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Structure Formation and Macrorheology of Nanofilled Composites of Polypropylene/Co-polyamide/Mixed Oxide

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The influence of the content of additive of the nanosize combined substance aluminium oxide/silica on the formation of microfibrillar structure within the thermodynamically incompatible blend of polypropylene/co-polyamide (PP/CPA) is studied. As established, nanoparticles (NPs) of Al_2O_3/SiO_2 are an effective modifier in the entire studied range of their concentrations (0.1–3.0 wt.%). The mixed oxide exhibits a synergistic result: the average diameter of PP microfibrils ($\bar{d}$) decreases by ≅ 2 times. At the same time, the content of nanofiller is only of 0.1 wt.% that is an order of magnitude less than when using NPs of its individual components. The most subtle and homogeneous morphology is formed in the composition containing 1.0 wt.% of the modifier: the value of $\bar{d}$ has a minimum value (1.2 μm *versus* 4.0 μm for the original blend), the share of microfibrils is the maximum (97.0%), and the value of the index of variability (dispersion) decreases by ≅ 5 times. As shown, the change in microrheological processes in the presence of a nanoadditive affects significantly the macrorheological characteristics of melts of filled polymer dispersions. Mixed oxide nanoparticles increase the degree of deviation from the Newtonian flow regime of three-component systems. The formation of anisotropic structures (PP microfibrils) in mixtures of PP/CPA/mixed oxide causes a drop in the effective viscosity compared to the melts of the original components. At the same time, the elasticity of the melts of the modified compositions increases and the values of the extrudate expansion coefficient (B) reach values higher than the additive ones. The indicators of the maximum deformation of the melt jet of nanofilled systems in the longitudinal tensile field ($F_{\max}$) also increase. The dependences of B and $F_{\max}$ on the composition of the mixture have an extremum at a mixed oxide content of 1.0 wt.% due to the formation of PP microfibrils with the highest degree of anisotropy.

Досліджено вплив вмісту домішки нанорозмірної комбінованої речовини оксид Алюмінію/кремнезем на формування мікрофібрилярної структури в термодинамічно несумісній суміші поліпропілен/співполіамід (ПП/СПА). Встановлено, що наночастинки (НЧ) Al_2O_3/SiO_2 є ефективним модифікатором в усьому дослідженому діяпазоні їхніх концентрацій (0,1–3,0 мас.%). Змішаний оксид проявляє синергічну дію: середній діяметер ПП-мікрофібрил ($\bar{d}$) понижується у ≅ 2 рази. Водночас вміст нанонаповнювача складає всього 0,1 мас.%, що на порядок менше, ніж за використання НЧ окремих його складових. Найбільш тонка й однорідна морфологія формується у композиції, що містить 1,0 мас.% модифікатора: величина $\bar{d}$ має мінімальне значення (1,2 мкм проти 4,0 мкм для вихідної суміші), доля мікрофібрил є максимальною (97,0%), а величина показника варіябельности (дисперсії) зменшується у ≅ 5 разів. Показано, що зміна мікрореологічних процесів у присутності нанодомішки значною мірою впливає на макрореологічні характеристики розтопів наповнених полімерних дисперсій. Наночастинки змішаного оксиду підвищують ступінь відхилу від Ньютонового режиму течії трикомпонентних систем. Формування анізотропних структур (ПП-мікрофібрил) у сумішах ПП/СПА/змішаний оксид зумовлює падіння ефективної в'язкости порівняно з розтопами вихідних компонентів. Водночас еластичність розтопів модифікованих композицій підвищується і величини коефіцієнта розширення екструдату (B) сягають значень, вищих за адитивні. Зростають також показники максимальної деформації струменя розтопу нанонаповнених систем у поздовжньому розтягувальному полі ($F_{\max}$). Залежності величин B і $F_{\max}$ від складу композиції мають екстремум за вмісту змішаного оксиду у 1,0 мас.%, що зумовлено формуванням ПП-мікрофібрил з найвищим ступенем анізотропії.

Key words: polypropylene, co-polyamide, mixed oxide, mixture, melt, morphology, viscosity, elasticity, deformation.

Ключові слова: поліпропілен, співполіамід, змішаний оксид, суміш, розтоп, морфологія, в'язкість, еластичність, деформація.

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1. INTRODUCTION

The addition of mineral nanofillers into the blend of polymers is an effective method of creating universal materials with new functional characteristics. Today, the issues of developing theories and concepts regarding the influence of nanoparticles on the compatibility of polymer dispersions, regulating the morphology and properties of nanocomposites, and creating practical methods of their preparation and potential opportunities are widely researched in the world [1–6]. Such nanocomposites are used as barrier, packaging materials, for the manufacture of car parts, medical devices, computer cases, in biotechnology, in LED, in lithium batteries, *etc*.

Blends of polymers, as a rule, are thermodynamically incompatible, so, the properties of products based on them largely depend on the morphology of the component of the dispersed phase in the matrix. The geometric shape, dimensional characteristics and homogeneity of the distribution of various types of structures in the polymer dispersion are determined by thermodynamic and/or kinetic factors. At the same time, selective localization of nanoparticles in one of the phases or at the boundary of their separation is also an important factor [3, 4]. The main thermodynamic parameter that controls the placement of NPs in the system is the wetting of their surface by component melts [5]. The authors of Ref. [6] showed that, depending on the number of silanol groups on the surface of hydrophilic silicon dioxide in a blend of polylactide/co-polymer of ethylene with vinyl acetate (PLA/EVAC), they accumulated in the dispersed phase, in the matrix (PLA), or in the interfacial space. A reinforced composite was obtained by mixing in a melt PLA polyolefin elastomer and clay modified with silver NPs [7].

A correlation was established between the compatibility of the components, the morphology and mechanical properties of the material, the improvement of which is achieved due to the preferential localization of the modified clay at the boundary of the phase separation. Changing the morphology and reducing the size of the dispersed phase domains in thermodynamically incompatible mixtures of different chemical nature, when natural and organomodified clays are introduced into them, made it possible to increase the mechanical parameters of nanocomposites [8–12].

The simultaneous introduction of natural and modified clay into the PLA/natural rubber (NR) blend creates a continuous morphology, with the natural clay being mainly placed in the matrix, and the organomodified clay in the dispersed phase [12]. Due to the selective localization of both types of clays, a synergistic increase in strength and reduction in brittleness of the PLA/NR composition is achieved (elongation at break is greater than 100%). The thermodynamically balanced distribution of nanoadditives, which is dictated by the wetting parameter, is hindered by the high viscosity of polymer melts. The final localization of NPs in a two-phase polymer system is often determined by kinetic phenomena. Using the example of the PLA/polyethylene/silica mixture, it was established that the selective placement of NPs at the phase separation boundary is characteristic of nanoadditives with a high affinity for one of the components, if they are previously introduced into a polymer with low compatibility. Simultaneous mixing of all ingredients contributes to uniform distribution of NPs in the mixture, and two-stage mixing contributes to preferential localization in one of the phases or on the border of their separation [13]. Different types of polypropylene structures in the polyvinyl alcohol (PVA) matrix were obtained by changing the sequence of adding silver/silica NPs to the composition [14].

With the preliminary introduction of nanoparticles into the PP melt, a dispersed type of structure is formed; when added to the dispersion medium, mutually continuous morphology is formed; with simultaneous mixing of all components, a layered structure of concentrically arranged rings is formed.

Studies on the effect of mineral nanoadditives on the formation of microfibrillar structure in thermodynamically incompatible polymer blends have shown that the morphology of the system depends on the chemical nature of polymers and NPs, their size and content, as well as on the conditions of preparation of compositions [15–27]. Addition in the blend of PP/CPA and PP/PVA of silicas with different specific surface areas and functional groups [17–19], metal oxides [20–22], complex substances Ag/SiO_2, Ag/Al_2O_3 [23,24] and TiO_2/SiO_2 [25, 26] makes it possible to obtain nanofilled fibrils, adjust their dimensional characteristics and the properties of products made from them. All investigated nanofillers have a compatibilization effect, namely, the average diameter of PP microfibrils decreases almost in 2 times, and their mass fraction increases to ≥ 90.0 wt.%. The formation of a finer microfibrillar structure also occurred when thermo- or organically modified montmorillonite was introduced into the PP/polystyrene blend [27]. The diameters of microfibrils, the uniformity of their distribution, and the ratio between other types of structures in the extrudate (particles, films) depend on the content and chemical nature of mineral nanoadditives. Reducing the diameters of nanofilled PP microfibrils and increasing the homogeneity of their distribution contributes to the improvement of the performance characteristics of filter materials (increasing cleaning efficiency and precision). Complex threads based on them have higher strength and dimensional stability. The presence of silver nanoparticles in the structure of microfibrils gives products made of them antimicrobial properties.

The purpose of the work is to regulate the microfibrillar structure of the polypropylene/co-polyamide blend by introducing nanoparticles of the combined aluminium oxide/silica substance and to study its effect on the macrorheological properties of the melts of the modified compositions.

2. OBJECTS AND METHODS OF RESEARCH

The studies were performed using a thermodynamically incompatible blend of PP/CPA with a composition of 30 wt.%/70 wt.%. The dispersed phase was polypropylene of brand TATREN HG 1007 with a melt flow index of 10 g/10 min (230°C/2.16 kg, ISO 1133-1) and a melting point of 169°C. Dispersion medium—PA-6/66 copolyamide (co-polymer of caprolactam and hexamethylene adipinate in a ratio of 50:50) with a melting point of 170°C, relative viscosity in sulfuric acid of 2.34, content of low molecular-weight compounds of 4.5 wt.%. As nanofiller, a combined substance was chosen—pyrogenic silica, on the surface of whose particles aluminium oxide NPs (Al_2O_3/SiO_2) were applied. The sample was synthesized at the O. O. Chuiko Institute of Surface Chemistry of the National Academy of Sciences of Ukraine. The specific surface of the mixed oxide was of 293 m^2/g, and the aluminium-oxide content was of 164.0 $\mu g/m^2$. The ingredients were mixed on a worm-disc extruder in two stages. The calculated amount of mixed oxide was pre-dispersed in the melt of the dispersed phase, and then the resulting granules (PP/nanoadditive) were mixed with the matrix polymer granules. The concentration (C) of Al_2O_3/SiO_2 nanoparticles in the composition was of 0.1–3.0 by mass.%. The effective viscosity (η) of the melts was determined using a capillary microviscometer in the shear-stress range (τ) $(0.1-5.7)\cdot 10^4$ Pa at a temperature of 190°C. Viscometry results were processed using generally accepted methods, taking into account the Rabinovich–Weissenberg correction, when constructing true flow curves. The flow regime (the index of deviation from the Newtonian flow n) was determined by the tangent of the angle of inclination of the tangent at a given point of the flow curve to the abscissa axis. Calculations were performed using a specially developed program [28].

The elastic properties of melts of individual polymers and blends were evaluated by the values of the coefficient of swelling (expansion) of the extrudate obtained under the conditions of free flow of the melt from the forming hole (B_0) and of the extrudate annealed according to the method [29] (equilibrium swelling B_{eq}). The equilibrium state was reached under annealing conditions, when the extrudate was kept for a short time in silicone oil (to eliminate the effects of gravity and surface tension) at temperatures close to the melting point of PP and CPA. The values of B_0 and B_{eq} were calculated as the ratio of the diameters of the original and annealed extrudates to the diameter of the die hole. The ability of the melt to longitudinal deformation was determined by the value of the maximum degree of extraction ($F_{\max}$), which was estimated as the ratio of the speed of receiving the melt jet to its linear speed in the die. Extraction of the matrix polymer from the composite extrudates was carried out in a Soxhlet apparatus with a 70% aqueous solution of ethyl alcohol. The morphology of the compositions was studied using a polarizing optical microscope using microphotographs of transverse and longitudinal sections of the extrudates. To quantify the microstructure, the sizes of all types of structures (microfibrils, particles, films) in the PP residue after the extraction of the matrix polymer from the extrudate mixture were determined under a microscope. For each sample, the number of types of structures that were measured was at least 1000 pieces. The obtained data were processed by the methods of mathematical statistics and the mass fraction of each type of structure, the average diameters ($\bar{d}$) of microfibrils and particles, the dispersion of the distribution (σ^2) of microfibrils were calculated and the curves of their distribution by diameter were constructed.

3. RESULTS AND DISCUSSION

3.1. The Influence of the Mixed-Oxide Concentration on the Rheological Properties of the Melt of the PP/CPA Blend

The conducted studies showed that the melts of all investigated systems are abnormally viscous liquids, which is evidenced by the nature of the flow curves and the value of the deviation index from the Newtonian regime (Fig. 1, Table 1).

The PP melt exhibits the greatest viscosity anomaly, and the flow of the CPA melt approaches the Newtonian regime (the n values are of 2.0 and 1.2, respectively). At the same time, the influence of the deformation rate on the effective viscosity of the mixture is much higher than on the η of the matrix component. On the dependence curve $\lg\eta = f(\lg\tau)$, the 'structural' section is steeper. Nanoparticles of the mixed oxide practically do not affect the nature of the flow of the PP melt, and the introduction of nanoadditives into the mixture is accompanied by an increase in the viscosity anomaly. This is due to the two-phase nature of polymer systems, the expansion of the spectrum of relaxation terms in them, and the intensity of the formation and destruction of the melt structure during its flow [30].

As can be seen from the Table 1, the values of the effective viscosity of co-polyamide and polypropylene melts differ by 2.8 times. The addition of a low-viscosity component causes a natural decrease in η of the mixture. However, the viscosity of the PP/CPA melt falls below the additive values: by 4.6 and 1.6 times compared to η of the matrix and the dispersed phase component, respectively. This indicates the separation of one of the ingredients into an individual phase during the flow of a two-phase system [30]. When introduced into the composition of 0.1–3.0 wt.% of nanofiller, the viscosity values of the melts remain lower than η of the original components, which indirectly indicates the invariance of the morphology of the melt in the presence of mixed oxide NPs. In the flow conditions, under the action of shear and tensile stresses, the layers of individual polymers in the flow move, but not the segments of their mac-

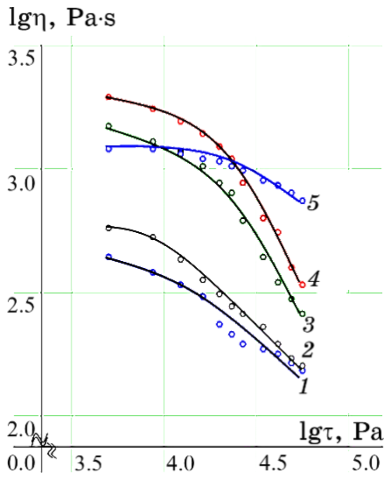


Fig. 1. Dependence of melt viscosity on shear stress: *1*—PP/CPA/NP 1.0 wt.%, *2*—PP/CPA, *3*—PP, *4*—PP/NPs 1.0 wt.%, *5*—CPA.

TABLE 1. Rheological properties of the studied systems.

Name of the polymer, mixture	Content of Al_2O_3/SiO_2, wt.%	Flow regime	Melt viscosity, Pa·s	η_{PP}/η_{CPA}	B_{PP}/B_{CPA}	Maximum deformation, %
PP	0	2.0	260	—	—	269
CPA	0	1.2	740	—	—	541
PP/CPA	0	1.5	160	0.35	1.29	99
PP/CPA/NPs	0.1	1.7	120	0.40	1.21	102
PP/CPA/NPs	0.5	1.7	135	0.43	1.14	106
PP/CPA/NPs	1.0	1.8	150	0.45	1.07	128
PP/CPA/NPs	2.0	1.8	160	0.49	1.0	121
PP/CPA/NPs	3.0	1.8	165	0.51	0.93	118

romolecules. The sliding of the components on the surface of the phase separation, due to their incompatibility, is one of the reasons for the decrease in the viscosity of the melts of the original and nanofilled mixtures.

At the same time, the dependence $\eta = f(C)$ for modified systems has a complex nature. With a nanoadditive content of 0.1 wt.%, the viscosity of the system becomes minimal, and with an increase in the concentration of the mixed oxide up to 3.0 wt.%, value of η increases (Table 1). The established decrease in melt viscosity may be related to the effect of small additives, which is due to a change in the thermodynamic parameters of the system, primarily, the compatibility or incompatibility of the components at the boundary of phase separation [31]. A further increase in the value of η of the nanofilled composition is the result of the structuring of its melt due to the formation of physical or chemical bonds between functional groups on the surface of Al_2O_3/SiO_2 nanoparticles with amino, oxide, and carboxyl groups of co-polyamide macromolecules.

Generalization and comparison of the results regarding the influence of the nanofiller content on the viscosity of the melts of the studied compositions was carried out with the use of temperature-concentration frequency superposition (adduction). The method is based on the fact that the change in the effective viscosity of the melt is determined by the complex of relaxation properties of the system in the initial state, when the value of η is maximal, and the flow process is described by Newton's equation [30]. The degree of change in the structure of the melt during its flow is estimated by the ratio of viscosities: at given values of stress and shear rate and the maximum Newtonian (η_N). For this, the following reduced co-ordinates are used: $\eta_r = \eta / \eta_N$, $\dot{\gamma}_{np} = \eta_N \dot{\gamma}$, where η_N is maximum Newtonian viscosity, $\dot{\gamma}$—shear rate gradient, η_{np}—reduced viscosity, $\dot{\gamma}_{np}$—the reduced shear rate gradient.

In cases, where the Newtonian segment of the curve was not reached in the experiment, η_N was found by the method of extrapolation of the dependence $\lg\eta$–$\lg\tau$, when $\lg\tau \to 0$. Generalization of viscosity properties for PP/CPA compositions with 0.1–3.0 wt.% of mixed oxide showed that there is invariance for them in relation to the additive content (Fig. 2).

As can be seen from Fig. 2, in the co-ordinates $\lg(\eta/\eta_N)$–$\lg(\eta_N \dot{\gamma})$ the points are quite close located near one general curve for all concentrations of the nanofiller. The existence of a universal dependence of η in the reduced co-ordinates indicates that the relaxation

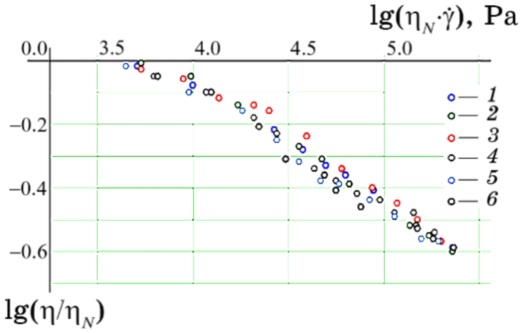


Fig. 2. Dependence of melt viscosity on shear rate in the reduced co-ordinates for PP/CPA/NP mixtures. Points *1–6* correspond to the NPs' content, wt.%: 0 (*1*), 0.1 (*2*), 0.5 (*3*), 1.0 (*4*), 2.0 (*5*), 3.0 (*6*).

spectra of the melts of the modified mixtures are similar to each other, and their rheological behaviour is described by the same functional dependence as that of the original blend. Thus, in the investigated systems, the influence of the composition of the mixture on the effective viscosity of the melt is fully manifested through the maximum Newtonian viscosity, and the possibility of concentration superposition in the melts is determined by the difference in the sensitivity of the components to the shear intensity.

Under conditions of shear flow, polymer melts develop significant highly elastic deformations and the resulting normal stresses. The swelling of the extrudate (increasing the diameter of the jet) that came out of the moulding nozzle is a manifestation of the elastic properties of polymer systems. Judging by the values of the swelling coefficient, the elasticity of the polypropylene melt is 1.3 times higher than that of co-polyamide, due to the greater mobility of the macromolecule chains of non-polar PP compared to polar CPA (Table 1). The melts of the original and nanofilled systems are characterized by increased elasticity, in comparison with the same indicator for the original components (Fig. 3).

This is due to the fact that the elastic properties of melts of polymer blends are related to the orientation and deformation in the direction of flow not only of segments of macromolecules in each phase, but also of ellipsoids of the dispersed phase. The process of relaxation of the accumulated stresses occurs non-immediately, and under normal conditions, due to the increase in the viscosity of the melt and the flow of crystallization or vitrification processes, the accumulated deformations and stresses are partially 'frozen'. As can be seen in Fig. 3, the swelling values of the extrudates of the initial and nanofilled samples under conditions of free flow from the die (B_0) are smaller than the equilibrium values (B_{eq}). At the

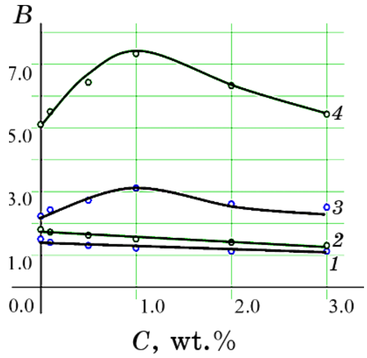


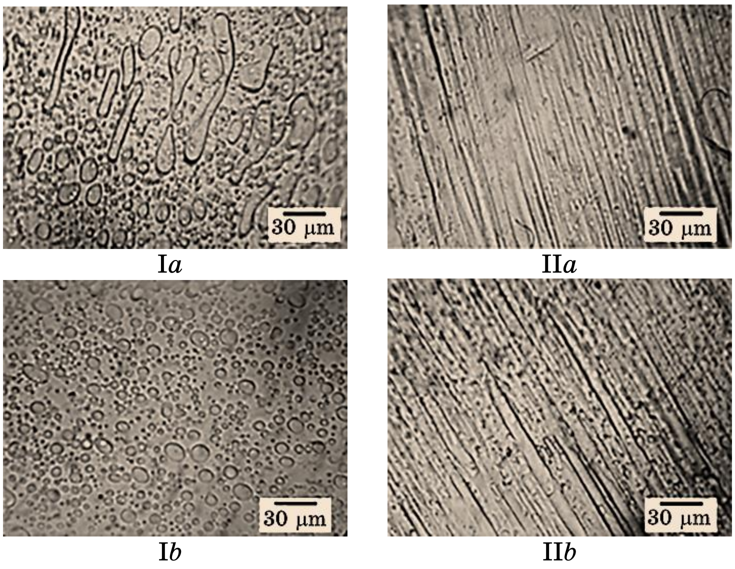
Fig. 3. Dependence of swelling of polypropylene extrudates (*1*—B_0, *2*—B_{eq}) and PP/CPA blend (*3*—B_0, *4*—B_{eq}) on the content of mixed oxide.

same time, the degree of growth of the equilibrium values of the swelling coefficient for two- and three-component mixtures is significantly higher than that of an individual component. Mixed oxide nanoparticles have different effects on the elastic properties of the PP melt and the PP/CPA blend. The B_{eq} values of nanofilled polypropylene melts decrease in the entire range of concentrations due to a decrease in the mobility of macromolecule segments in the presence of Al_2O_3/SiO_2 nanoparticles (Fig. 3). At the same time, the elasticity of the melts of the modified compositions increases by 14–43%, judging from the equilibrium swelling values of the extrudates. The dependence $B = f(C)$ passes through the maximum, which is reached at an additive content of 1.0 wt.%. The extreme nature of the dependence of the elastic properties of melts of polymer blends on the content of nanoadditives has been described for many systems [5, 16–19, 23–26]. The formed structures of the dispersed phase are new relaxing elements, and they make the main contribution to the elasticity of the system. Equilibrium swelling values reach their greatest values, when structures with the maximum degree of anisotropy are formed. This occurs under the condition of formation of microfibrillar morphology during the flow of the melt. The increase in elasticity of melts of PP/CPA/NPs compositions indirectly indicates that mixed oxide nanoparticles contribute to the formation of thinner polypropylene microfibrils in the CPA matrix.

The accumulation of significant highly elastic deformations by polymer melts determines another important feature of their rheological properties in the viscous-flow state, namely, the ability to stretch (the so-called longitudinal flow). The formation of fibres and films can be considered as a process of uniaxial deformation. The technological parameter that characterizes the ability of polymer melts and their blends to longitudinal stretching is the indicator of the maximum degree of drawing $F_{\max}$. The higher the value of $F_{\max}$, the better the systems' ability to uniaxial deformation. The results of the study showed that the melt of the original CPA is stretched in the field of the longitudinal velocity gradient to the greatest extent (Table 1). The fibre-forming properties of all the studied mixtures deteriorate, compared to the original components, which is due to the heterogeneity of their structure and a decrease in the viscosity of the melts. The addition of mixed oxide nanoparticles improves the uniaxial deformation of melts of modified compositions. At a concentration of nanoadditives of 1.0 wt.%, the value of deformation becomes maximum, and then slightly decreases with an increase in the content of Al_2O_3/SiO_2 up to 3.0 wt.%. The better deformation properties of three-component compositions are the result of an increase in the strength of nanofilled jets, which occurs due to an increase in the viscosity of their melts and a change in morphology in the field of the longitudinal velocity gradient. During the extraction process, solid Al_2O_3/SiO_2 nanoparticles are not deformed and increase the resistance to the flow of the melt, which leads to an increase in the value of the longitudinal viscosity of the system. At the same time, already formed anisotropic structures of polypropylene undergo further deformation. An increase in the degree of anisotropy of PP microfibrils also contributes to the longitudinal stretching of the composition melt jets.

3.2. The Influence of the Mixed Oxide Concentration on the Processes of Structure Formation in the PP/CPA Blend

The dispersed phase of the polymer blend is deformed and destroyed under the conditions of mixing and processing, which leads to the formation of a wide range of its shapes and sizes. The final morphology of the system is the result of a dynamic balance between the phenomena of deformation and decay, on the one hand, and coalescence, on the other. As can be seen in Fig. 4, the binary blend is characterized by a coarser and more inhomogeneous structure of the polymer of the dispersed phase in the dispersion medium. In three-component systems, nanoparticles of mixed oxide act as compatibil-



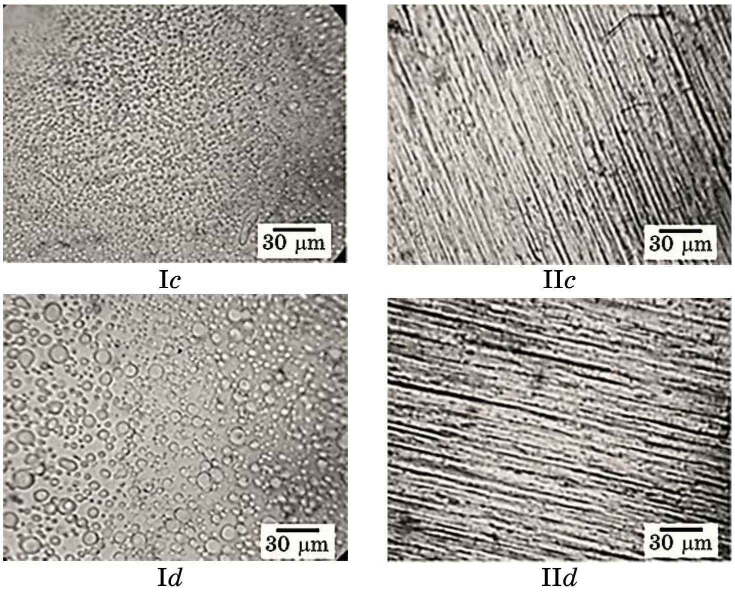
I*a*

II*a*

I*b*

II*b*

Fig. 4. Microphotographs of transverse (I) and longitudinal (II) sections of extrudates of PP/CPA/NPs mixtures according to the content of mixed oxide, wt.%: 0.0 (*a*), 0.1(*b*), 1.0 (*c*), 3.0 (*d*).



I*c* II*c*

I*d* II*d*

Continuation of Fig. 4.

TABLE 2. Influence of the concentration of the mixed oxide on the microstructure of extrudates of the PP/CPA/NPs mixture.

Content of Al_2O_3/SiO_2, wt.%	Types of structures					
	Microfibrils			Particles		Films, wt.%
	$\bar{d}$, μm	wt.%	δ^2	$\bar{d}$, μm	wt.%	
0	4.0	82.5	2.6	3.8	4.9	12.6
0.1	2.1	87.9	0.9	1.8	4.7	7.4
0.5	1.8	91.6	0.6	1.5	3.1	5.3
1.0	1.2	97.0	0.5	1.3	1.3	1.7
2.0	2.3	96.5	0.7	1.9	2.1	1.4
3.0	2.5	95.9	0.7	2.1	2.8	1.3

izers (emulsifiers) in the entire studied range of concentrations.

In the presence of nanoadditives in the amount of 0.1–3.0 wt.% the degree of PP dispersion in the CPA matrix increases and most of the drops acquires the correct round shape. Microfibrillar morphology is formed in the nanofilled mixtures, as well as in the original one. Examination under a microscope of polypropylene residues after the extraction of the matrix polymer from the extrudates of the mixtures showed that, in addition to microfibrils, other types of structures are also formed in them: films and micron-size particles (Table 2).

Microfibrils are the predominant type of structure in the extrudates of two- and three-component systems. The morphology of PP/CPA/NPs compositions is more subtle and homogeneous. Addition to the blend of only 0.1 wt.% of mixed oxide nanoparticles causes a decrease in the average diameter of polypropylene microfibrils and the value of the dispersion of their diameter distribution by $\cong 2$ and 5 times, respectively (Table 2). At the same time, the share of fibrils with $\bar{d} \leq 1.0$ µm increases by 4.4 times, coarse structures disappear, and the curve of distribution of microfibrils by diameters sharply narrows (Fig. 5).

In our earlier studies, it was shown that when modifying the PP/CPA blend separately with nanoparticles of silica or aluminium oxide, a similar result (decrease in $\bar{d}$ of microfibrils to 2.0 and 2.2 µm, respectively) was achieved, provided that their content is an in order higher [17, 21]. Thus, the obtained results indicate that when using the combined substance silicon dioxide/aluminium oxide as nanofiller, its components show a synergistic effect in the direction of reducing the dimensional characteristics of the component of the dispersed phase. In this case, the modifying effect is determined by the content of the additive in the mixture, and the dependence $\bar{d} = f(C)$ is of an extreme nature. At a concentration of mixed oxide of 1.0 wt.% share of PP microfibrils is the maximum and is of 97.0%, and their average diameter is the minimum, *i.e.*, 1.2 µm (Table 2). Further increase in the content of Al_2O_3/SiO_2 nanoparticles to 3.0 wt.% leads to coarsening of the microfibrillar morphology of the compositions. Such nature of the dependence of the degree of dispersion of the component of the dispersed phase on the content of the modifying additive is characteristic of classical compatibilizers, as well as mineral nanofillers [17–19, 21, 25–27]. This is due to the fact that, when the critical concentration is reached, the modifier is separated into a separate phase, while its surface activity decreases.

The synergistic effect of the combined substance aluminium ox-

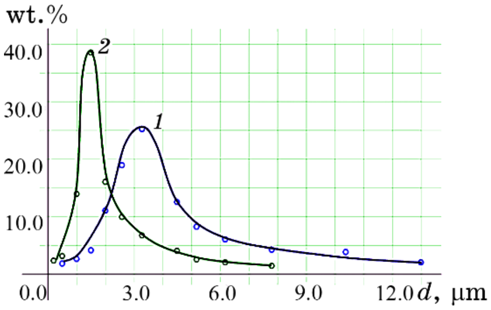


Fig. 5. Curves of distribution of microfibrils by diameters from extrudates of mixtures: *1*—PP/CPA, *2*—PP/CPA/0.1 wt.% NPs.

ide/silica on the *in situ* formation of thinner and more homogeneous PP microfibrils in the CPA matrix is primarily related to the effect of the nanoadditive on the course of interphase phenomena. It is known that modifying additives capable of exhibiting specific interactions (hydrogen, dipole–dipole, chemical, *etc.*) with one or both ingredients of the mixture improve the compatibility of components, suppress coalescence, and reduce interfacial tension [30, 32]. Silicas containing a metal oxide phase on the surface retain their properties and at the same time have additional active centres in their structure [33]. It is the increased chemical activity of Al_2O_3/SiO_2 nanoparticles, compared to individual components, that ensures their synergistic effect. The maximum impact of nanoadditives on interphase processes is achieved, when they mainly fill the surface of separation of components. Poor wetting of the Al_2O_3/SiO_2 mineral additive (which has a polar surface) by the melt of nonpolar polypropylene, as well as two-stage mixing of the components, contributed to the migration and selective localization of mixed oxide NPs in the interphase zone between the polypropylene droplets and the co-polyamide matrix.

The second factor that changes the balance in the processes of deformation, disintegration and coalescence of droplets of the component of the dispersed phase in the matrix is a change in the ratio of viscosities and elasticities of their melts [30]. Table 1 shows that with an increase in the concentration of Al_2O_3/SiO_2 in the mixture, the values of η_{PP}/η_{CPA} increase, and B_{PP}/B_{CPA} decrease, approaching to one. This contributes to the formation of PP fibrils of smaller diameters, since the deformation of polymer droplets with the formation of a jet occurs most efficiently when the values of viscosities and elasticities of the dispersed phase and the dispersion medium are close. Micron-size particles (PP drops) are the result of the disintegration of jets of the smallest diameters, as the most thermodynamically unstable. The formation of films is facilitated by the migration of the component with lower viscosity to the walls of the capillary. When the ratio of viscosities of nanofilled PP and CPA increases, the proportion of films decreases (Tables 1, 2).

4. CONCLUSIONS

It is shown that the introduction of the complex substance Al_2O_3/SiO_2 in the amount of 0.1–3.0 wt.% into the polypropylene/co-polyamide blend melt allows you to control the process of *in situ* formation of PP microjets in the CPA matrix. Aluminium oxide/silica nanoparticles exhibit a compatibilization effect in the compositions at all studied concentrations, which causes a decrease in the diameters of microfibrils in the modified systems and an increase in the homogeneity of their diameter distribution. The maximum effect is achieved with a nanoadditive content of 1.0 wt.%, while 97.0 wt.% of polypropylene forms microfibrils, the average diameter of which is of 1.2 µm, and the dispersion of the distribution decreases by $\cong 5$ times. Mixed oxide is a more effective structural modifier compared to silica and aluminium oxide nanoparticles. A two-times decrease in the value of $\bar{d}$ is achieved with a content of nanoadditive in the composition of 0.1 wt.%, which is an order of magnitude less than when using individual substances. The synergistic effect is due to the presence of additional active centres on the surface of nanoparticles of the Al_2O_3/SiO_2 combined substance, compared to its components.

It was established that the change in the microstructure of nanofilled compositions affects the macrorheological properties of their melts, namely, the effective viscosity decreases, and the ability to longitudinal deformation and elasticity increase. The decrease in the values of η of the modified melts is the result of the predominant influence of the process of forming PP liquid jets in the CPA matrix over the structuring of the melt due to the formation of connections between the functional groups of the nanoadditive and macromolecules of co-polyamide. The dependence curves of B and $F_{\max}$ on the concentration of the mixed oxide have an extremum at its content of 1.0 wt.%. The formation of anisotropic PP structures in the CPA matrix and the relaxation of the stresses accumulated by them at the exit from the forming hole determine the high values of the swelling coefficient of extrudates—5.4–7.3 of nanofilled compositions. Polypropylene microfibrils are new relaxing elements in the system, and they make the main contribution to its elasticity.

The invariance of the dependence of the effective viscosity on the shear rate in the reduced co-ordinates was established for PP/CPA/mixed oxide compositions. The existence of a concentration superposition confirms that the nanoparticles of the additive do not change the nature of the relaxation spectrum of the melt of the original blend, and the influence of its content on the η of three-component compositions is manifested through the maximum Newtonian viscosity.

Regulating the microstructure of incompatible polymer blends by introducing complex nanoadditives into their melts is an effective method of developing nanocomposites with predetermined morphology and properties, as well as creating new thin-fibre materials with improved characteristics based on them.

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