REGULARITIES OF PRODUCING OF NANO-FILLED POLYROPYLENE MICROFIBERS

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

[1]*Kyiv National University of Technologies & Design, N.-Danchenko srt. 2, 01011 Kyiv, Ukraine*
[2]*Chuiko Institute of Surface Chemistry, NAS of Ukraine, General Naumov srt. 17, 03164 Kyiv, Ukraine*
mfibers@ukr.net

Abstract: *The research of the concentration influence of the titanium oxide/silica (TiO_2/SiO_2) combined nanodispersing additive on the rheological properties and the structure-formation processes in a mixture of polypropylene/copolyamide (PP/CPA) has been conducted. Established, that during the flow of melt takes place the allocation of components on phases with the formation of liquid jets (PP microfibers) in the CPA matrix. Changing of content of nano-additive in the mixture melt allows us to control the process of fiber formation in the direction to increasing the fraction of microfibers and reducing their average diameter. The maximum effect of fiber formation improving was achieved at concentration of TiO_2/SiO_2 in a mixture of 1.0 wt%. Nano-filled compositions are characterized by low viscosity, the increased elasticity and spinnability of melt. Complex threads from nano-filled polypropylene microfibers have high hygienic properties thanks to a developed specific surface.*

Key words: *mixture of polymers, nano-additive, fiber formation, microfibers, viscosity*

1   INTRODUCTION

Modifying the properties of synthetic fibers and threads by reducing of the filaments diameter to micro- and nanosize and an introduction to their structure of nano-fillers is a promising trend in technology of chemical fibers. Formation of microfibers by processing of polymer mixture melt is a simple effective method of obtaining filament yarn and staple fibers with diameters from fractions of tenths to a few micrometers. Fiber formation of component of the dispersed phase in the matrix has enough general character and described for many pairs of polymers. However, this phenomenon is most clearly realized subject to the requirements of the components mixtures properties and the conditions of deformation. Thermodynamically incompatible polymers are mixed that in the terms of processing form the polymer dispersion of droplets of one in another. This transition layer has a sufficient extension that ensures the transfer of stress from the matrix to the dispersed phase. One of the traditional methods of influence on the interphase phenomena is addition of a third component – compatibilizator, that promotes interaction between the phases and the formation of a stable fine dispersion and consequently, leads to improved process of fiber formation [1]. In recent years have been shown the compatibilized action of nano-additives (decrease in surface tension) in molten polymer mixtures. It allows you to manage the processes of structure-formation in the processing of polymeric dispersions and products to provide them with a set of new properties [2-4].

The purpose of the research is: impact of complex nano-additive of titanium oxide/silica on process of polypropylene (PP) fiber formation in copolyamide (CPA) matrix, on the rheological properties of their molten mixtures and on the characteristics of complex threads from PP microfibers.

2   EXPERIMENTAL

2.1   Materials used

For research were used: isotactic polypropylene as fiber forming component, copolyamide – matrix polymer (copolymer of caprolactam and hexamethylene-adipinate in the ratio 50:50) and the mixture PP/CPA of composition 30/70 wt%. Both polymers are industrial polymers, which are produced in large volumes. Characteristics of PP, CPA and mixture PP/CPA are represented in Table 1. Complex substance titanium oxide/silica (TiO_2/SiO_2) was used as nano-additive.

Table 1 Characteristics of initial polymers

Polymer	Melting temperature [°C]	Viscosity [Pa·s] *	Swelling of extrudate (B) *	Maximum degree of stretch (F_{max}) *
PP	169	260	2.0	270
CPA	170	740	1.4	630
PP/CPA	-	170	5.1	102

*at shear stress $5.69{\cdot}10^4$ Pa

Pyrogen silica nanoparticles were covered by nanoparticles of titanium oxide. The nano-additive titanium oxide/silica (TiO_2/SiO_2) has a specific surface area 62 m^2/g and content of TiO_2 7.0 wt%. Mixed oxide was obtained by compatible high-temperature pyrolysis of $SiCl_4$ and $TiCl_4$. The concentration (C) of nano-additive in mixture is of (0.5÷3.0) wt% by weight of polypropylene.

2.2 Methods used

Mixing components were performed on the worm-disc-extruder. In the gap between the movable and immovable discs of it there are intense shear and tensile stress, which contributes to a thin uniform dispersion of dispersed phase component. For maximum concentration of nano-additive in the structure of PP microfibers, it was pre-dispersed in the melt of dispersed phase, and the obtained granules PP/nano-additives were mixed with the matrix polymer (CPA). Rheological properties of melt: viscosity (η) and non-Newton flow index (n) was studied using capillary micro-viscozimeter at a temperature of 190°C in the range of shear stress τ (0.10÷5.69).10^4 Pa. The degree of deviation of flow regime from Newtonian was characterized by the value of «n», which is defined as the the slope of the tangent to the x-axis at a given point of the curve of flow. Melt elasticity was evaluated by largest equilibrium swelling of extrudates "B" as defined by the method [5]. The ability of melts to the longitudinal strain was characterized by a maximum degree of stretch, which was calculated as the ratio of the speed of a jet taking to the linear speed of the melt in the die (F_{max}). Research of remnants of polypropylene after matrix extraction was performed using an optical microscope brands MBI and scanning electron microscope GEOL GSM-35. Quantitative characteristics of the processes of structure-formation in extrudate were evaluated under a microscope by counting the number of all types of polypropylene structures and determining their size in the residue after extraction of matrix polymer. Experimental data were processed by methods of mathematical statistics, resulting in determining the average diameter of the microfibers and particles (d), the variance of their distribution by diameter (σ^2) and a mass fraction of each type

of structure. Complex threads of nano-filled PP microfibers were obtained by extraction of matrix polymer by the inert solvent with respect to fiber forming polymer. Composite threads were formed on a laboratory bench with jet stretch 1000% and stretched at 150°C with multiplicity of stretching [6]. The strength at break (P) and breaking elongation (ε) of filament yarn was determined by using tensile testing machines of type KT 7010 AZ. Elastic modulus (E) was calculated by the formula:

$$E = L_0 P_{3\%} / (L_1 - L_0) S \qquad (1)$$

where L_0 – initial length; L_1 – length of thread after elongation of 3%; S – cross-sectional area of thread; $P_{3\%}$ – thread strength at elongation at 3%. The size of the specific surface area (S_{BET}) of polypropylene microfibers was determined by thermogravimetric method by building the sorption-desorption isotherms of moisture relative on humidity of environment, and S_{BET} was calculated by the equation BET [4, 7].

3   RESULTS AND DISCUSSION

The investigation showed that during the flow of melt of initial and nano-filled mixtures there is the effect of phase distribution of components. The polymer of dispersed phase is allocated in the form of thin streams, which are stretched by the flow of the other polymer (matrix). Thus, the structure of extrudate (monothread) coming out of the die hole is a holistic phase of disperse medium, reinforced with thin streams of dispersed phase, which are remaining as a bundle of PP microfibers after dissolving the matrix polymer (Figrure 1).

Microscopic studies have shown along with the microfibers of continuous lengths, polypropylene forms other types of structures, such as particles, films, short microfibers, fine-fiber outer shell (Table 2).

Addition to melt mixture PP/CPA (0.5÷3.0) wt% of TiO_2/SiO_2 allows you to adjust the extrudate morphology of modified mixture. Data in Table 2 show the compatible effect of nano-additive: increases the uniformity and dispersion degree of component dispersed phase.

Table 2 The characteristics of the microstructure of mixture extrudates PP/CPA/TiO_2/SiO_2 [*]

The content of additive in mixture [wt %]	Continuous fibers			Short fibers		Particles		Films [wt%]	Shell [wt%]
	d [μm]	[wt%]	σ^2 [μm^2]	d [μm]	[wt%]	d [μm]	[wt%]		
0	4.0	79.5	2.6	3.2	10.8	4.1	2.7	4.1	2.9
0.5	2.7	82.7	1.2	2.4	9.0	2.9	2.6	3.3	2.4
1.0	1.8	94.0	1.2	2.0	1.1	2.4	1.2	1.8	2.0
1.5	2.2	89.9	1.7	2.1	2.3	2.6	3.4	2.5	1.9
3.0	2.5	85.4	1.9	2.3	4.7	3.1	5.8	2.2	1.9

[*]at τ = 5.69·10^4 Pa

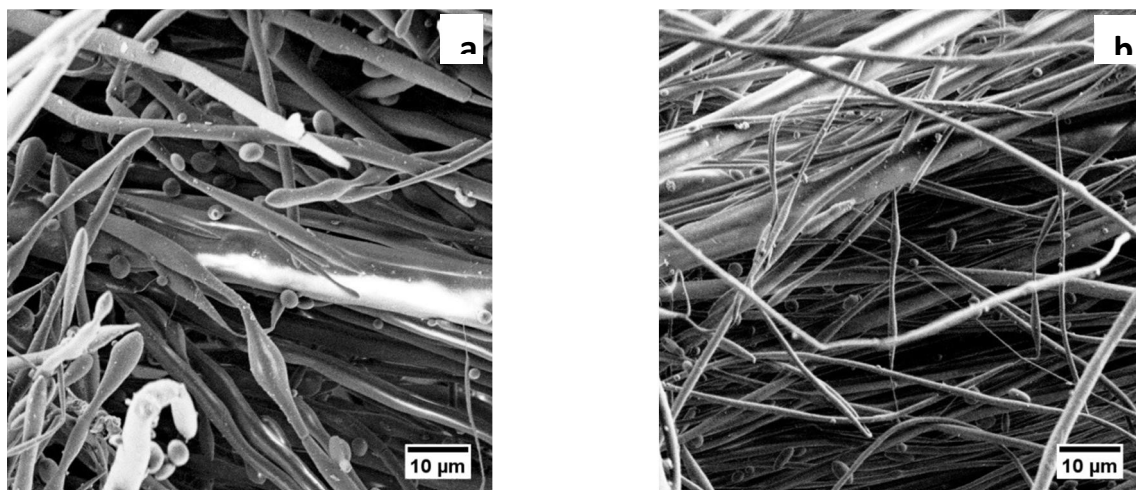**Figure 1** Electron microphotographs of polypropylene microfibers. Content TiO$_2$/SiO$_2$: a) 0.0 wt%; b) 1.0 wt%

There is also a fiberization improvement in all investigated range of concentrations of TiO$_2$/SiO$_2$: average diameter microfibers continuous length is reduced from 4.0 µm (for the original mixture) to (1.8÷2.7) µm (depending on the concentration of additives), increases the uniformity of distribution by diameter, according to the value of σ^2, increases mass fraction of polypropylene, which forms microfibers. Thus the concentration of nano-filler significantly influences on the size of microfibers and the ratio of types of structures in the extrudate − the diameters of particles and microfibers reach their minimum values and the number of microfibers is the maximum at the content of additive of 1.0 wt%.

Increasing the degree of dispersion of drops of dispersed phase polymer in the presence of 3.0 wt% hydrophilic and hydrophobic silica in the mixtures of polypropylene/polystyrene (PP/PS) and polypropylene/copolymer of ethylene and vinyl acetate (PP/EVAC) was described by Elias [2]. The change of process of structure-formation of the component dispersed phase in the presence of nano-fillers the authors associate with the formation of the advanced transition layer at the interphase area of mixture and with decreasing values of surface tension. The effect is enhanced when nanoparticles are preferentially localized in the interphase area. Thus, it was found that the preliminary introducing silica nanoparticles in PP melt, hydrophilic SiO$_2$ nanoparticles migrate from the volume of PP to the phase or polystyrene or EVAC, and this determines the decrease of surface tension at the interphase area. Addition of nanoparticles of titanium oxide in a mixture melt of poly(ethylene terephthalate)/PP allows you to adjust the diameter and length of polyester fibrils in a matrix of polypropylene [3]. In the presence of nano-additive the diameter is decreasing and their length is increasing. The authors of [4] has found

that additives of pyrogenic silicas exhibit the compatibilization effect on mixture melt polypropylene/copolyamide and decrease the value of interphase tension. This promotes the formation of liquid jets (microfiber) of PP smaller diameters and their stabilization.

Effect of nanoparticles TiO$_2$/SiO$_2$, obviously, is also associated with the formation of advanced transition layer at the interphase area of mixture PP/CPA and with a decrease of the value of interphase tension. The significant compatibility effect is achieved thanks to the prevaling localization of nanoparticles TiO$_2$/SiO$_2$ in the interphase area. It is known that the nano-fillers are pushed from the melt volume to the interphase area of polymers when they are premixed with a component that has worse polymer affinity to the surface of nanoparticles [2]. Hydrophilic nanoparticles of TiO$_2$/SiO$_2$ are poorly wettable by nonpolar polypropylene melt, and they migrate to the interphase area and affect on the properties of the transition layer and the processes of structure-formation.

Formation of fine-fiber outer shell is caused by the fact that during the flow of polypropylene in the nozzle, as liquid with a much lower viscosity, is pushed to the walls and forms a thin boundary layer. The formation of fiber shell of continuous length, filled with microfiber, has practical importance, such as the formation from a mixture of polymers the composite film and getting out of it the filter material after extraction of matrix polymer. Such shell protects the filtration layer from separation of fibers by the filtering liquid and their removal to the filtrate.

The performed investigations showed that addition of nanoparticle TiO$_2$/SiO$_2$ affects the rheology of initial polypropylene of melts and also mixture PP/CPA (Figure 2).

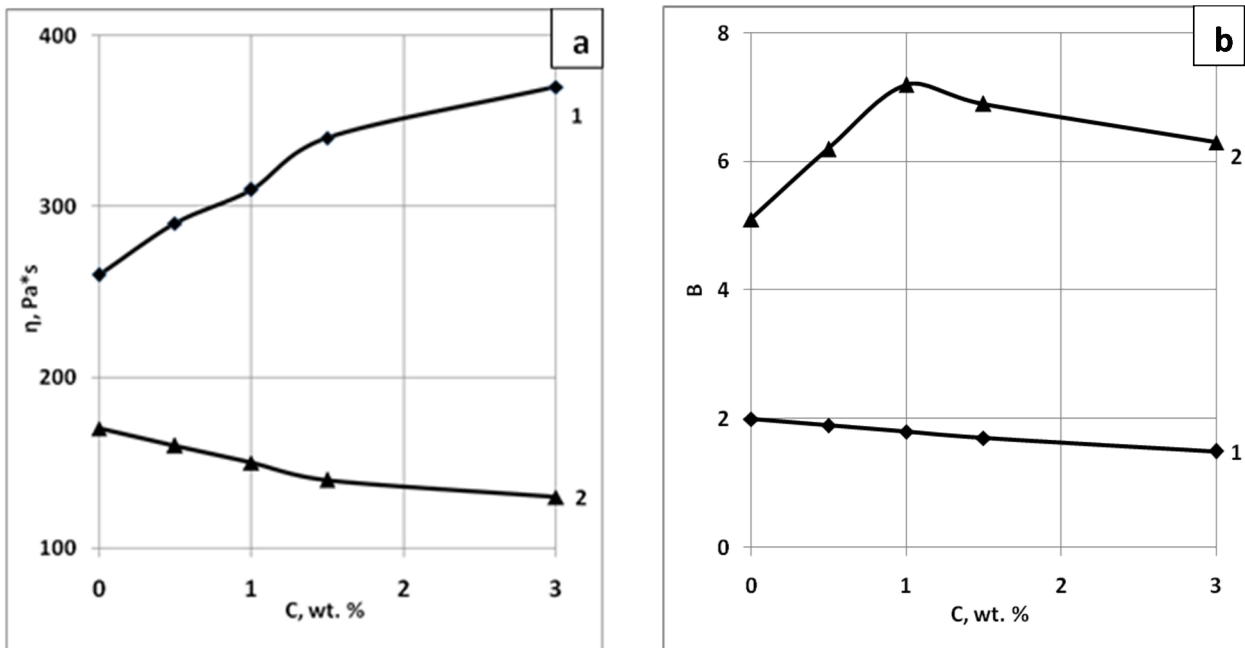**Figure 2** The influence of concentration of nano-additive TiO$_2$/SiO$_2$ on viscosity (a): of melts PP (1), the mixture of PP/CPA (2) and extrudate swelling (b): of PP (1) and mixture of PP/CPA (2)

As can be seen from Figure 2a, PP melt viscosity increases in overall range of concentrations of additives, thus appears effect of filling melt with solid substance. Such regularity, as a rule, occurs when filling melts by individual polymers. The melt viscosity of modified mixture decreases by (2.0÷5.7) times compared with η of the initial PP and CPA (Table 1, Figure 2a). The sharp drop in viscosity indicates a change in the mechanism of the flow of mixture melt – the transition from segmental movement of polymer macromolecules in the stream to stratified (layered) flow of individual components. Thus the decrease viscosity of melts of researched mixtures can be explained changing their structure. Allocation of PP in a separate phase to form a continuous surface between the components promotes the decrease of the viscosity through sliding of polymer along the surface phase separation. Secondly, for the implementation of flow of the mix with deformed particles is required smaller pressure drop (corresponding lower melt viscosity) than during the flow of individual polymers. Creating the anisotropic structure of component of the dispersed phase and their orientation in the direction of flow also contribute decrease of η of mixture melt [6, 7]. Reduced viscosity of melts of nano-filled compositions compared to η the initial mixture PP/CPA in the entire range of concentrations of TiO$_2$/SiO$_2$ (Figure 2a) is obviously connected with the change in processes of structure-formation of PP in matrix CPA in the presence of nanoparticles of additives. The initial polymers and their mixtures are viscoelastic non-Newtonian fluids. The nature of the modified melt flow of PP and PP/CPA mixture almost not varies depending on the content of nano-filler at all studied concentrations and obeys the Ostwald de Waele correlation (non-Newton flow index (n) is in the range of 1.6÷1.8).

An important feature of polymer melts and their mixtures, which can not be explained in terms of classical fluid mechanics, is the extrudate swell (increase in size of the jet) after exiting from the forming hole. While addition of additives TiO$_2$/SiO$_2$ in PP melt equilibrium value "B" decreases with increasing of content of nano-additive (Figure 2b), indicating a decrease in the elasticity of the melt by limiting mobility of macromolecules chains. Significant growth of extrudate swelling bi- and three-component mixtures is associated with deformation and orientation in the direction of flow of segments of macromolecules in each phase and also the droplets of dispersed phase themselves. They are the new relaxing elements, typical characteristic only for two-phase systems. The maximum degree of anisotropy is achieved when the dispersed phase forms a liquid jet (microfibers) of continuous length. In a number of studies have been shown that the value of the equilibrium swelling indirectly characterize the process of fiber formation component of the dispersed phase in the matrix. The index "B" is greatest when the microfiber is the only type of structure in the extrudate and their diameters are the smallest [1, 4]. As shown in Figure 2b, the swelling value of ternary compositions in (1.2÷1.4) times higher than for the original mixture.

Dependence "B" = f (the content of TiO_2/SiO_2) is an extreme nature. The maximum is reached in mixture $PP/CPA/TiO_2/SiO_2$ of content 30/70/1 wt%, whereby fiber formation is implemented in a best way: the average diameter of microfibers is minimum (1.8 μm), and they are the predominant type of structure in extrudate (Table 2). Increasing the fraction of films causes decrease in swelling. Thus formed anisotropic structure (microfibers) are the major contributions to the highly elastic deformation during the flow of polymer dispersions. The total elastic energy, when leaving the capillary, is higher for the composition with the deformable drops, which leads to an increase of swelling in several times in comparison with the "B" of initial polymers.

Forming of fibers can be considered as an process of uniaxial stretching. An important technological feature of melts of polymers and their mixtures which indicates the fiber forming properties, is the value of the maximum degree of stretching F_{max}: the higher its permissible value, the better the ability of the material to recycling or spinnability system. The obtained results indicate that the value of longitudinal strain melt of bi- and three-component mixtures falls sharply compared with F_{max} of the initial components (Table 1, Figure 3).

Minimum spinnability has a melt PP/CPA, due to the incompatibility of polymers and the weak interaction between components in the interphase area. Addition of nano-additive in an amount (0.5÷3.0) wt% is accompanied by an increase of $F_{max.}$ It is related to the increasing of melt viscosity and with improved fiber formation of PP in matrix of CPA. It is known that anisotropic structures increase the ability of melt to longitudinal strain [8]. Simultaneously, there is also significant increase of spinnability of polypropylene melt filled with solid nanoparticles of additive. Revealed regularity can be explained by a change in the processes of crystallization of polypropylene in the presence of nano-additive and forming of more perfect form of supramolecular structures. Results of the complex threads properties study of initial PP microfibers and filled with nanoparticles of TiO_2/SiO_2 are shown in Table 3.
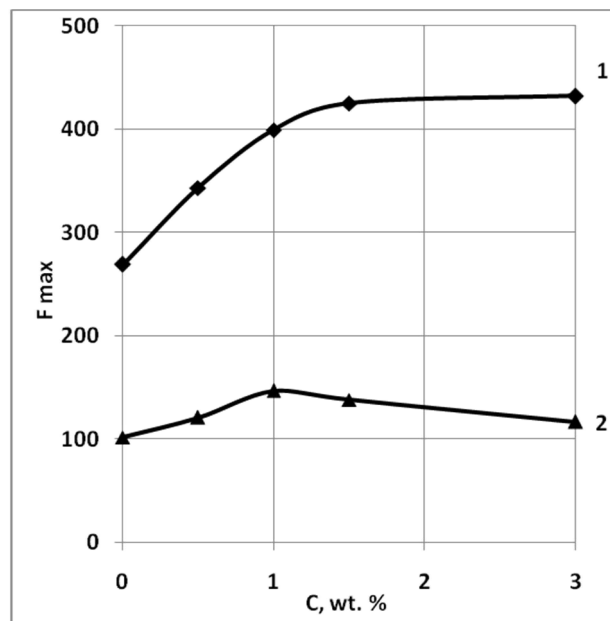

Figure 3 The dependence of the maximum degree of stretching melts PP (1) and mixture PP/CPA (2) on the concentration of nano-additive TiO_2/SiO_2

The obtained data show that the properties of complex threads formed from polymer mixture melts, is largely determined by the type of structures of dispersed phase in the matrix. As expected, addition of nano-additive improves strength and initial elastic modulus of modified threads.

The maximum values of mechanical properties are achieved at additive content 1.0 wt%, when the fiber formation of PP in matrix of CPA is implemented in a best way. It is known that polypropylene is hydrophobic polymer with an equilibrium water absorption of (0.1÷0.2) wt%. For nano-filled PP microfiber hygroscopicity increases approximately 2.5 times in comparison with the original microfibers, and (15÷20) times compared to textile polypropylene threads, obtained by traditional technology. This is due to the increase of specific surface of modified PP microfibers (Table 3).

Table 3 The influence of TiO_2/SiO_2 additives on complex threads properties

Content of TiO_2/SiO_2 [wt%]	Strength [MPa]	Elastic modulus [MPa]	Elongation [%]	Surface area S_{BET} [m²/g]
0	160	2800	13.3	84
0.5	190	3500	11.8	135
1.0	240	3800	12.6	190
3.0	220	3400	11.7	210

4   CONCLUSIONS

Were investigated physical and chemical regularities of obtaining of polypropylene microfibers filled with complex nano-additive TiO_2/SiO_2, by processing of polypropylene/copolyamide mixture melts. It was established that during flow of melts of initial and nano-filled mixtures there is an effect of phase distribution of components: a polymer of dispersed phase forms a thin jets that remain in the form of microfibers beam after extraction of the matrix polymer from composite monothread. Nanoparticles in quantity (0.5÷3.0) wt% not only does not interfere the implementation of process of fiber formation during flow of melts PP/CPA, but also improve it – the mass fraction of microfibers increases, their diameter and quantity of undesirable structures (films, particles) decreases.

Ability to longitudinal strain of melts of modified compositions in all the studied range of concentrations of additive is lower than in nano-filled polypropylene, but the spinnability of ternary mixtures is sufficient for the formation fibers or films from them.

The obtained complex threads of PP microfibers filled with nano-additive TiO_2/SiO_2 are characterized by high hygienic properties (due to a developed specific surface) and mechanical indexes similar to textile polypropylene threads.

5   REFERENCES

1. Rezanova V., Tsebrenko M.: Influence of binary additives of compatibilizers on the micro- and macrorheological properties of melts of polypropylene-copolyamide mixtures, Journal of Engineering Physics and Thermophysics 81(4), 766-773, 2009

2. Elias L., Fenouillot F., Majeste J.C., Cassagnau P.H.: Morphology and rheology of immiscible polymer blends filled with silica nanoparticles, Proceeding of 19th Congres Francais de Mecanique, August 2009, Marseille, 1-6

3. Utracki L., Wilkie C.: Polymer blends handbook, London: Springer New York, Heidelberg, Dordrecht, 2373, 2014

4. Tsebrenko M., Rezanova V., Tsebrenko I.: Polypropylene microfibers with filler in nano state, Chemistry & Chemical Technology 4(3), 253-260, 2010

5. Utracki L., Bakerdjiane Z., Kamal M.: A method for the measurement of the true die swell of polymer melts, J. Appl. Polymer Sci 19(2), 481 - 501, 1975

6. Han C.: Multiphase flow in polymer processing, New York: Academic Press, 459, 1981

7. Lutsik P., Malkin E., Abarji I.: Heat- and mass transfer at processing textile: Naukiova dumka, Kyiv, 259, 1993

8. Paul D., Bucknall C.: Polymer blends, New York: John Wiley & Sons, INC, 618, 2000