THE INFLUENCE OF NANO-ADDITIVES ON THE FORMATION OF MATRIX-FIBRILLAR STRUCTURE IN THE POLYMER MIXTURE MELTS AND ON THE PROPERTIES OF COMPLEX THREADS

N.M. Rezanova[1], V.G. Rezanova[1], V.P. Plavan[1] and O.O. Viltsaniuk[2]

[1]Kyiv National University of Technologies & Design, N.-Danchenko str. 2, 01011 Kiev, Ukraine
mfibers@ukr.net
[2]Vinnitsa National Pirogov Memorial Medical University, Pirogov str. 56, 21018 Vinnitsa, Ukraine
admission@vsmu.vinnica.ua

The influence of concentration of additives silver/silica (Ag/SiO_2) and silver/alumina (Ag/Al_2O_3) on the processes of structure-formation in the thermodynamically incompatible mixtures of polypropylene/copolyamide (PP/CPA) and the properties of complex threads from nano-filled PP microfibers were researched. Nano-fillers, that were used, show the compatabilization action in the mixture, reducing the value of interfacial tension and increasing the degree of dispersion and deformation of drops of disperse phase. This leads to a decrease in the average diameter of PP microfibers and reduction of mass fraction of films and particles, which the more perfect matrix-fibrillar structure is forming. The researched silver-containing nano-additives provide to complex threads an antimicrobial properties and improve their mechanical properties.

Keywords: *polymer mixtures, nano-additives, microfibers, interfacial tension, complex threads.*

1 INTRODUCTION

Increasing requirements for properties of textile materials and expansion of fields of their use led to search methods of obtaining of fibers and threads with a given set of parameters. The priority way is to develop methods of obtaining of nano-filled ultrafine fibers. The use of substances in nanostate can effectively solve the problem of increasing strength, elasticity, providing incombustibility, electrical, magnetic, optical, sorption, antimicrobial properties, etc. [1, 2]. As nano-fillers are widely used carbon nanotubes, nanoparticles of metals and metal oxides, silica and alumina. In recent years developed bifunctional nano-additives in which nanoparticles of metals or oxides are inflicted on the surface of mineral sorbents [3, 4]. Such substances exhibit antimicrobial activity silver-containing drugs combined with high sorption and anti-toxic properties. Their use minimizes consumption of silver, hence the reduction in toxicity and cost of silver-containing drugs. Reducing the diameter of individual filaments in complex threads to micro- and nanoscale improves product quality and reduces material consumption of production. Super-thin synthetic fibers can be obtained by different methods: melt - spinning, melt - blowing, processing of polymer mixture melts and electrospinning. Formation of microfibers and complex threads by processing of polymer mixture melts allows you to adjust their properties as by characteristics of the nano-fillers, and through their influence on fiber-formation of the component of the dispersed phase in the matrix [5-8]. Materials from ultrafine fibers retain all the positive properties inherent to products made of synthetic fibers: strength, shape stability and high durability. At the same time, because of the very small diameter of the individual filaments in the tissues of them, can form many air voids. Thanks to them, there is a free exchange of air between the skin and the environment, and such fabrics have high hygienic properties (fabric is "breathing") [9].

Purpose of the work is to research the influence of bifunctional nano-additives on the processes of structure-formation in molten mixtures of polypropylene/copolyamide as well as their impact on the properties of complex threads from microfibers.

2 EXPERIMENTAL

2.1 Materials used

To obtain complex threads from polypropylene microfibers was used a mixture of polypropylene/copolyamide (PP/CPA) content 30/70 wt.%. Characteristics of input polymers are given in the work [6]. To modify PP microfibers were chosen bifunctional inorganic antimicrobial substances in nanostate - silver/silica (Ag/SiO_2) and silver/alumina (Ag/Al_2O_3), their characteristics are shown in Table 1.

Table 1 Characteristics of nano-additives

Name	Specific surface of oxide [m^2/g]	The average particle size [nm]	Content of Ag [$\mu g/m^2$]	Specific surface of nano-additive [m^2/g]
silver/silica	320	17	16.3	296
silver/alumina	145	10	9.5	134

The concentration (*C*) Ag/SiO_2 and Ag/Al_2O_3 was in mixtures (0.5÷3.0) wt.% from mass of polypropylene. Nano-additives were received by restoring with glucose of ions Ag^+, deposited on the surface of pyrogenic silica (SiO_2) and alumina (Al_2O_3) from a water-alcohol solution of silver nitrate. The used additives combine bactericidal activity of silver and sorption properties of base components.

2.2 Methods used

Nano-filled composition were prepared with the help of the combined worm-disk extruder brand LGP-25, at this the additives previously were entered into polypropylene. The impact of nano-additives on fiber-formation of PP in matrix of CPA was evaluated using an optical microscope brands MBD by the method described in the [6]. At this were determined the mass fraction of the PP, which is spent on the formation of different types of structures (microfibers, particles, films) and the average diameter of microfibers. The kinetics of disintegration of liquid jets of PP (microfibers) in the CPA matrix was studied using a microscope equipped with a heating table. Longitudinal sections of the extrudates of mixtures were placed on it and were photographed the various stages of the process of destruction of the jets when heated. The radii (*R*) of jets and the distances between the centers of drops (*r*), which formed, were determined from the micrographs. The results were treated by the classical theory of Tomotika and were calculated the coefficient of instability (*q*), lifetime (decay) (t_l), adjusted decay (t_l/R) of jets and the value of interphase tension ($\gamma_{\alpha\beta}$). The complex threads were formed on research-industrial extrusion machine with 1000% spinneret extractor hood and were stretched at 150°C with multiplicity 6. Complex threads from nano-filled PP microfibers were obtained by extraction of the matrix polymer with solvent inert with respect to fiber-forming polymer. The strength at break (*P*) and modulus of elasticity (*E*) of complex thread was determined as described in [6]. Research of antibacterial activity of nano-filled threads from PP microfibers was made on the World Health Organization recommended test-strains of microorganisms and fungi by standard methodics [10, 11]. Suspensions of microorganisms were prepared using the device Densi-La-Meter (Czech Republic). Antibacterial activity of samples of microfibers was examined by two methods. The first method consisted in the diffusion of the active substance into the nutrient medium (method of "wells"). To do this, threads from PP microfiber were kept in saline (in a ratio 1:5) for 2 hours at 37°C, then the resulting liquid is poured into the wells of culture medium placed in a Petri dish. Microbial load amounted to 1.10^7 bacterial cells per 1 ml of medium and is established by the standard of McFarland. For the study was taken 18-24 hours culture of microorganisms. The antimicrobial activity of modified PP threads was determined by the diameter of the zone delayed the growth of microorganisms around the hole (*D*), in millimeters. According to the second method were studied the features of the growth of microorganisms on the surface of microfibers by playback of contamination of cultures. The threads were placed in casein-soy broth at a ratio of 1.10^7 of colony-forming units per milliliter [CFU/ml], incubated in an thermostat during 48 hours, after this, was made seeding on agar and was counted the number of microorganisms grown on nutrient medium. The criterion of evaluation was the decrease of number of viable colonies of cells of microorganisms in the corresponding period of time after the contamination, which is defined as the logarithm of the number of colonies.

3 RESULTS AND DISCUSSION

Formation of microfibers by processing molten polymer mixture is a special type of structure-formation in which is happening process of deformation and merging of drops polymer of dispersed phase into microfiber. They must maintain its stability in the channel of the forming hole and after the exit from it. Deformation, coalescence of drops, the thermodynamic instability of jets and the degree of compatibility of ingredients on the interphase area are effective factors to create the desired structure of the polymer dispersion. The final morphology is the result of a balance between the processes of deformation and desintegration on the one hand, and coalescence - the other. It is known that during the flow the dispersion medium is acting on drop dispersed therein with power that can deform it, provided that there is sufficient interaction between two polymers of mixture in the transition layer. From the fundamental relationships that describe thermodynamic equilibrium in dispersed systems, follows, that the most effective factor, that allows you to adjust the parameters of the phase structure, is the affinity of components. The value of surface tension at the interphase area is an indirect characteristic of degree of compatibility of polymers.

Compatibilization effect of nano-additives in polymer mixtures is described in several papers and it is associated with increasing of affinity between macromolecules of components at the interphase area [5-7].

Experimental results on the effects of nano-additives silver/silica and silver/alumina on decay of PP liquid jets in the matrix of CPA evidence their significant impact on the value of interphase tension throughout all the range of concentrations that were studied: $\gamma_{\alpha\beta}$ falls from 2.60 mN/m for the initial mixture to 0.47 and 0.27 mN/m for mixtures filled with Ag/SiO_2 and Ag/Al_2O_3 respectively (Table 2).

At this compatibilization effect depends upon the concentration of nano-additives and it is the maximum for the nano-filler content of 0.5 wt.%. Further increase in the concentration of Ag/SiO_2 and Ag/Al_2O_3 leads to an increase the value of interfacial tension. Extreme dependence $\gamma_{\alpha\beta} = f\ (C)$ is due to the fact that upon reaching its critical amount the additive is allocated in a separate phase, and its surface activity decreases. The efficiency of nano-additives depends on their chemical nature: the maximum reduction $\gamma_{\alpha\beta}$ occurs when into the mixture melt is entered additive based on alumina. This result is due to fact that in polymer mixtures compatibilization action is determined by selective localization of nanoparticles at the interphase area. Thus the effect is the higher, the greater the difference between polymer-philic of the components of mixture [5, 12]. Higher hydrophilic of surface of aluminas is probably contributes to more intense pushing of them to the interphase area.

The liquid jet (cylinder) is thermodynamically unstable and breaks up into drops in the event of appearance on its surface excitation of wave nature, provided that the amplitude of the wave coincides with the radius of the jet. Its decay time (lifetime) is directly proportional to the diameter of the initial cylinder and inversely proportional to the value of surface tension. So, other things being equal, decrease of interfacial tension value provide stability of jets smaller diameters that contribute to the formation of more thin microfibers. Data presented in Table 2, confirm a significant increase of the lifetime and adjusted lifetime of polypropylene microfibers in nano-filled mixtures PP/CPA and reduction of unstability coefficient, compared with initial mixture. Stability of microfibers depends upon the concentration of nano-additives: value t_l/R is maximum when their content is 0.5 wt.%. Changing the value of interfacial tension between the components is one of the factors regulating the morphology of polymer dispersions. The performed investigations of the microstructure of extrudates of initial and nano-filled mixtures showed, that addition of bifunctional nano-fillers into the mixture PP/CPA does not change the nature of structure-formation of polymer of dispersed phase in the matrix. For all studied compositions there is formation of a matrix-fibrillar morphology (Table 3).

Table 2 Characteristics of decay kinetics PP microfibers in the matrix of CPA

Nano-additive		$\gamma_{\alpha\beta}$	q	t_l [s]	t_l/R [s/μm]
name	content [wt.%]				
without additives		-	0.0348	32.6	24.5
Ag/Al_2O_3	0.5	0.27	0.0187	57.4	46.3
	1.0	0.32	0.0193	55.2	38.9
	1.5	0.41	0.0224	51.8	36.4
	3.0	0.51	0.0241	49.1	33.5
Ag/SiO_2	0.5	0.47	0.0198	50.9	32.9
	1.0	0.54	0.216	47.5	31.6
	1.5	0.65	0.0252	45.1	30.5
	3.0	0.73	0.0265	41.8	28.8

Table 3 Influence of nano-additives on microstructure of extrudates of mixture PP/CPA

Nano-additive		Microfibers		Films [wt.%]	Particles [wt.%]
name	content [wt.%]	d [μm]	[wt.%]		
without additives		3.8	90.3	7.0	2.7
Ag/Al_2O_3	0.5	1.9	96.8	1.3	1.9
	1.0	2.2	95.1	3.5	1.4
	1.5	2.5	94.0	4.7	1.3
	3.0	2.8	93.7	5.2	1.1
Ag/SiO_2	0.5	2.4	95.1	3.6	1.3
	1.0	2.7	94.2	4.6	1.2
	1.5	3.2	93.9	5.2	0.9
	3.0	3.4	92.8	6.3	0.9

Researched nano-additives improve process of fiber-formation PP in matrix of CPA: reduces the average diameter of microfibers and reduces mass fraction of films and particles in comparison with the initial mixture. At this the ratio between the types of structures and diameters of microfibers depends upon the concentration of nano-additives and their chemical nature. The positive effect of nano-fillers on fiber-formation is due to the stabilizing effect of nanoparticles on the finest PP microfibers by increasing the lifetime of the liquid jet and the reduction of the interfacial tension (Table 2).

Mechanical properties of complex threads, formed of the investigated mixtures, are shown in the Figure 1.

Adding of nano-fillers into the structure of PP microfibers leads to improvement of quality threads: their tensile strength and modulus of elasticity are increasing. This dependence is the logical and it is due to a number of factors. First, the addition of high-modulus nano-disperse additives increases the strength and resistance to deformation due to the effect of filling. Secondly, reducing the diameters of filaments in complex threads also helps to strengthen them. We have previously shown that the maximum mechanical properties have yarns, in which microfibers are the predominant type of structure [6, 7]. At this, presence of films impairs quality of threads. For nano-fillers concentration in a mixture of more then 1.5 wt.% the growth rate slowed down, which may be due to the process of aggregation of nanoparticles. Effect of modification by the additive Ag/SiO_2 is more pronounced versus Ag/Al_2O_3, due to its larger specific surface area. It is known that silica provide a significant improvement of mechanical properties of filled compositions. At this reinforcing action of silica correlates with the size of its specific surface area (S_{BET}): module increases when $S_{BET} \geq 50$ m^2/g, and the degree of reinforcement increases with increasing of specific surface [13].

Test results of antimicrobial activity of saline after withstanding of complex threads from nano-filled PP microfibers in it are shown in Table 4.

According to the methodic [10] were evaluated the antimicrobial effect by the following criteria: D<10 - microorganism is insensitive to the drug; 10<D<15 - low sensitivity; 15<D<25 - microorganism is sensitive to the drug. The obtained data indicate, that PP microfibers filled with nanoparticles Ag/Al_2O_3 and Ag/SiO_2, are showing insignificant antimicrobial activity towards all studied test-strains of microorganisms and fungi - the diameters of delay of their growth around the holes lie within (12.3÷14.7) mm. At the same time, we know that the antibacterial activity of the initial Ag/SiO_2 is high - about 10 times higher compared to silver ions [3]. Low sensitivity of saline solution in this case may be due to the fact that silver nanoparticles are in the pores of base oxide and are slowly diffusing into it.

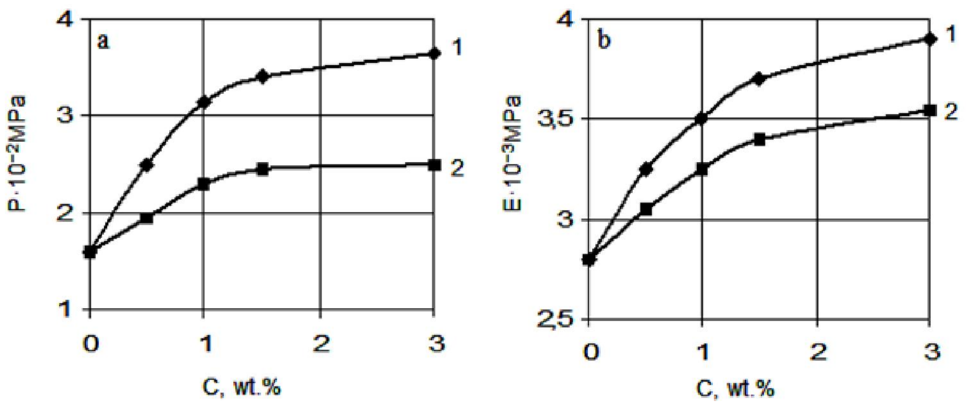

Figure 1 The impact of the concentration of nano-additives on the strength P (a) and elastic modulus E (b) of threads from PP microfibers: 1– Ag/SiO_2; 2 – Ag/Al_2O_3

Table 4 Antimicrobial activity of nano-filled threads, defined by the method of diffusion in agar

Name and composition of the mixture [wt.%]	Diameters of the zones stunted growth [mm]					
	Staphylococcus aureus ATCC 25923	*Escherícha coli ATCC 25922*	*Pseudomonas aeruginosa ATCC 27853*	*Proteus vulgaris ATCC 4636*	*Basillus subtilis 6633*	*Cadida albicans ATCC 885/653*
PP/CPA 30/70	**the growth of microorganisms and fungi**					
PP/CPA/Ag/Al_2O_3 30/70/0.5	14.1±0.9	14.7±0.2	13.0±0.5	12.9±0.6	14.0±0.4	13.9±0.8
PP/CPA/Ag/SiO_2 30/70/3.0	13.9±0.8	13.0±0.4	12.8±1.1	12.3±0.7	14.2±0.1	13.6±1.0

Table 5 Antibacterial activity of nano-filled complex threads, defined by contamination method

Exposition [days]	Δ [CFU/ml]					
	PP/Ag/Al_2O_3			PP/Ag/SiO_2		
	Staphylococcus aureus ATCC 6538 (5.60)*	*Pseudomonas aeruginosa ATCC 9027* (5.60)*	*Cadida albicans ATCC 885/653* (5.60)*	*Staphylococcus aureus ATCC 6538* (5.74)*	*Pseudomonas aeruginosa ATCC 9027* (5.65)*	*Cadida albicans ATCC 885/653* (5.60)*
Initial seeding	0.98	0.95	0.95	1.06	0.96	0.98
2	3.21	2.21	2.21	3.27	2.26	2.43
7	not found	3.91	4.0	4.05	3.65	3.30
14	microorganisms and fungi are not found					

* logarithm of the microbial load [CFU/mL]

Antibacterial action of nano-filled complex threads from PP microfibers, which is defined by the method of contamination as the difference (*Δ*) between the values of logarithms of microbial load and number of viable colonies of cells of microorganisms through an appropriate time period, is shown in the Table 5. This value after two days shall be not less than 2, and after 7 days - not less than 3. In the future, the number of viable bacteria colonies should not grow.

For studies were selected complex threads formed from mixtures containing 0.5 wt.% Ag/Al_2O_3 and 3.0 wt.% Ag/SiO_2. The results show that the modified threads exhibit high antimicrobial and antifungal activity towards *Staphylococcus* reference strains of microorganisms and fungi of the genus *Cadida* (Table 5). Complex threads filled with nanoparticles Ag/Al_2O_3 are more effective compared with Ag/SiO_2 because alumina itself has high antimicrobial activity to some strains of microorganisms that is shown in the work [14].

4 CONCLUSIONS

It was established, that the addition of nano-fillers silver/silica and silver/alumina into the mixture polypropylene/copolyamide provides reduction of surface tension at the interphase zone, increasing of lifetime and reduction of instability of liquid jets of PP in matrix of CPA. Compatibilization action of additives depends upon their chemical nature and content. Nanoparticles Ag/Al_2O_3 are more effective compared to the Ag/SiO_2 and have the maximum impact on phase morphology of modified mixture at concentration of 0.5 wt.%, which corresponding to a minimum value of interfacial tension. Reducing the average diameter of the microfibers and increase their mass fraction due to a decrease spending for the formation of new surfaces and the stabilizing effect of nanoparticles on the finest microfiber PP by increasing the lifetime of almost 2 times.

It is shown that the complex threads of nano-filled PP microfibers are characterized by high tensile strength and elastic modulus that is connected with the effect of filling and with decreasing diameters of filaments. Modification of threads with silver-containing nano-additives provides them with anti-microbial properties and ability to protect against pathogenic organisms. The developed complex threads from nano-filled PP microfibers can be used to create new materials for medical purposes.

5 REFERENCES

1. Andrady A.L.: Science and technology of polymer nanofibers, John Wiley & Sons, Inc., Hoboken, New Jersey, USA, 2008, 404 p., ISBN-10: 0471790591
2. Biomedical Applications of Polymeric Nanofibers, R. Jayakumar, S.V. Nair (Eds.), New York: Springer, 2012, XII, 288 p., ISBN 978-3-642-27147-2
3. Egger S., Lehman R.P., Height M.J., Loessner M.J., Schuppler M.: Antimicrobial Properties of a Navel Silver-Silica Nanocomposite Material, Applied and Environmental Microbiology 75(9), 2009, pp. 2973-2976
4. Bohatyrov V.M., Oranskaya E.I., Galaburda M.V., Gerashhenko I.I., Osolodchenko T.P., Yusypchuk V.I.: Silica nanocomposites with compounds of silver, copper, zinc and their antimicrobial properties, Chemistry, Physics and Technology of Surface 7(1), 2016, pp. 44-58, (in Russian)
5. Li W., Karger-Kocsis J., Schlarb A.K.: Dispersion of TiO_2 Particles in PET/PP/TiO_2 and PET/PP/PP-g-MA/TiO_2 Composites Prepared with Different Blending Procedure, Macromol. Mater. Eng. 294, 2009, pp. 582-589
6. Rezanova N.M., Plavan V.P., Rezanova V.G., Bohatyrov V.M.: Regularities of producing of nano-filled polypropylene microfibers, Vlakna a Textil (Fibres and Textiles), 23(4), 2016, pp. 3-8
7. Tsebrenko M., Rezanova V., Tsebrenko I.: Polypropylene microfibers with filler in nano state, Chemistry & Chemical Technology 4(3), 2010, pp. 253-260
8. Sangroniz L., Palacios J.K., Fernandez M., Eguiazabal J.I., Santamaria A., Muller A.J.: Linear and non-linear rheological behavior of polypropylene/polyamide blends modified with a compatibilizer agent and nanosilica and its relationship with the morphology, European Polymer Journal 83, 2016, pp. 10-21
9. Krichevskij G.E.: Nano-, bio- and chemical technologies and production of a new generation of fibers, textiles and clothing, Moscow: Izvestiya, 2011, 528 p, (in Russian)
10. Volyanskyj Yu.L., Grytsenko I.S., Shyrobokov V.P.: Studying of the specific activity of antimicrobial

medical drugs: Methodic guidelines, Kyiv, State Pharmacological Center, 2004, 39 p., (in Ukrainian)

11. Determination of the sensitivity of microorganisms to antibacterial drugs, Methodic guidelines, Kyiv, MOZ of Ukraine, 2007, № MB 9.9.5-143-2007, (in Ukrainian)
12. Xiu H., Bai H.W., Huang C.M., Xu C.L., Li X.Y., Fu Q.: Selective localization of titanium dioxide nanoparticles at the interface and its effect on the impact toughness of poly(L-lactide)/poly(ether)urethane blends, eXPRESS Polymer Letters 7(3), 2013, pp. 261-271
13. Manson J., Sperling H.: Polymer blends and composites, New York: Plenum Press, 1976, 440 p.
14. Williams M.: Ions, not particles, make silver toxic to bacteria: News Releases, 2012, Access mode: http://news.rice.edu/2012/07/11/ions-not-particles-make-silver-toxic-to-bacteria-3