with parameters of deformation-strength characteristics by 1.1 – 1.2 times exceeding the parameters of the matrix thermoplastics have been developed. The developed composites based on polymer blends are effective for manufacturing structural elements for automotive components and metal-polymer belt conveyors used in various industries.

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