ISSN 1027-5495. Functional Materials, 26, No.2 (2019), p. 389-396.
doi:https://doi.org/10.15407/fm26.02.389

Polypropylene fine-fiber filter materials modified with nano-additives

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

[1]Kyiv National University of Technology and Design, 2
Nemirovich-Danchenko Str., 01011 Kyiv, Ukraine
[2]Vinnitsa National Pirogov Memorial Medical University, 56 Pirogov Str.,
21018 Vinnitsa, Ukraine

Received November 10, 2018

Properties of fine-fiber filter materials (FM) obtained by extraction of matrix polymer from a microfibrillary composite in the form of a film formed by extrusion of polypropylene(PP)/copolyamide(CPA)/nano-additive mixtures were studied. The main structural unit of FM is polypropylene microfiber (microfibrill), filled with mineral silica-based nano-additives. Modified FMs are characterized by high efficiency of air purification of mechanical particles of 0.3 μm and higher. The possibility to adjust the precision of filters by reducing the diameters of PP fibrils formed *in situ* and to increase their mass fraction is shown. This was achieved by introducing of nano-additives of different chemical nature into the mixture of PP/CPA and changing their concentration. Nanoparticles in the structure of filter materials contribute to their hydrophilicity and specific surface increasing, and also provide adsorption capacity, and antimicrobial action against a number of microorganisms and fungi.

Keywords: polymer mixtures, nano-additives, microfibrille, filter material.

Исследованы свойства тонковолокнистых фильтрующих материалов (ФМ), полученных экстракцией матричного полимера из микрофибриллярного композита в виде пленки, сформированной методом экструзии смесей полипропилен(ПП)/сополиамид(СПА)/нанодобавка. Основной структурной единицей ФМ являются полипропиленовые микроволокна (микрофибриллы), наполненные минеральными нанодобавками на основе кремнезема. Модифицированные ФМ характеризуются высокой эффективностью очистки воздуха от механических частиц размером 0,3 мкм и выше. Показана возможность регулирования прецизионности фильтров за счет уменьшения диаметров сформированных *in situ* ПП фибрилл и увеличением их массовой доли. Наночастицы в структуре фильтровальных материалов способствуют повышению их гидрофильности и удельной поверхности, а также обеспечивают адсорбционную способность и антимикробное действие по отношению к ряду микроорганизмов и грибов.

Модифіковані нанодобавками поліпропіленові тонковолокнисті фільтрувальні матеріали. *Н.М.Резанова, В.Г.Резанова, В.П.Плаван, О.О.Вільцанюк.*

Досліджено властивості тонковолокнистих фільтрувальних матеріалів (ФМ), одержаних екстракцією матричного полімеру із мікрофібрилярного композиту у вигляді плівки, сформованої методом екструзії сумішей поліпропілен(ПП)/співполіамід(СПА)/нанодобавка. Основною структурною одиницею ФМ є поліпропіленові мікроволокна (мікрофібрили), наповнені мінеральними нанодобавками на основі кремнезему. Модифіковані ФМ характеризуються високою ефективністю очищення повітря від механічних частинок розміром 0,3 мкм і вище. Показано можливість регулювання прецизійності фільтрів за рахунок зменшення діаметрів сформованих *in situ* ПП фібрил та збільшення їх масової долі. Наночастинки у структурі фільтрувальних матеріалів сприяють підвищенню їх гідрофільності і питомої поверхні, а також надають адсорбційну здатність та антимікробну дію до низки мікроорганізмів і грибів.

1. Introduction

Modification of the properties of synthetic fibrous materials by reducing the diameters of individual filaments to micro- and nanosizes is one of the most studied areas in the technology of polymers, since it allows to provide a complex of new characteristics and reduce material consumption for their production. Materials from micro- and nanofibres store all the positive quality indicators inherent in products made of synthetic fibers: strength, high wear and tear strength, and so on. At the same time, due to the very small diameter of individual filaments, they acquire unique properties. By processing the polymers mixture melts, a new class of composites is received in which the component of the dispersed phase forms micro- or nanofibrils in the matrix of another component *in situ*. Composites with diameters of fibers of 10 to 100 μm are called microfibrillary (MFC); if the range of diameters falls below 100 nm — nanofibrillary (NFC). At the same time, it has been found that microfibrils often have diameters from 100 to 1000 nm, and they are also referred to NFC [1]. Superfine fibers and new fibrous materials are obtained by extracting of matrix polymer from the MFC and NFC using a solvent inert to the fibrous component [1–4]. Thus, from the composites of polytetrafluoroethylene/polylactic acid (PTFE/PLA) and polybutylene terephthalate/polypropylene (PBT/PP) in the content ratio of 20/80 wt. %, using the dissolution of PLA with chloroform, and PP — with xylene of temperature 140°C, the nanofibers of PTFE and PBT with diameters from 100 to 600 nm are obtained [3]. Biodegradable fiber material for medical use from polylactic acid fibrils in the sizes from 400 nm to 1 μm was obtained by processing of the PLA/polyvinyl alcohol of 40/60 wt. % mixture [4]. In this method, it is environmentally advisable to use soluble in water or in non-toxic organic substances as a matrix component of polymers [4–6].

It is known that the diameter of the microfibrils and their length, as well as the formation of other types of structures (particles, films) are determined by the rheological properties of the components of the mixture and the degree of their interface interaction. One of the classic methods to influence on the interphase phenomena is the injection of the third component — substances that are capable of physical and/or chemical interaction with the ingredients of the mixture. In recent years, the compatibilizating effect of nano-additives in the polymer mixture melts (reduction of the surface tension) has been shown, which allows for controlling the processes of structure-formation during the processing of polymer dispersions and for providing a complex of new properties to the products thereof. Thus, by the processing of the nano-filled PP/CPA melt mixtures of 30/70 wt. % into the composite monothreads and films with the subsequent removal of CPA with an aqueous solution of ethyl alcohol, complex threads with a high specific surface and hygienic properties at the level of natural fibers were obtained [7, 8] as well as precision filter materials [9]. The injection of nanoparticles (NP) into the melt of a mixture of polymers allows us to combine the unique properties of superfine fibers and substances in the nanoscale and to create qualitatively new materials with predicted characteristics.

The purpose of the work is to modify the properties of fine-fiber materials obtained by processing the mixture melts of polypropylene/copolyamide by injecting silica-based nano-fillers.

2. Experimental

2.1. Materials used

For the research, industrial polymer samples were used: isotactic polypropylene as a fiber-forming component; copolyamide (a copolymer of caprolactam and hexamethylene adipinat in the ratio of 50:50 as a matrix polymer; their mixture in the contents ratio of 30/70 wt. %; and nano-filled systems with a nano-additives concentration (C) of (0.5÷3.0) wt. % of the polypropylene. The following inorganic compounds were selected as nano fillers: pyrogenic silica (SiO_2); and two-phase systems of silver/silica (Ag/SiO_2) and titanium oxide/silica (TiO_2/SiO_2), (Table 1). The Ag/SiO_2 nano-additive is obtained by glucose restoration of Ag^+ ions deposited from aqueous-alcoholic solution of silver nitrate on the surface of SiO_2 particles [10]. In industrial conditions, the mixed TiO_2/SiO_2 oxide is obtained by compatible high-temperature pyrolysis of $SiCl_4$ and $TiCl_4$ vapors in air-hydrogen flame at a temperature ≥1000°C. The indicated method provides a high degree of purity (>99 %) and dispersion of particles (10÷100) nm. At the interface of titanium oxide/silica, a significant amount of Si–O–Ti bonds is formed [11].

Table 1. Characteristics of used nano-additives

Name of nano-additive	Average particle size, nm	Content of the modifying substance, $\mu g/m^2$		Specific surface area, m^2/g
		Ag	TiO_2	
Pyrogenic silica	10	–	–	324
Silver/silica	17	16.3	–	296
Titanium oxide/silica	51	–	4.3	62

2.2. Methods used

The mixing of the components was carried out in an LGP-25 worm-disk extruder. In the gap between the movable and stationary discs of the extruder there are intense shear and tensile stresses that contribute to the fine uniform dispersion of the disperse phase component. To ensure maximum concentration of nano-additives in the microfiber structure, it was pre-dispersed in the melt of PP. Granules of PP/nano-additive were mixed with a matrix polymer (CPA) on the same extruder. To study the process of structure-formation of PP in the matrix, strands from the investigated mixtures were formed on LGP-25. Extraction of CPA from the strands was carried out in 70 % aqueous solution of ethyl alcohol at a temperature (70±5)°C in the Soxhlet apparatus. The residues of PP were analyzed using a MBI-15 optical biological microscope and GEOL GSM-35 scanning electron microscope. Structure formation in the strands was evaluated by counting the number of all types of PP structures in the microscope and determining their sizes. Experimental data were processed by methods of mathematical statistics; then the average diameter of microfibers (d) and their mass fractions (W) were counted. The specific surface (S_{BET}) of polypropylene microfibers was determined by a thermogravimetric method by constructing isotherms of moisture sorption-desorption versus relative humidity of the medium. The S_{BET} value was calculated using the BET equation [12]. Hygroscopicity of PP microfibers was estimated by the weight method according to the standard procedure.

Composite films, which are semi-finished products for filtering materials, were formed on the worm press through a "fish tail" type flat-slit head with a jet drawing of 200 %. Samples of FM were prepared from the composite films by removing the CPA in the conditions described for the strand microfiber. The retention ability of the filtering materials was evaluated by the efficiency of atmospheric air purification from mechanical impurities using the counter of AZ-5 aerosol particles in the range of their sizes of (0.3÷1.0) μm. The efficiency of the filtration was calculated as the ratio of the number of retained particles of the corresponding diameter to their number in the air. Permeability of FM was evaluated on a laboratory bench using distilled water at a pressure of $0.5 \cdot 10^5$ Pa. Specific productivity was determined as the volume of the filtrate passing through the filter layer per unit time from the unit of its working surface.

Studies on the antibacterial activity of FM filled with Ag/SiO_2 nanoparticles were carried out on the test strains of microorganisms and fungi recommended by WHO according to standard methods [13, 14]. Suspensions of microorganisms were prepared using the Densi-La-Meter device. The antibacterial activity of the samples of microfibers was investigated in two ways. According to the first method, the peculiarities of microorganism growth on the surface of the FM were studied by reproduction of the contamination by cultures. The samples of FM were placed in a soy-casein broth at a rate of $1 \cdot 10^7$ colony-forming units per a milliliter (CFU/ml), then they were incubated in a thermostat for 48 h; after that they were sowing on agar, and the number of microorganisms that sprouted on a nutrient medium was counted. The evaluation criterion was the reduction of the number of viable colonies of the cells of microorganisms for the appropriate period of time after contamination; this was defined as the logarithm of the number of the colonies. The second method was based on the diffuse of the active substance into the nutrient medium. For this purpose, the samples of FM were kept in a physiological saline (at the ratio of 1:5) for 2 h at a temperature of 37°C, and then the resulting liquid was poured into the wells of the nutrient medium. The microbial loading was $1 \cdot 10^7$ microbial cells per 1 ml of medium and set by the McFarland standard. For the research, the 18–24 h cul-

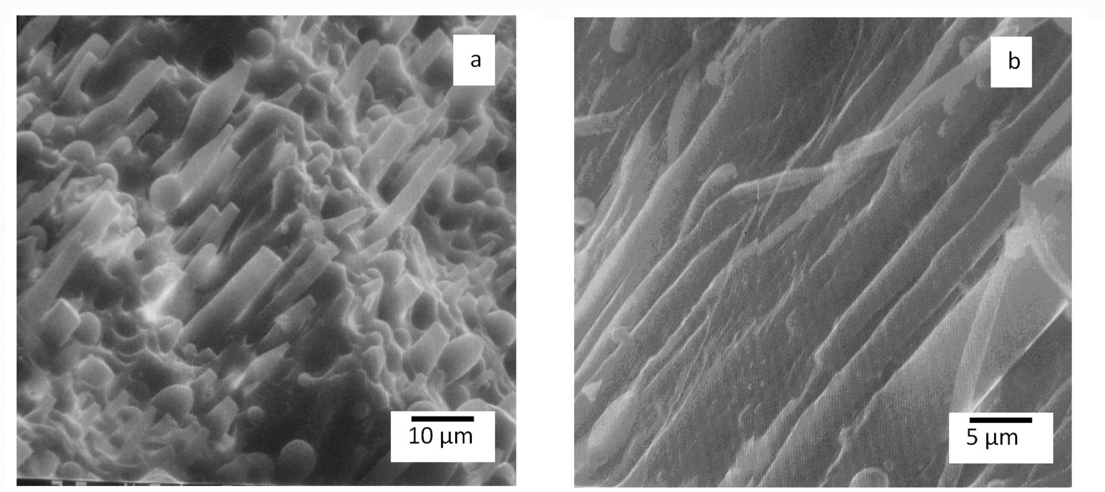

Fig. 1. SEM images of transverse (a) and longitudinal (b) chips of strand from the mixture with SiO_2 content 1.0 wt. %.

ture of microorganisms was taken. The antimicrobial activity of the modified FM was determined by the diameter of the zone of growth retardation of microorganisms around the wells (*D*), in millimeters. According to the technique used [13], filter materials are sensitive to the drug, provided that *D* exceeds 10 mm.

3. Results and discussion

Microfiltration using fine-fibrous filter materials is one of the simplest, most reliable and cost-effective methods for cleaning of gas and liquid media. The main indicators characterizing FM, namely, retaining ability (efficiency) and permeability (specific productivity) are determined by the size and form of the elements which they are made from. The average pore diameter of the filtering layers is the lower, the smaller the size of the structural elements, and their shape is the more homogeneous, the more geometrically monotonous and regular is the shape of the structures that form the FM.

It is known that in the mixing and processing of polymer mixtures into products, the component of the disperse phase is deformed and destroyed with the formation of particles in a wide range of sizes and shapes (spherical, ellipsoidal, cylindrical, and ribbon) or their combinations [2, 3]. The final morphology of the system is the result of a dynamic balance between the phenomena of deformation and capillary instability, on the one hand, and coalescence — on the other. For *in situ* formation of fibrils (microfibers) of one polymer in the matrix of another, liquid drops of the dispersed phase must deform and merge into the streams in the direction of flow and maintain a stable shape until the solidification.

Studying the microstructure of strands and residuals of PP after extraction of CPA from them showed that in the mixing of components on a worm-disc extruder, *in situ* formation of the fibrils of a component of the disperse phase (PP) in the dispersion medium (CPA) occurs. The injection of mineral nano-additives does not change the nature of the structure-formation of PP in the matrix of copolyamide. SEM images of transverse and longitudinal cleavages of a strand from the $PP/CPA/SiO_2$ mixture in the ratio of 30/70/1 wt. % clearly shows the formation of polypropylene fibrils in the CPA matrix (Fig. 1).

The performed microscopic studies showed that the dominant type of structure in the strands is the PP microfibrils. At the same time, the particles and films are formed in a small amount. The injection of all of the investigated nano-fillers helps to reduce the microfiber average diameter (Fig. 2), and to increase the mass fraction of microfibers (Fig. 3) over the entire concentration range. The maximum effect is achieved with the content of an additive of 1.0 wt. %. As can be seen from Fig. 2, 3, the modifying effect of the nano-fillers depends on the chemical nature and it is the most pronounced for TiO_2/SiO_2 nanoparticles where the average diameter of the PP microfibrils is minimal, and their mass fraction is maximal. The mixed oxide is more polar in comparison with silica, due to the formation of Ti–OH and Si–O–Ti functional groups on its surface [11], the fact which additionally complicates the interaction with the melt of nonpolar polypropylene.

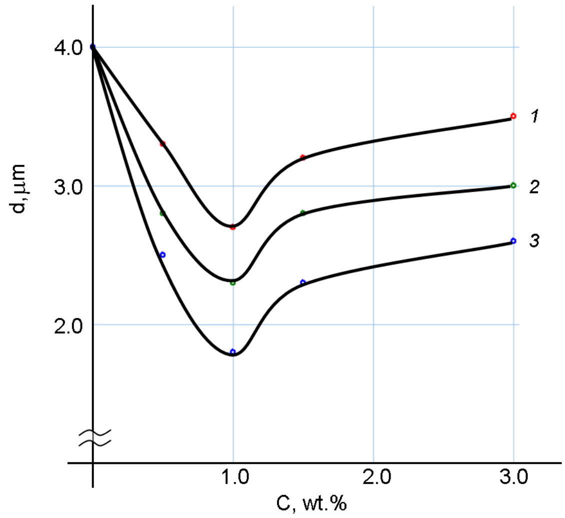

Fig. 2. Influence of concentration and chemical nature of nano-additives on the average diameter of microfibers: *1* — Ag/SiO_2; *2* — SiO_2; *3* — TiO_2/SiO_2.

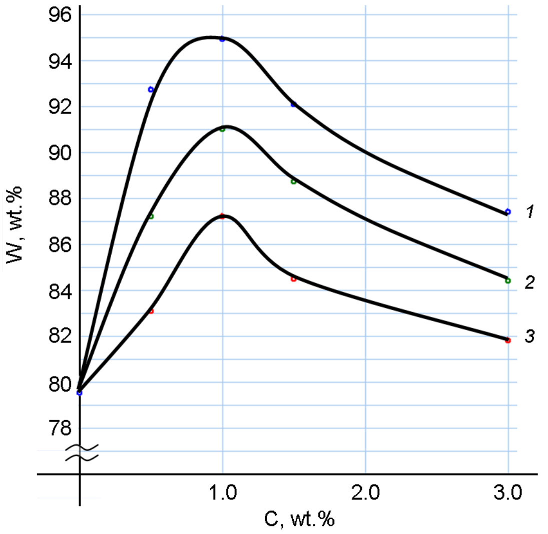

Fig. 3. Influence of concentration and chemical nature of nano-additives on microfibers mass fraction: *1* — Ag/SiO_2; *2* — SiO_2; *3* — TiO_2/SiO_2.

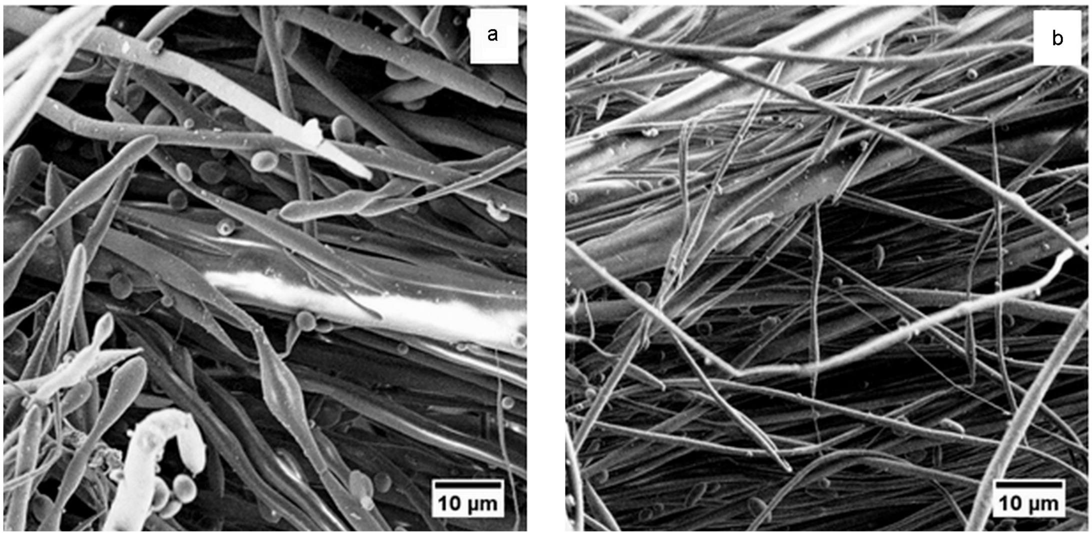

Fig. 4. SEM images of polypropylene microfibers. Content TiO_2/SiO_2, wt.%: a) 0; b) 1.0.

The nanoparticles are pushed out of the PP melt to the interphase area of the components and localized in it. It is known that the predominant placement of the NP at the interphase has the greatest effect on the processes of structure-formation in the polymer mixture melts by reducing the surface tension [15]. The formation of microfibrils of minimum diameters is caused also by the fact that in addition to the compatibilization effect, solid nanoparticles in the PP jets prevent the decomposition of finest of them into drops. From electronic microphotographs it is seen that when introducing TiO_2/SiO_2 nanoparticles, the microfibers become thinner and acquire the regular cylindrical shape. In this case, "varicose" fibers are practically absent, which are formed as a result of uncompleted decomposition of the melt jets of the dispersed phase (Fig. 4).

In order to obtain filtering materials from the granules of the output and nanofilled mixtures, a composite film was formed. In the process of extrusion, granules of the mixtures are melted, and the PP jets are decomposed into drops. Subsequently, they experience longitudinal shear deformation, merge with the formation of cylinders (fibrils) and are oriented in the direction of flow when the melt mixture

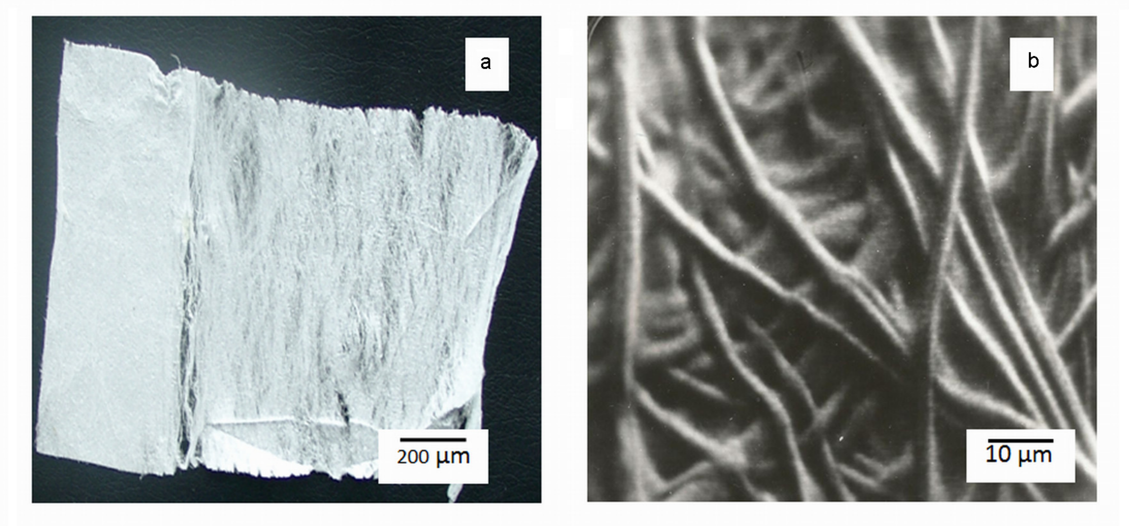

Fig. 5. Microphotography of the appearance of FM (a) and SEM image of its surface layer (b).

Table 2. Influence of nano-additives on the efficiency of atmospheric air purification and the productivity of filter materials

Name of additive	Efficiency, % (by particle size, µm)						Productivity*, $m^3/m^2 \cdot h$
	0.3	0.4	0.5	0.6	0.8	1.0	
Without additives	78.6	83.5	85.9	87.8	91.9	99.4	4.05
SiO_2	99.9	100	100	100	100	100	10.65
Ag/SiO_2	99.3	99.9	100	100	100	100	10.84
TiO_2/SiO_2	99.9	100	100	100	100	100	12.23

* at a pressure of $0.5 \cdot 10^5$ Pa.

passes through a flat-slit head. As a result, a polymeric composite with a microfibrillary structure, which took place in the strands, is formed. After extraction of the matrix polymer from the films, a non-woven fabric was received, whose main structural unit was the initial and nano-filled PP microfibers (Fig. 5). Fig. 5a shows an image of an FM sample stretched in a transverse direction; from the figure it is seen that the microfibers within the layer are parallel to each other and retain the orientation in the direction of extrusion. At the same time, in the surface layer the microfibrils partially lose their parallelism due to the features of the CPA extraction process in the Soxhlet apparatus (Fig. 5b). Using the processing of initial and three-component mixtures containing 1.0 wt. % of nano-filler, samples of FM with a filtering layer thickness of (200±20) µm were obtained. The analysis of the results of evaluating the filtration effeciency of atmospheric air from mechanical particles (0.3÷1.0) µm in size shows that the injection of nano-additives in the structure of polypropylene microfibers provides an increase in the precision and efficiency of FM (Table 2).The modified filter materials detain mechanical impurities sized of 0.5 µm and above with an efficiency of 100 %. This improvement of one of the main indicators of filters is due, first of all, to an increase in the uniformity of the filtering layer structure due to the almost twofold decrease in the average microfiber diameter and shape improvement. In addition, when cleaning media from mechanical impurities sized ≤ 1.0 µm through fibrous filter materials, the so-called "sieve" effect does not play a significant role [16]. The precision filtration occurs due to a number of physico-chemical processes — the effect of touching, adsorption, and Brownian diffusion. Due to this factors, the FM can hold particles 5 times smaller than pore size. The decisive significance of the adsorption process is demonstrated by the sharp increase in the specific surface area up to 84 m^2/g for the initial microfibers and up to (190÷244) m^2/g for the nano-filled PP ones, compared with the fibers formed according to the classical technology (Table 3).

Table 3. Influence of nano-additives on the value of specific surface and hygroscopicity of polypropylene microfibers

Name of additive	Specific surface, m^2/g	Hygroscopicity, %
Without additives	84	0.17
SiO_2	244	0.35
Ag/SiO_2	230	0.31
TiO_2/SiO_2	190	0.48

The permeability of the filters is determined by the pressure drop across both sides of the filtering partition and the material resistance to the filtered medium. Studies on the productivity of FM in distilled water showed its growth for the samples which structure contains nanoparticles of the initial and modified silica (Table 2). This is an unexpected result, since increasing the precision and efficiency of filters of any class is usually accompanied by a decrease in their permeability. The increase in productivity, apparently, is due to a decrease in the hydraulic resistance of the filter layer due to the better hydrophilicity of the nano-filled PP microfibers (Table 3). An additional factor that provides the maximum productivity of the FM modified with mixed oxide, obviously, is the ability of materials with additives of TiO_2 nanoparticles to self-cleaning like leaves of plants, insect wings, etc. [17].

Depending on the application, the filtering materials, in addition to the basic indicators, must meet a number of additional requirements. It is important that the filter layer is not a source of growth of microorganisms, has antimicrobial properties, can withstand sterilization etc. Results of the study of adsorption of bacteria from aqueous solutions by the investigated FM and nanosized silica are given in Table 4. Comparison of the obtained data shows that the adsorption capacity of the developed fibrous materials is at the level of silica, which is known to be an effective adsorbent and is widely used in medicine.

The biological activity of the developed materials was studied by the methods of contamination and diffusion of the active substance into the culture medium using the samples formed from a mixture containing 3.0 wt. % of Ag/SiO_2. In the first method, the antimicrobial action was defined as the difference between values of logarithms of microbial load and the number of viable colonies of the cells of microorganisms over the appropriate period of time. According to the method [14] for biologically active materials, this value should be at least 2 after two days, and at least 3 after 7 days. Further, the number of viable colonies of bacteria should not increase.The modified filter materials exhibit high antimicrobial and antifungal activity against reference strains of *Staphylococcus* microorganisms and *Candida* fungi (Table 5). In another method, a physiological solution was tested after keeping of FM samples in it. The results showed that the developed fine-fiber materials were sensitive to all the museum test-strains of microorganisms and fungi — the diameters of their growth retardation lie in the range of (12.3÷14.7) mm.

The nano-filled polypropylene filtering materials withstand 20-time sterilization with acute vapor and chemical reagents (water-alcohol solutions and hydrogen peroxide) and are regenerated by a reverse current by 80 %.

An important advantage of the method of obtaining a fine-fiber filter material by extraction of a matrix polymer from MFC is the possibility of increasing the working surface of the filter. It should be emphasized, that, in contrast to other methods, in this case the composite film (i.e., MFC) is corrugated, but not the finished filtering material. Thus, the possibility of mechanical damage and contamination of the filter layer is eliminated.

Table 4. Adsorption properties of modified filter materials

Sample name	Number of bacteria before processing, CFU*/ml	Number of bacteria after processing, CFU*/ml	Adsorption ability, %
FM modified by SiO_2	$1.0\cdot10^8$	$2.0\cdot10^6$	98.0
FM modified by Ag/SiO_2	$1.0\cdot10^8$	$8.9\cdot10^5$	99.2
FM modified by TiO_2/SiO_2	$1.0\cdot10^8$	$7.2\cdot10^5$	99.3
Silica A-300	$1.0\cdot10^8$	$5.7\cdot10^5$	99.4

* number of colony-forming units

Table 5. Antibacterial activity of filter materials modified by nanoparticles Ag/SiO_2

Exposure, the day	Reduction of lg K, (CFU/ml)		
	Staphylococ-cus aureus ATCC 6538 (5.74)*	*Pseudomonas aeruginosa ATCC 9027* (5.65)*	*Cadida albicans ATCC 885/653* (5.60)*
Primary sown	1.06	0.96	0.98
2	3.27	2.26	2.43
7	4.05	3.65	3.30
14	Microorganisms and fungi have not been detected		

* logarithm of microbial loading, (CFU/ml)

4. Conclusions

The possibility of forming a composite film with a matrix-fibrillar structure was established by processing of nano-filled mixtures of polypropylene/copolyamide on a worm extruder through a flat-slit head of the "fish tail" type. By extraction of copolyamide from MFC a fine-fiber material made of polypropylene microfiber filled with mineral nano-additives was produced. It was shown that the introduction of the investigated nanofillers improved the homogeneity of the filter layer by increasing the mass fraction of microfibers and reducing their average diameter. The developed FMs are characterized by increased precision and efficiency of filtration with a simultaneous increase in their productivity by a factor of (2.6÷3.0) caused by a decrease in the hydraulic resistance of the filtering layer. Due to the developed specific surface area, the modified FMs exhibit adsorption capacity for bacteria at the same level as silica. The presence of silver-containing nano-additives in the structure of materials provides an antimicrobial effect on the museum strains of microorganisms and fungi. Thus, the fine-fiber FMs with nano-filled polypropylene microfibers are deep action precision materials which can be used for purification of drinking water, liquid and gas technological environments of food and medical industries.

References

1. S.Thomas, R.Mishra, N.Kalarikka, Micro and Nano Fibrillar Composites (mfcs and nfcs) from Polymer Blends, Woodhead Publishing, Sawston (2017).
2. L.A.Utracki, C.A.Wilkie, Polymer Blends Handbook, Springer NY Heidelberg Dordrecht, London (2014).
3. Vu Anh Doan, Masayuki Yamaguchi, *Recent Res. Devel. Mat. Sci.*, **10**, 59 (2013).
4. R.J.Shields, D.Bhattacharyya, S.Fakirov, *J. Mater. Sci.*, **43**, 6758 (2008).
5. N.H.A.Tran, H.Brunig, M.A.Landwehr et al., *J. Appl. Polym. Sci.*, **133**, 442 (2016).
6. N.H.A.Tran, H.Brunig, R.Boldt et al., *Polymer*, **55**, 6354 (2014).
7. N.M.Rezanova, V.P.Plavan, V.G.Rezanova et al., *Vlakna a Textil*, **4**, 3 (2016).
8. N.M.Rezanova, V.G.Rezanova, V.P.Plavan et al., *Vlakna a Textil*, **2**, 37 (2017).
9. P.A.Hlubish, V.M.Irkley, N.M.Rezanova et al., High-tech, Competitive, Environmentally Oriented Fibrous Materials and Products from Them, Aristey, Kyiv (2007).
10. N.M.Rezanova, V.P.Plavan, L.S.Dzubenko et al., *Nanosyst., Nanomat., Nanotechn.*, **16**, 55 (2018).
11. Chemistry of the Surface of Silica, ed. by A.A.Chuyko, IHP NANU, Kyiv (2001).
12. R.V.Lutsik, E.S.Malkin, I.I.Abarji, Heat and Mass Transfer in the Processing of Textile Materials, Naukova Dumka, Kyiv (1993).
13. Yu.L.Volianskiy, I.S.Hritsenko, V.P.Shirobokov, Study of Specific Activity of Antimicrobial Drugs. Method. Instr. State Pharmacological Center, Kyiv (2004).
14. Determination of the Sensitivity of Microorganisms to Antibacterial Drugs. Method. Instr. MB 9.9.5. Ministry of Health of Ukraine, Kyiv (2007).
15. Polymer Blends, ed. by D.R.Paul, C.B.Bucknall, John Wiley & Sons, Inc., New York (2000).
16. Filters and Filtration Handbook, ed. by Ch.Dickenson, 3-rd ed. Elsevier Adv. Tech., Oxford (1992).
17. V.E.Geller, *Chem. Fibers*, **2**, 3 (2013).