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Bacteria of the genus *Bacillus* as a method of directed modification of polycaproamide fibers

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In this paper, studies are presented that indicate the feasibility and effectiveness of the use of the genus *Bacillus* microorganisms for the directional modification of physicomechanical properties (strength, nominal stretching) of polycaproamide fibers and the production of high-strength polymer-matrix composites. Bacteria of the genus *Bacillus* can affect the structure of the surface of the fibers by increasing the nanoroughness and the amorphous layer. It is possible to use *Bacillus brevis*, *Bacillus subtilis*, *Bacillus mesentericus* and others strains to improve the consumer characteristics by the direct biodegradation of polycaproamide fibers.

Key words: fiber, surface, modification, microorganisms.

Introduction

Currently, the main direction of technical progress in the industry of chemical fibers is not so much the development of new types of polymers but the modification of the known chemical fibers and the creation of composite materials. When creating new composite materials, the interaction of the components is controlled by various methods, for example, by mechanical, chemical, radiation effects. However, the application of these methods is connected with considerable technological and ecological restrictions. It is especially difficult to reach the effect at the modification of modern high-strength fibers. At present, the method of biomodification, based on the effect of the products of the vital activity of microorganisms on a chemical fiber, is applied. Taking into account the almost unlimited spectrum of microorganisms and the mild conditions of exposure, the possibility of directional modification of the known fibers is opened, with the aim of giving them new, pre-defined properties, improving the quality of finished products and expanding their field of application [1, 2].

Materials and methods

Modifications were made to polycaproamide fibers tex 93 produced by the branch "Plant Khimvolokno" JSC "Grodno Azot", which are used for the production of cord fabrics and the reinforcement of composite materials. The diameter of the polyamide fiber is 31 ± 2 μm.

For the microbial modification of fibers, bacteria of the genera *Bacillus* (*Bacillus brevis, Bacillus subtilis, Bacillus mesentericus, Bacillus cerculans, Bacillus thuringiensis, Bacillus polymixa, Bacillus albus, Bacillus pumilus, Bacillus sphaericus, Bacillus mycoides)* were used from the collection of microorganisms of the Department of Ecology of the Faculty of Biology and Ecology, the Yanka Kupala State University of Grodno. As the culture medium for the bacteria, the meat-peptone broth (MPB), the synthetic medium Evans supplemented with caprolactam [5], the synthetic (minimal) medium stabilized with polyvinyl alcohol were used [4]. The treatment of the fibers was carried out by culturing microorganisms in the liquid nutrient media in Erlenmeyer flasks, volume 100 cm^3, in the number of 1 g of fiber on a shaker at 120 °C for 7, 14 and 21 days [3]. After that, the fibers were washed with distilled water until the nutrient medium and the waste products of the microorganisms were

completely washed out. Next, the moisture from the samples was removed by drying at a temperature of 20–25 °C during 24–48 hours.

The change in the fiber surface structure was studied by optical methods (inverse metallographic microscope MMP-1600T, Microtestmines, Belarus), confocal laser (OLYMPUS Lext OLS 4000, Japan) and atomic force microscopy (NT206, Microtestmushins, Belarus).

The size of the biomodified layer of the polyamide fiber was determined as the amount of amorphous fiber (in μm) of the fiber observed visually and measured using the "Ruler" tool of the Adobe Photoshop CS6 version 13.0.1 and the standard ruler OLYMPUS Lext OLS 4000 microscope.

The fiber strength test was carried out using a ZWICK / ROELL Z010 (Zwick Roell Group) testing machine designed to conduct static tests and to determine the physical properties of materials for axial stretching, compression, bending.

Endo- and exothermic transitions were investigated by differential scanning calorimetry (Discovery DSC, TA Instruments, USA).

The thermogravimetric analysis of the fibers was carried out by using a Discovery TGA thermogravimetric analyzer.

Results and discussion

When microscopic fibers were examined by means of optical microscopy, the greatest changes in the structure of the fiber as compared to the control were detected in 6 samples out of 18, which were taken for the further studies (Table 1).

Table 1. Scheme of culturing samples

Fiber sample number	Kind of microorganism	The nutrient medium	Cultivation time, day
1	*Bacillus brevis*	Evans medium	21
2	*Bacillus brevis*	MPB	14
3	*Bacillus subtilis*	MPB	14
4	*Bacillus mesentericus*	Evans medium	21
5	*Bacillus mesentericus*	Evans medium	7
6	*Bacillus mesentericus*	minimal medium	14

Fiber microscopy with the help of a laser confocal microscope indicates that the modification of fibers with a *Bacillus brevis*, *Bacillus subtilis*, *Bacillus mesentericus* strains leads to the formation of more developed surfaces with a shallow fibril-like structure (Fig. 1).

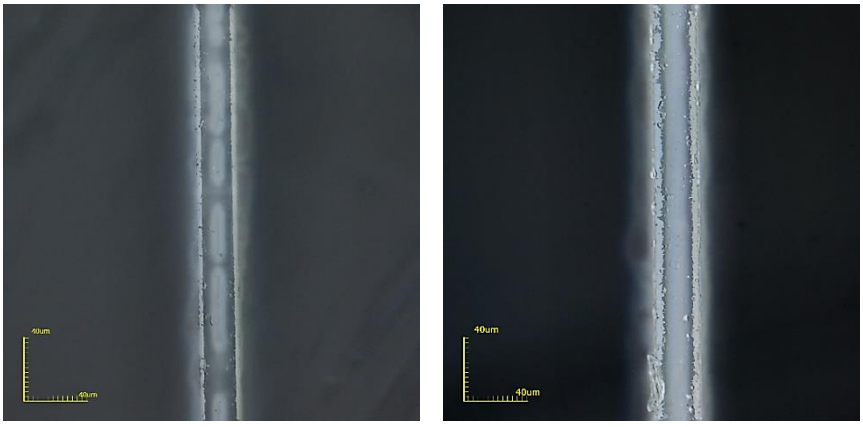

Fig. 1. The surface of the polyamide fiber of the control sample (left) and sample No. 4, modified with *Bacillus mesentericus* bacteria (right).

The size of the amorphous layer of the samples studied increases by a factor of 2 in the case of culturing *Bacillus subtilis* on the MPB for 14 days as compared with the unmodified sample (Fig. 2).

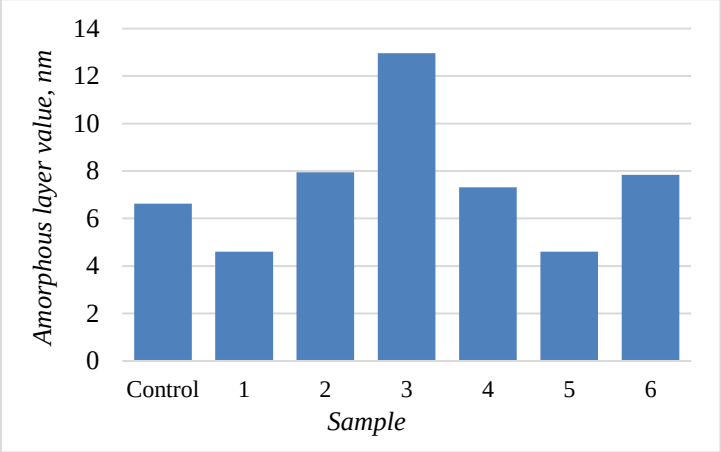

Fig. 2. Amorphous layer of control and biomodified samples.

When studying the nanoroughness using an atomic-force microscope, the number of depressions and protrusions on the surface of the samples under study was also taken into account (Table 1).

Table 2. The number of protrusions, depressions and nanoroughness of polyamide fiber

Sample fiber	Number of protrusions, pcs.	Number of depressions, pcs.	Nanoroughness, nm
Control	8	5	118,71
1	31	17	292,53
2	17	15	214,41
3	21	9	160,48
4	27	14	236,69
5	13	13	170,06
6	14	10	110,90

The greatest change in the nanosurface (up to 2.5 times) of the modified samples was observed upon exposure to fibers by strains *Bacillus mesentericus, Bacillus. brevis* (Fig. 3) for 14–21 days on a synthetic environment of Evans with the addition of caprolactam and a minimal medium stabilized with polyvinyl alcohol.

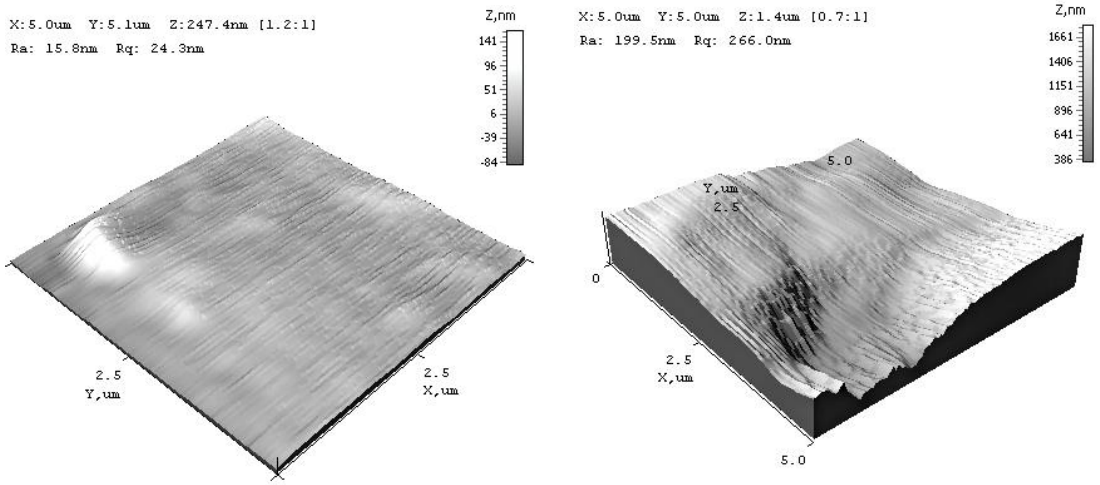

Fig. 3. 3D model of the surface of the control sample (left) and sample No. 1, modified with *Bacillus brevis* bacteria.

By the biomodification of a polyamide fiber, its nominal tension is increased 2.3 times as compared with the control sample (Table 2). The increase in the nominal tensile strength and the

strength (up to 60 % when exposed to the strain *Bacillus brevis* and *Bacillus subtilis* for 14–21 days on the media used) of polyamide fibers may indicate the improvement in the consumer characteristics of the modified fibers. Also, an increase in strength by 20 % (in comparison with the control sample) was recorded in the works of I. M. Korin [4].

When using modified polyamide fibers to create high-strength composites, it is of interest to reduce the nominal tensile strength during a short-term modification (sample 4 when exposed to the *Bacillus mesentericus* strain).

Table 2. Physical properties of materials with axial tension

Sample fiber	Stress at a tension of 1 %, MPa	Strength, N / tex	Relative elongation at break, %
Control	3.630 ± 0.104	0.143 ± 0.001	9.5 ± 3.7
1	0.573 ± 0.104	0.171 ± 0.001	19.1 ± 3.7
2	0.673 ± 0.104	0.083 ± 0.001	21.7 ± 3.7
3	1.010 ± 0.104	0.154 ± 0.001	20.2 ± 3.7
4	1.470 ± 0.104	0.091 ± 0.001	8.3 ± 3.7
5	0.609 ± 0.104	0.082 ± 0.001	No gap
6	0.493 ± 0.104	0.072 ± 0.001	No gap

Such changes in the properties of polyamide fibers after biomodification are due to a change in the chemical nature of the fiber surface [0, 1]. It is known that in the process of vital activity microorganisms produce a wide range of enzymes, organic acids, surface-active and other substances, change the pH of the medium. This can lead to the rupture of intra- and intermolecular hydrogen bonds in chains and cause conformational changes in macromolecules, *i.e.* lead to a change in the composition of chemical groups and their amount on the surface. Possible is a slight enzymatic hydrolysis of the amide bond, since it is known that bacteria of the genus *Bacillus* are producers of proteolytic enzymes. In addition, some enzymes of the genus *Bacillus* bacteria are capable of transferring the chemical groups and cross-linking of the molecules.

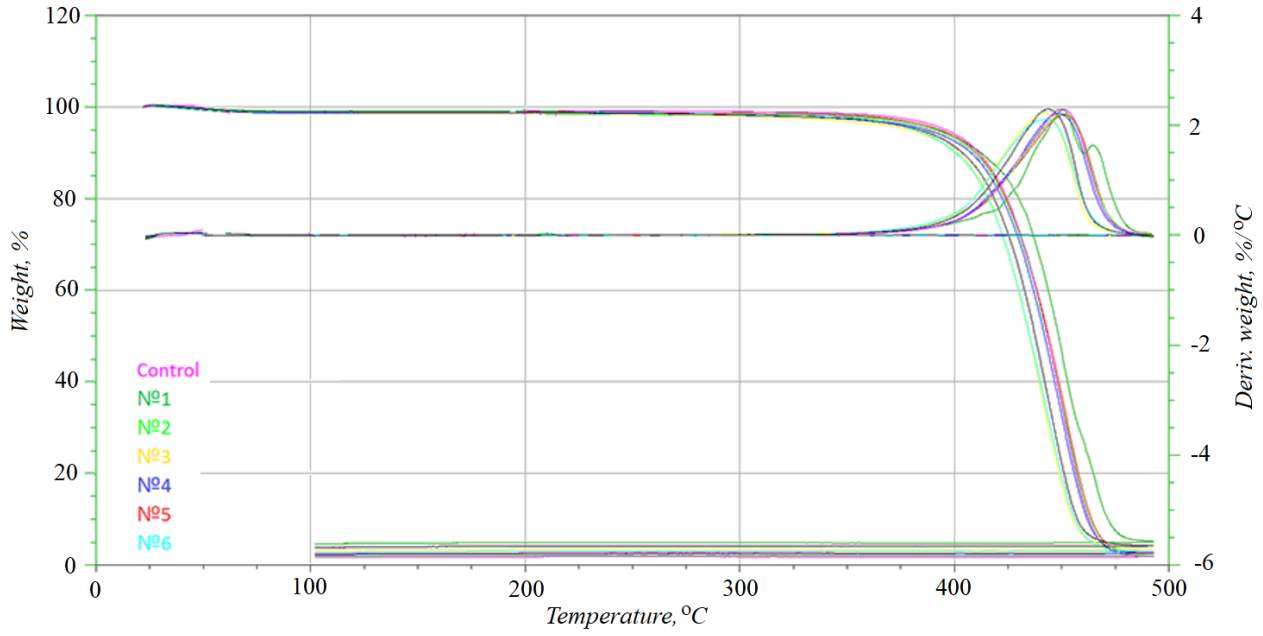

Fig. 4. Curves of thermogravimetric analysis of biomodified and control samples.

As a result of the study of endo- and exothermic transitions, it was revealed that the melting points of the samples under study did not change significantly. The enthalpy of some biomodified samples was reduced (for example, when the *Bacillus brevis* strain was grown on the MPB for 14 days – by 20.3 %), while the others were increased (for example, when the strain

Bacillus mesentericus was cultured on the Evans medium for 7 days – by 53.8 %) (Table 3).

Table 3. Changes in the oxidation temperature of modified fiber samples during a dynamic thermal analysis

Sample fiber	Oxidation temperature, ºC	Thermal peak, ºC	Melting enthalpy, J/g
Control	39,91	213,29	50,84
4	39,94	214,13	40,53
8	39,80	216,10	78,17

From the course of thermogravimetric analysis of the fibers it is seen that the mass of both the initial and the modified samples does not change to the temperature of 380 °C, which indicates its thermal stability (Fig. 4). At a temperature above 380 °C, a decrease in the mass of the samples is observed with the release of volatile products from the polymer, proceeding in two stages: more slowly in the temperature range 380–420 ºC and faster at 420–500 °C. In the first stage of decomposition, the mass of the samples is reduced on average by 15.2 %, whereas in the second stage the control and composite samples undergo almost a complete decomposition.

Conclusions

Thus, the results of the study of the effect of the genus *Bacillus* microorganisms on the surface and the physico-mechanical characteristics of the polyamide fiber have shown that using different strains cultivated on different nutrient media it is possible to control the mechanical parameters of the fibers. For example, in the production of yarns it is of interest to increase the strength of the monofilament (for example, in the case of sample No. 1) and in some cases the elongation at break (sample No. 3). Also, in the production of composites, an increase in the surface roughness of the fiber (sample No. 1), promoting adhesion, and a decrease in the elongation at break (sample No. 4) are of interest.

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BAKTERIJŲ *BACILLUS* NAUDOJIMAS TIKSLINEI POLIKAPROAMIDINIO PLUOŠTO MODIFIKACIJAI

S a n t r a u k a

Šiame darbe tyrimais įrodyta, kad bakterijos *Bacillus* yra veiksmingos modifikuojant polikaproamidinių pluoštų fizikines ir mechanines savybes (stiprumo, tąsumo) ir gaminant didelio stiprumo polimerinių matricų kompozitus. Bakterijos *Bacillus* geba veikti pluošto paviršiaus struktūrą didindamos nanošiurkštumą ir amorfinio sluoksnio storį. Nustatyta, kad *Bacillus brevis*, *Bacillus subtilis*, *Bacillus mesentericus* ir kt. padermes galima naudoti polikaproamidinio pluošto vartojimo charakteristikoms gerinti, vykdant kryptingą pluoštų biodestrukciją.

Reikšminiai žodžiai: pluoštas, paviršiaus modifikavimas, mikroorganizmai.