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Investigation of the influence of nanomodifying additives on the molding process and physical and mechanical properties of complex polypropylene yarns

S.M.Bereznenko[1], N.V.Sadretdinova[1], N.M.Bereznenko[2], L.B.Bilotska[1]

[1]Kyiv National University of Technologies and Design, 2 Nemyrovycha-Danchenka Str., 01011 Kyiv, Ukraine
[2]The State Research Institute of Ministry of Internal Affairs of Ukraine, 4A Ievhena Hutsala lane, 01011 Kyiv, Ukraine

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The article presents the results of the study of indicators that affect the process of formation of complex polypropylene yarns modified by Ag, Cu, Fe and (Ag + Cu) nanoparticles with antimicrobial action. The impact of the above additives on the change of the main physical and mechanical properties of the obtained nanomodified complex polypropylene yarns is shown, in particular, breaking load and change in linear dimensions. The paper also pays attention to the study of the temperature impact on the change of linear dimensions of polypropylene yarns containing nanoparticles. The study demonstrates the possibility of using the proposed nanomodified complex polypropylene yarns for the manufacture of materials and products with antimicrobial properties without losing their physical and mechanical properties. It is also important that the obtained nanomodified polypropylene complex yarns can be further processed into products.
Keywords: complex polypropylene yarns, nanomodification, antimicrobial properties, breaking stress, heat setting.

Дослідження впливу наномодифікуючих добавок на процес формування і фізико-механічні властивості комплексних поліпропіленових ниток. *С.М.Березненко, Н.В.Садретдінова, Н.М.Березненко, Л.Б.Білоцька*

Досліджено формування комплексних поліпропіленових ниток, модифікованих наночастинками з антимікробною дією Ag, Cu, Fe, (Ag + Cu). Показано вплив вищевказаних добавок на зміну основних фізико-механічних властивостей одержаних наномодифікованих комплексних поліпропіленових ниток, зокрема розривального навантаження та зміну лінійних розмірів. Вивчено вплив температури на зміну лінійних розмірів поліпропіленових ниток з вмістом наночасток. Встановлено необхідність попередньої термофіксації для забезпечення стабільності лінійних розмірів ниток у процесах наступної переробки. Проведені дослідження демонструють можливість використання запропонованих наномодифікованих комплексних поліпропіленових ниток для виготовлення матеріалів та виробів з антимікробними властивостями без втрати фізико-механічних показників останніх. Одержані наномодифіковані поліпропіленові комплексні нитки можуть у подальшому перероблятися.

Изучено получение комплексных полипропиленовых нитей с антимикробным действием, модифицированных наночастицами Ag, Cu, Fe, (Ag + Cu). Показано влияние вышеуказанных добавок на изменение основных физико-механических свойств полученных наномодифицированных комплексных полипропиленовых нитей, в частности разрывного напряжения и изменение линейных размеров. Исследовано влияние температуры на изменение линейных размеров полипропиленовых нитей с содержанием наночастиц. Определена необходимость предварительной термофиксации для обеспечения стабильности линейных размеров нитей в процесах последующей переработки. Показана возможность использования предложенных наномодифицированных комплексных полипропиленовых нитей для изготовления материалов и изделий с антимикробными свойствами без потери их физико-механических свойств. Полученные наномодифицированные полипропиленовые нити могут в дальнейшем перерабатываться.

1. Introduction

Antimicrobial materials and products based on fibrous carriers are widely used in many spheres of human life and the environment [1, 2]. To obtain antimicrobial fibers and yarns, various modification methods are used, including nanotechnologies: impregnation; formation of fibers from solutions and melts of polymers containing antiseptic substances (antibiotics, enzymes); introduction of nanoparticles (NPs) of various chemical nature and geometric shapes into the structure of yarns; application and fixing of NPs on the surface of yarns [3, 4]. Each of the methods has its advantages and disadvantages, and the world scientific community continues to work hard to overcome them [5]. The introduction of NPs metals, their oxides or combined additives into synthetic monofilaments in the process of molding is quite effective and promising. Significant interest in these developments is due to the fact that particle-filled polymer fibers and yarns have a wide spectrum of bactericidal action against pathogenic microflora, show virucidal and fungicidal activity over a long period of use [6, 7]. Another method involves dressing with surfactants, which are carriers of useful properties and can be adsorbed by fibers or modify their structure. In this way, it is possible to change the properties of the fiber surface in situ and influence the processes occurring at the interface [8].

Along with the development and improvement of modification methods, an important task of scientific research in the textile industry is to study the mechanical and physico-chemical properties of modified fibers [9–11]. Since modification processes complement and complicate the production technology of fibers and yarns, it leads to changes, sometimes negative, in their structure and properties.

The aim of the work is to study the effect of antimicrobial modifiers on the physical and mechanical properties of polypropylene monofilament yarns when using various modification methods to ensure that they can be processed by existing knitwear and textile equipment.

2. Experimental

In the study, the following substances were used to create nanomodified polypropylene complex fibers:

— thermoplastic polymer polypropylene (hereinafter referred to as PP) (Technical spesificatons in the territory of Ukraine 54008400-97, Grade A);

— as antimicrobial substances – silver (Ag), copper (Cu), and iron (Fe) nanoparticles in the low-melting surfactant PEG-115 (hereinafter referred to as surfactants) in the form of a paste; Ag nanoparticles, a mixture of silver and copper (Ag + Cu) in alcohol solution and silver Ag and iron Fe aqueous solution.

Nanoparticles of Ag, mixtures of silver and copper (Ag + Cu) in alcohol and silver Ag and iron Fe aqueous solutions were provided by the V.M.Bakul Institute of Superhard Materials (ISM of the National Academy of Sciences of Ukraine) following the agreement on scientific and technical cooperation. For obtaining highly concentrated silver suspensions, the method of single-stage preparation of suspensions of nanoscale particles of electrically conductive materials was used, where they are organized in the process of plasma dispersion of metals, alloys and other electrically conductive materials by a localized plasma jet and, in a single-stage technological cycle, are introduced (implanted) by the same jet into glycerol located in a vacuum chamber. At the same time, 75 % of metal particles have a size that ranges from 30 to 60 nm.

In order to create a modified thermoplastic composition based on polypropylene modified with metal nanoparticles, a method was used that is characterized by simplicity of implementation and does not require new equipment.

Nanoparticles of Ag, Cu, (Ag + Cu) in an alcohol solution and Ag and Fe in an aqueous solution were applied immediately to PP

Table 1. Characteristics of PP granules modified with metal nanoparticles

Sample characteristics	Dispersion environment	Surfactant content	* Modifier content in surfacant
Unmodified polypropylene (control sample)	–	–	–
Polypropylene modified with silver (Ag)	PEG-115	1.0	$4 \cdot 10^{-4}$
Polypropylene modified with silver (Ag)	PEG-115	0.5	$2 \cdot 10^{-4}$
Polypropylene modified with silver (Ag)	Water	1.0	$4 \cdot 10^{-4}$
Polypropylene modified with silver (Ag)	Alcohol	1.0	$4 \cdot 10^{-4}$
Polypropylene modified with silver (Ag)	Glycerin	1.0	$4 \cdot 10^{-4}$
Polypropylene modified with copper (Cu)	PEG-115	1.0	$4 \cdot 10^{-4}$
Polypropylene modified with copper (Cu)	PEG-115	0.5	$2 \cdot 10^{-4}$
Polypropylene modified with a mixture (Ag + Cu)	Alcohol	1.0	$4 \cdot 10^{-4}$
Polypropylene modified with a mixture (Ag + Cu)	Alcohol	0.5	$2 \cdot 10^{-4}$
Polypropylene modified with iron (Fe)	Water	1.0	$4 \cdot 10^{-4}$
Polypropylene modified with iron (Fe)	Water	0.5	$2 \cdot 10^{-4}$

* — by calculation.

granules, thoroughly mixed until the alcohol and aqueous solution completely evaporated at room temperature. The surfactant content varied from 0.3 % to 1 %.

The obtained experimental samples of mixtures were dried in a drying cabinet at a temperature of 60°C for 1 h before further processing. To obtain a granulate modified with Ag, Cu, Fe, (Ag + Cu) nanoparticles, the vein was immersed in water with a temperature of 20±3°C on a laboratory LSP extruder, followed by grinding the vein into granules of 3.0÷3.5 mm in size. The estimation of granularometric composition wasn't made, but for a more uniform distribution of nanoparticles in the polymer mass, double granulation of the treated granules was performed at the following parameters: cylinder temperature 250°C, nozzle temperature 240°C. The characteristics of the obtained granules are given in Table 1.

3. Results and discussion

Complex polypropylene fibers were made from the obtained PP granules with antimicrobial properties modified with nanoscale Fe (Ag + Cu) particles using a periodic molding process on an extrusion machine of the UFTP brand and drawing on a draw-twister bench of the VSTV brand. Soviet-made laboratory equipment was used in the study.

Before forming PP fibers, modified polypropylene granules were dried in a vacuum drying cabinet at 80°C for 3 h.

Parameters of forming polypropylene yarns on the UFTP machine:

— melt supply rate, g/min – 15.3

— forming speed, m/min. – 100

— temperature by zones, °C: cylinder — 255±3, measuring pump — 250±3, die set — 250±3

— number of die holes – 12

— oiler ASH-12, %, no more than – 3.

Parameters for drawing polypropylene yarns on the VSTV bench:

— draw multiplicity, – 3.6÷5.4

— drawing temperature, °C – 110±3

— drawing speed, m/min. – 40±50

The obtained complex yarns modified with metal nanoparticles are shown in Fig. 1.

When manufacturing clothing and its elements using nano-modified complex yarns, it is necessary to consider the influence of Ag, Cu, Fe nanoparticles on the process of forming and drawing complex polypropylene fibers, as well as the physical and mechanical properties of the resulting fibers in order to assess the possibility of their use for the manufacture of textile materials.

3.1. The investigation of the temperature effect on physical and mechanical properties of modified PP yarns

One of the most important characteristics of synthetic yarns is their heat resistance, which causes changes in the physical and mechanical properties of yarns under the influence of elevated temperatures. Of particular interest are studies on

Fig. 1. Complex filaments modified with metal nanoparticles.

the heat resistance of modified polypropylene yarns at thermofixation temperatures of 80, 110 and 140°C (Table 2), the heat treatment of which was carried out on a rigid frame under tension for one hour.

Data given in Table 2 indicate that when the thermal fixation temperature increases to 140°C, the relative breaking load increases in the initial and modified PP samples of yarns containing different amounts of metal nanoparticles, regardless of their state (paste, alcohol, water solution). Thus, during heat treatment (in the temperature range from 80 to 140°C), the physical and mechanical properties of PP yarns improve, which makes it possible to use them at elevated temperatures in products for various purposes.

3.2. The research of the effect of heat treatment temperature on the change in linear dimensions of modified PP yarns

Considering the further use of polypropylene yarns modified with Ag, Cu and Fe nanoparticles in the production of textile materials and products for various purposes based on them, it became necessary to determine the change in the linear dimensions of the resulting yarns.

When processing PP yarns into products (non-woven materials, fabrics, knitwear), the latter after hot and wet treatments (dying, finishing, washing, etc.) significantly reduce in size. The change in linear dimensions is accompanied by an increase in the thickness of the fibers and increased elongation when they break.

In order to prevent or partially reduce changes in the linear dimensions of products when they are treated in wet and hot environments, the yarns must be previously subjected to additional heat treatment at temperatures slightly higher than the treatment temperature of the products.

The best results are achieved if the yarns are thermally fixed under tension or on rigid cores, which limit the possibility of

Table 2. Indicators of the breaking load of PP filaments modified with metal nanoparticles

Type of yarn	Dispersion environment	Relative breaking load, cN/ tex at temperature			
		20°C	80°C	110°C	140°C
PP (initial)	–	35.8	36.2	35.7	36.5
PEG-115 + Ag					
PP + 0.3 %	paste	34.5	36.8	40.5	39.8
PP + 0.5 %	paste	33.7	36.0	39.5	39.9
PP + 1.0 %	paste	37.5	39.5	42.4	40.8
PP + Ag	alcohol	38.5	39.2	40.6	39.8
PP + Ag	water	17.3	17.5	19.9	20.8
PEG-115 + Cu					
PP + 0.3 %	paste	35.9	36.8	39.5	39.2
PP + 0.5 %	paste	36.7	38.9	38.8	39.0
PP + 1.0 %	paste	37.7	36.8	39.5	41.2
PEG + Ag + Cu					
PP + 1.0 %	alcohol	36.5	36.9	38.9	37.2
PEG-115 + Fe					
PP + 1.0 %	water	35.7	38.9	39.0	40.8

Table 3. Temperature dependences of changes in the linear dimensions of nanomodified PP yarns

Type of yarn	Dispersion environment	Change in linear dimensions, % at temperature		
		80°C	110°C	140°C
PP (initial)	–	4.4	6.1	9.5
PEG-115 + Ag				
PP + 0.3 %	paste	2.4	5.5	8.5
PP + 0.5 %	paste	2.8	5.4	11.3
PP + 1.0 %	paste	4.3	6.9	11.8
PP + 1.0 %	alcohol	3.6	6.2	13.4
PP + 1.0 %	water	4.8	7.2	10.8
PEG-115 + Cu				
PP + 0.3 %	paste	4.2	7.0	10.5
PP + 0.5 %	paste	3.9	6.5	11.3
PP + 1.0 %	paste	3.2	6.9	11.1
PEG-115 + Ag + Cu				
PP + 0.5 %	alcohol	2.6	5.0	9.2
PP + 1.0 %	alcohol	2.6	5.0	9.2
PEG-115 + Fe				
PP + 0.5 %	water	2.4	5.3	9.4
PP + 1.0 %	water	2.4	5.3	9.4

Table 4. Dependences of changes in the linear dimensions of nanomodified PP yarns on the temperature thermofixation

Thermofixation temperature, °C	Type of sample	Change in linear dimensions, %, at test temperature	
		80°C	110°C
80	PP + (1 % PEG-115 + Ag)	1.24	3.68
	PP + (1 % PEG-115 + Cu)	1.05	3.0
	PP + (1 % PEG-115 + Fe)	1.0	2.3
110	PP + (1 % PEG-115 + Ag)	0.64	2.04
	PP + (1 % PEG-115 + Cu)	0.44	2.28
	PP + (1 % PEG-115 + Fe)	0.68	2.32
140	PP + (1 % PEG-115 + Ag)	0.72	1.4
	PP + (1 % PEG-115 + Cu)	0.4	1.16

changing the linear dimensions of the yarns. It is known that the higher the thermal fixation temperature of the fiber, the smaller the change in linear dimensions during further operations [6]. At this stage, the effect of the heat treatment temperature on the change in the linear dimensions of polypropylene yarns containing nanoparticles of various metals (Ag, Cu, Fe) was studied. The change in the linear dimensions of PP yarns in the free state was determined by holding samples in a thermal cabinet for one hour at temperatures of 80, 110 and 140°C (Table 3).

The data obtained (Table 3) indicate that in the free state, the change in the linear dimensions of the initial and modified with metal PP yarns increases by more than 2 times with an increase in temperatures from 80 to 140°C. To reduce the change in the linear dimensions of PP yarns, preliminary thermofixation was performed in a fixed state at temperatures of 80, 110 and 140°C (Table 4).

Table 5. Physical and mechanical properties of modified PP yarns

Sample	Thermofixation at 100°C	Linear density, tex	Breaking load, cN	Breaking elongation, %	Relative breaking load, cN/tex
PP + 0.5 % (PEG-6000 + 0.5 % Cu)	–	27.0	1014.8	24.1	37.6
	+	27.6	1245.2	19.4	45.1
PP + 1 % (PEG-6000 + 1 % Cu)	–	23.5	1005.6	28.3	42.8
	+	28.9	1336.0	19.7	46.2
PP + 1 % (PEG-6000 + 10 % Ag)	–	28.8	958.0	23.8	33.3
	+	26.8	1088.0	21.3	40.6

The data shown in Table 4 indicate that preliminary thermofixation with an excess of the thermofixation temperature over the temperature of subsequent processing by 30°C can significantly reduce the indicators of changes in the linear dimensions of PP filaments in comparison with fibers in which there was no previous thermofixation (Table 5). These data should be considered when choosing the conditions for thermofixation of PP yarns during subsequent processing.

In addition to introducing Ag, Cu, and Fe nanoparticles into PP yarns from alcohol and aqueous solutions, we tested the method of introducing Ag, Cu, and Fe nanoparticles into PP complex yarns, when nanoparticles were previously introduced into a solid carrier (PEG-6000).

3.3. The investigation of PP fibers modified with metal nanoparticles obtained by thermal vacuum spraying of metals

A more promising and effective method of introducing nanoparticles, in our opinion, is the method of vacuum thermal spraying, in which metal particles are dispersed and then condensed. Using this method, experimental samples of Ag and Cu nanopreparations were obtained, which were introduced into a solid carrier (PEG-6000). The nanoparticle size was about 70 nm or less.

The thermoplastic polymer composition modified with Ag and Cu nanoparticles was obtained in the following way. A modifying preparation (PEG-6000) was applied to heated PP granules in the form of a white powder, on which Cu (Ag) nanoparticles were pre-applied by vacuum thermal spraying, thoroughly mixed, cooled at room temperature and processed on a laboratory screw press (LSP) according to the standard method. The advantage of the above method for obtaining thermoplastic fiber is that the modifying preparation PEG-6000 with Cu (Ag) nanoparticles did not need to be dissolved with ethyl alcohol, which greatly simplifies the technology for obtaining yarns.

The formation of PP fibers modified with Cu (Ag) nanoparticles was performed on a UFTP machine at the following parameters:

— melt feed speed, g/min 15.3
— molding speed, m/min 80
— molding temperature by zone (cylinder, metering pump, spinneret unit), °C 250±2
— Oil-ASH-12 max, % 3
— number of spinneret holes 12
— diameter of spinneret holes, mm 0.5

Thermal drawing of PP yarns was carried out on the bench for drawing-out of yarn VSTV at the following parameters:

— draw multiplicity 5.0
— heater temperature, °C – 110±3
— drawing speed, m/min 40
— number of twists, T/m-40

The physical and mechanical properties of the drawn PP yarns are shown in Table 5.

When sewing clothes and its individual elements, it is necessary to treat them at high temperatures (above 100°C). This can result in deformation of the product due to change in linear dimensions of yarns. This makes it necessary to carry out termofixation before using them. As can be seen from the data in Table 5, the thermofixation of yarns at 100°C leads to an increase in the strength of yarns and a decrease in the breaking elongation. The changes in the linear dimensions of the modified yarns are shown in Table 6.

The data in Table 6 indicate that shrinkage depends on temperature and varies in the drawn PP yarns from 3.6 % to 7.1 %; and after thermofixation, there is a decrease in these indicators. Therefore, the introduction of nanoparticles into the com-

Table 6. Changes in linear dimensions of modified yarns

Sample	Thermofixation at 100°C	The change in linear dimensions, %, at test temperature		
		60°C	80°C	100°C
PP + 0.5 % (PE-6000 + 0.5 % Cu)	196	3.6	4.7	6.9
		–	–	4.0
PP + 1 % (PE-6000 + 1 % Cu)	–	3.6	4.4	5.8
	+	–	–	4.0
PP + 1 % (PE-6000 + 10 % Ag)	–	4.2	5.4	7.1
	+	–	–	3.6

position by vacuum thermal spraying is effective and demonstrates a reduction in shrinkage of the drawn PP yarns by 40–50 % after thermofixation of the yarn samples at 100°C.

4. Conclusions

The processes of PP fiber formation of complex yarns modified with Ag, Cu, and Fe nanoparticles have been investigated. The parameters of molding and thermo-orientation drawing of examined samples, as well as their physical and mechanical properties, were determined. It is shown that the obtained nanomodified PP complex yarns have satisfactory physical and mechanical properties and can be further processed on existing knitting and textile equipment. A method for stabilizing the linear dimensions of the obtained yarns by thermofixation was proposed. The studies carried out make it possible to use of nanomodified PP yarns for the manufacture of competitive materials and products with antimicrobial properties (atraumatic bandages, dressings, socks, bactericidal knitted, woven and nonwoven materials).

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