THE COMPATIBILITY FACTOR IN MATERIAL SCIENCE OF MIXED ENGINEERING NANOBLENDS

ФАКТОР СОВМЕСТИМОСТИ В МАТЕРИАЛОВЕДЕНИИ СМЕСЕВЫХ МАШИНОСТРОИТЕЛЬНЫХ НАНОКОМПОЗИТОВ

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Abstract: *Features of the structure of blends obtained by thermomechanical blending of thermoplastic components with different molecular structure are considered. The possibility of formation of structures with different levels of ordering (from heterophase structure with a pronounced boundary between the components to the macrogomogeneous structure with high compatibility of matrix and modifying components) is shown. Under injection of nanosize particles with different chemical composition into the blends, a synergistic effect of simultaneously increasing the parameters of tensile stress-strain and tribotechnical characteristics of items and its resistance to thermal oxidation is achieved. Nanosize particles in the active state perform the function of a physical compatibilizer, forming a cross-linked structure with physical bonds in the volume of the composite. The engineering nanoblends with increased performance parameters have been developed.*

KEYWORDS: NANOBLENDS, COMPATIBILITY, NANOSIZE PARTICLES, SYNERGISTIC EFFECT, PHYSICAL COMPATIBILIZER

1. Introduction

In the brand assortment of engineering materials a blends based on thermoplastic components with different chemical composition, structure, molecular weight are occupied a special place. Managing the compatibility parameters of the components of blends by using special technologies for producing composites or functional ingredients that regulate the intensity of interfacial interaction processes (compatibilizers) can be form a structure with set-up parameters of the organization that ensures the achievement of the required performance characteristics of the products under given conditions of their application [1-3].

At the same time, the structure of the blend in the depending on operational requirements for the products varies according to the homogeneity parameters – from the macrogomogeneous with the pronounced phases of the matrix and modifying components [3] to the macrohomogeneous one, in which, as a result of complete thermodynamic compatibility, the modifying component in the matrix is dissolved [1, 2]. Both fundamentally different types of structure of blends have their own peculiarities in the implementation of the specified parameters of performance characteristics, have found wide application in engineering practice and are not antagonists. Therefore, further development of scientific ideas on the mechanisms and kinetics of the formation of the structure of blends with a given level of ordering is have considerable interest for materials science and technology of polymeric functional materials. At the same time, both main types of blends with different levels of thermodynamic compatibility of components are characterized by the commonness of the basic features, the most important of which is the structure of the boundary layers of composites, which largely determines the parameters of the product performance characteristics. In the structure of the optimal level of ordering, the boundary layer between the components must possess the necessary parameters of stress-strain characteristics that can be realized only when controlling the intermolecular interaction processes using different approaches. In this aspect, studies of the influence of nanosize particles on interphase interaction processes are of particular interest, since their special energy state suggests the possibility of forming the structure of boundary layers with increased parameters of characteristics [4, 5].

The purpose of this paper is to evaluate the role of nanosize particles of various types in the formation of the structure of blends with different levels of thermodynamic compatibility.

2. Research methods

For the research we used polymer materials widely applied in engineering for the production of functional products of various design versions – polyamide 6 (PA 6) and polyethylene terephthalate (PET) produced at JSC Grodno Azot and JSC Mogilev Khimvolokno. To modify the matrix components were used aliphatic polyamides PA 11, PA 12 in the industrial supply state, fine-grained particles of carbon-containing components (colloidal graphite preparation KGP C-1, carbon nanotubes CNT, products of explosive synthesis – charge) and layer silicates – mica (phlogopite) and talc. The components were blended using a twin-screw extruder (Compex), a material cylinder of an injection molding machine with a screw extruder (Demag, Battenfeld), and a fluidized bed coating plant. The parameters of stress-strain, tribological and adhesive characteristics of composites were evaluated by using standard techniques on solid samples and coatings.

3. Results and discussions

Analysis of the physical and mechanical characteristics of blends obtained by thermomechanical blending of thermoplastic components PA6 + PET shows its nonmonotonic dependence on chemical composition (Fig. 1). In the range of small concentrations of the modifier (up to 0.5-1.0 wt. %) the effect of increasing the tensile strength, bending and wear resistance is observed. Earlier, similar effects were noted for thermoplast-thermoplast composites [3]. The effect of increasing the strength and tribological characteristics is probably due to the formation of modifying phase reinforcing aggregates (PET and PA, respectively) in the matrix and the processes of copolymerization mechanochemical reactions during the composite formation. This reactions lead to the formation of a copolymer product with increased resistance to external influences. Analysis of the morphology of the cleavage of samples cooled in liquid nitrogen confirms the presence of modifying phase aggregates with dimensions of 0.5-10 μm, depending on the ratio of composites in the mixture. PET and PA particles are close to spherical, and PA and PET particles are more various in shape and size (Fig. 2). At the ratio of components is close to 50:50 wt. % the phase inversion is observed, that to lead to a significant decrease of all parameters of physical and mechanical characteristics.

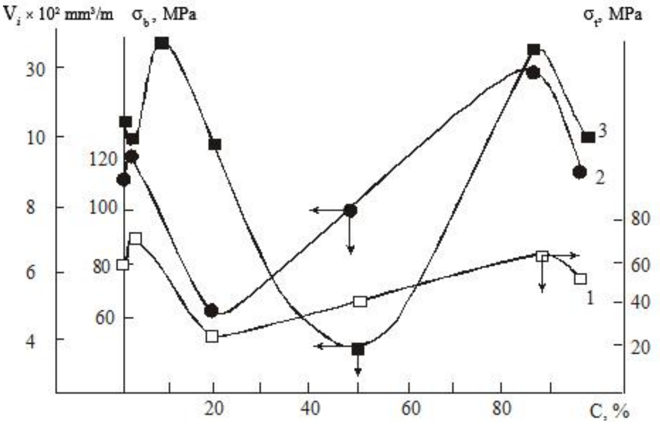

Fig. 1 Dependence of the tension (1), bending (2) stress and abrasion factor (3) on the content of PA 6 in PET

Thus, the traditional technology of thermomechanical blending provides the production of composite materials based on PA 6 and PET with high service characteristics. Such materials can be successfully used as binary matrices for engineering materials of various functional purposes include tribotechnical. The advantage of combined PA/PET matrices is a higher resistance to moisture and operating factors compared to polyamides, which causes an increase in the operational range of their use.

When introducing layered silicates into the composite PA 6 / PET mixture, it is possible to control the compatibility parameters of the components due to the influence of the factor of their increased energy activity [4].

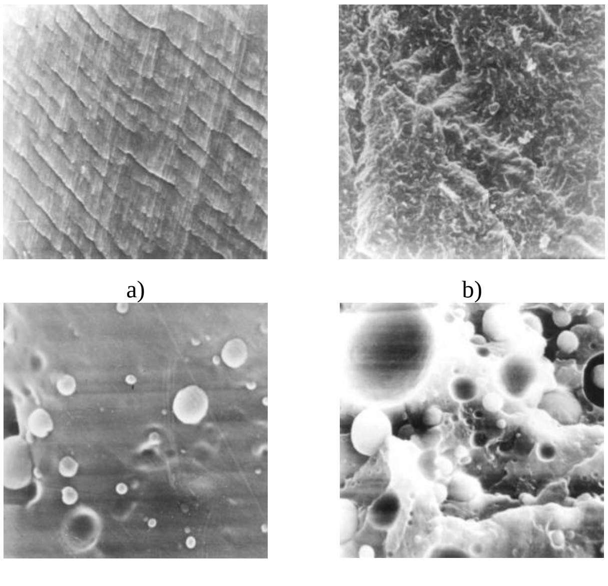

***Fig. 2** A typical view of cleavage in liquid nitrogen of PA 6 (a), PET (b) and composite materials PA 6 + 10 wt. % PET (c) and PA 6 + 50 wt. % PET (d)*

Modification of matrix polymers and blends (PA 6/PET) by layered silicates significantly increased their wear resistance and significantly reduced the coefficient of friction during operation without the supply of external lubrication (Fig. 3). It is obvious that during the blend formation is taking place the thermal degradation of silicate microparticles with the formation of nanosize plate aggregates [4], into the interlayer space of which the macromolecules of the matrix and modifying components penetrate.

The energy state of the plate aggregates determines the formation of a cross-linked structure with physical bonds that contribute to the increase of the operational characteristics parameters.

The carried out researches have allowed to develop blends PA 6 + 10 wt. % PET and PET + 10 wt. % PA 6. Under introduced into the matrices 5-20 wt. % dispersed particles of mica the synergistic effect of increasing the parameters of tribological and adhesion characteristics while maintaining high values of the parameters of stress-strain characteristics, estimated by the criterion $\sigma_t \geq$ 62-65 MPa is achieved.

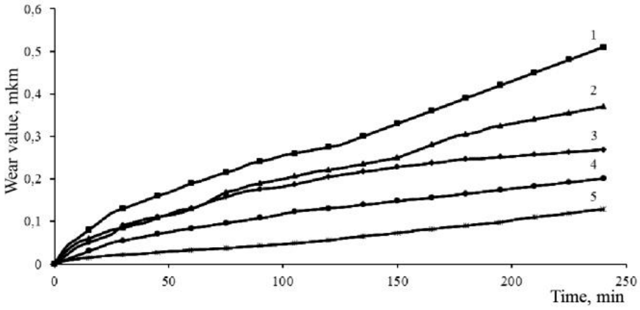

***Fig. 3** Dependence of the wear value of blends based on PA 6 on the time for the "finger-disk" test at p = 2.8 MPa, V = 1.1 m/s: 1 – PA 6; 2 – PA 6 + PTFE (90:10); 3 – PA 6 + talc (90:10); 4 – PA 6-L-FG30; 5 – PA 6 + mica (90:10)*

To control the compatibility parameters of components in composites based on aliphatic polyamides, carbon-containing particles of various production technologies – KGP C-1, CNT, charge, were used.

The data in Tables 1 and 2 show the effectiveness of the action of highly dispersed particles in blends based on aliphatic polyamides. A probable mechanism of modifying effect of carbon-containing modifiers is the formation of physical adsorption bonds in the transition layer of the composite according to the ideas presented in [4].

***Table 1: Parameters of stress-strain characteristics of blends based on the aliphatic polyamides (bending tests)**.*

Chemical composition of blend, wt. %	Characteristics value		
	E, MPa	σ_b, MPa	ε_b, %
PA6,6(84,5%) + PA6(10%) + PA12(5%) + KGP C1(0,5%)	2984,7	114,7	6,7
PA6,6(84,5%) + PA6(10%) + PA12(5%) + CNT(0,5%)	2797,8	109,7	6,1
PA6,6(84,5%) + PA6(10%) + PA12(5%) + шихта(0,5%)	2850,5	115,1	6,8

***Table 2: Parameters of stress-strain characteristics of blends based on the aliphatic polyamides (tensile tests)**.*

Chemical composition of blend, wt. %	Characteristics value	
	σ_t, МПа	ε_t, %
ПА6,6(84,5%) + ПА6(10%) + ПА12(5%) + КГП С1(0,5%)	78,84	3,9
ПА6,6(84,5%) + ПА6(10%) + ПА12(5%) + УНТ(0,5%)	54,19	2,1
ПА6,6(84,5%) + ПА6(10%) + ПА12(5%) + charge(0,5%)	77,78	3,8

Under injection of nanodispersed carbon-containing particles into the composite, which are mainly located in the interspherilite regions, the effect of increasing the resistance to thermal-oxidative destruction increases due to the formation of additional physical bonds of the adsorption type (Fig. 4).

In our opinion, the significant contribution of carbon-containing particles to the resistance to thermal oxidative aging of composites based on aliphatic polyamides is due to the energy state of nanoscale particles, which facilitates the formation of intermolecular physical bonds with the active centers of the macromolecule and a decrease in their activity in the processes of affinity for oxygen.

Thus, nanosize carbon-containing particles serve as a physical compatibilizer, contributing to the formation of a more perfect composite structure at different levels of organization.

A similar effect of the structuring effect of nanosize particles such as natural minerals (clays, zeolites) and diamond processing products is established in the works of Prof. A.A. Okhlopkova and co-workers [6] for the modification of polytetrafluoroethylene.

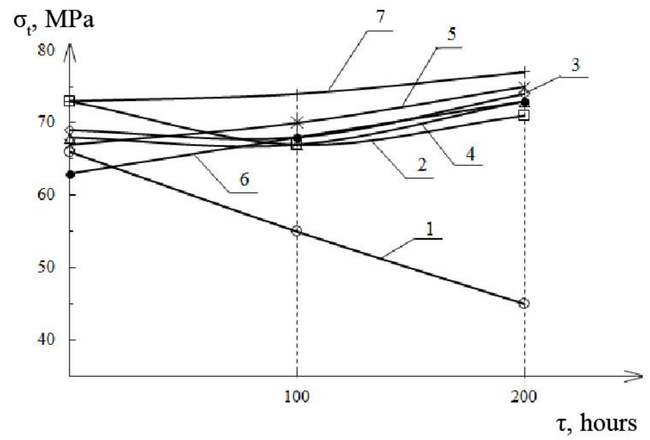

Fig. 4 *Dependence of the tensile strength parameter on the time of thermal oxidation at 423 K (150 °C) for composites:*
1 – PA 6.6-L;
2 – PA6.6 (94 %) + PA6 (5 %) + PA12 (1 %);
3 – PA6.6 (90 %) + PA6 (5 %) + PA12 (5 %);
4 – PA6.6 (85 %) + PA6 (10 %) + PA12 (5 %);
5 – PA6.6 (84.5 %) + PA6 (10 %) + PA12 (5 %) + KGP C-1 (0.5 %);
6 – PA6.6 (84.5 %) + PA6 (10 %) + PA12 (5 %) + CNT (0.5 %);
7 – PA6.6 (84.5 %) + PA6 (10 %) + PA12 (5 %) + charge (0.5 %)

Thus, the modification of blends based on aliphatic polyamides by nanoscale particles of different chemical composition, 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 for the realization of the synergistic effect is due to the interaction of active centers of nanoscale particles with the centers of polymeric macromolecules with the formation of adsorption type bonds [3-5]. The formation of such bonds changes the intensity of intermolecular interaction in composites based on mono- and blend matrices, which is manifested in the transformation of the structure of the composite at the intermolecular, supramolecular and interphase levels. Due to multi-level structural modification, resistance to the influence of operational factors, including to the processes of tribotechnical interaction in metal-polymer systems and elevated temperatures in the air environment, increases.

4. Conclusions

The established regularities in the formation of the structure of blends based on thermoplastic polymers made it possible to develop composite materials for the manufacture of items of various metal-polymer systems – coatings for friction joints of cardan shafts and turning chucks, elements of shutoff and control valves used in low pressure pipelines [7].

The established regularities can be realized with the use of industrial technological equipment – mixers, extruders, injection molding machines. That allows using the obtained data in practical material science.

5. References

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