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Biodegradation of polycaproamide textile materials

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The work solves the problem of biodegradation of synthetic polymers that have exhausted the resource of their work, and the choice of microorganisms that are capable of biodegradation. As synthetic polymers, the most common ones used for the production of clothing, decorative and technical fabrics, etc., polyamides are taken. For research purposes, polycaproamide (PCA) in the form of model porous-fibrous systems of different densities was used. As objects of microbiological impact, bacterial cultures adaptive to PCA fibers (microflora of active wastewater sludge, spontaneous microflora of nylon) were used. *Bacillus subtilis k1* was identified as the most active strain of PCA biodegradable bacteria. The presumptive mechanism of degradation with ε-aminocaproic acid release is established, in which bacteria affect the weak amide bond in the macromolecular chain of polycaproamide.

Keywords: bacteria-biodegraders, ε-aminocapronic acid, polycaproamide fibers

INTRODUCTION

Currently, elimination of polymer waste is an urgent problem. Most synthetic polymers were developed in due time as analogues of the well-known natural materials, for example, glass or metals, for the purpose of their full replacement and, therefore, they have high structural strength, hardness, durability, and biological resistance. In recent years, as the service life of polymeric materials depletes, the problem of their utilization began to arise, which has become more urgent. There are various recycling programs for this purpose, but nevertheless, when polymer waste enters the natural environment, the best way out is to assimilate it to carbon dioxide and water, as it happens with natural polymers. There are different mechanisms for this process, and the most famous is biodegradation. Biostability and biodegradability are two fundamentally different properties of materials in general, and polymers in particular. As a rule, polymers are highly biostable that gives rise to the problem of protecting the environment against polymer waste. The biostability of polymers can substantially be estimated by calculation methods, for example, by the rate of aging or by extrapolating the biodegradation process. Statements that polymers do not degrade for 200 to 400 years have not yet been verified as they are industrially produced since the mid-XXth century.

Bibliographic Review

Biostability of fibrous textile materials, including polyamide materials, has been studied in many works [1-3]. It has also been established that microorganisms can use synthetic polymers as a source of energy and nutrition [4-10].

Chemical fibers, unlike natural ones, do not have their own permanent and specific microflora. Therefore, in the biodegradation of these materials, the most common types of microorganisms characterized by increased adaptability can play a major role.

The emergence and progression of biological degradation of polyamide fibers is largely due to their properties and the properties of influencing microorganisms and their species composition. Basically, the type of microorganisms that damage polyamide and other chemical fibers is determined by the conditions of their operation that form the microflora, and its adaptive capabilities.

Extraction, cultivation and use of such adaptive strains is of both scientific and practical interest. Using strains of bacteria adaptive to nylon, the waste from polyamide production, products that have become obsolete, and potentially toxic substances, can be disposed which will make it possible to obtain secondary raw materials and solve the problem of environmental protection.

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Table 1. Indicators of physical and mechanical properties of nylon nonwoven needle-punched materials

Sample	Surface density, g/m^2	Breaking load, N		Breaking elongation, %	
		length	width	length	width
No.1	535 (0.7 tex)	1050	486	94.8	118.6
No.2	250 (0.3 tex)	347	461	70.9	117.7

The purpose of this work is to study biodegradation of synthetic polymers using an example of polyamide fibers and to identify strains of microorganisms that are capable of causing their biodegradation. To reveal the mechanism of action of microorganisms on synthetic fibers, nonwoven fibrous materials obtained from poly-ε-caproamide (PCA) were selected.

EXPERIMENTAL

The study included fibrous nonwoven materials from polycaproamide fibers obtained from the melt of secondary PCA, with linear density of 0.7 tex and 0.3 tex. The molecular weight of the polymer was 30-35 kDa. The canvas was bound mechanically by needle-punching machines. Table 1 shows the main parameters of nonwoven PCA fabrics included in the study. As objects of microbiological action on PCA materials, bacteria extracted from PCA fibers previously inoculated and damaged by microorganisms in activated sludge of wastewater, as well as damaged by spontaneous microflora formed on the fiber during its exposure in a humid chamber to a relative humidity of 100% and 30– 35 °C were used. PCA fibers served as sources of energy and nutrition for microorganisms in the metabolic process. Using the method of batch cultivation, 11 cultures were extracted from damaged polyamide fibers:

– cultures of bacteria extracted from fibers damaged by spontaneous microflora: 6a; 62a; 63a; 64a;

– cultures of bacteria extracted from PCA fibers damaged by microflora of active wastewater sludge: 5 nylon 2, 5 nylon 5, 5 nylon 6.

The degree of biological damage was assessed based on optical microscopy results by Yermilova's method [1] *via* quantifying the number of fiber damages. Fiber damage was divided into three categories: Class A – fouling by microorganisms and their metabolic products; Class B – more severe degradation: swelling, thinning, and wall damage; Class C – strong and deep damage to fibers by microorganisms: stratification and disintegration of fibers to separate conglomerates. Changes in the damage coefficient (degradation index) of the fiber in the range of 0 to 0.3 correspond to the initial changes in the fiber surface, without affecting its internal structure. If the coefficient falls within the range of 0.3 to 3.55, degradation is observed both on the surface and in the inner sections of the fibers, and at values ranged within 3.55 to 42.25 deep biological degradation of the fiber structure is observed at all its levels.

To assess the effect of bacteria on the structure and properties of materials, the samples were sterilized by UV-radiation for two hours and placed in sterile desiccators. They were inoculated with an aqueous suspension of daily pure cultures of bacteria (1.1 billion cells per 1 ml), kept in a thermostat at 35 °C to 37 °C and relative humidity of 100%.

To assess the ability of bacteria to degrade PCA fibers to ε-aminocaproic acid, a polarographic method was used. Fixed volumes of mineral media containing PCA fibers as a carbon source were sterilized. Then, they were inoculated with a daily broth culture of bacteria in a volume of 31×10^6 cells per 1 ml and incubated at 35 °C. Samples were taken every day and the content of ε-aminocaproic acid formed was determined. The content of ε-aminocaproic acid was determined on the polarograph PU-1 (Germany).

The amount of ε-aminocaproic acid formed under the action of bacteria was determined and measured in the studied media (initial and after inoculation for 10 days), as well as in the control media without bacterial inoculation. The ε-aminocaproic acid content was determined from a calibration curve. A method for determining the sorption capacity of polyamide fibers (CE), which is based on the neutralization reaction of basic or acidic groups with a 0.1N acid or alkali solution with back titration of the excess of acid or alkali was also used.

RESULTS AND DISCUSSION

Table 2 shows the research results. The most active culture turned out to be a bacterial strain under the code designation "6a" extracted from spontaneous microflora of nylon fibers. After 3 weeks of exposure, the biodegradation index (k = 0.52) verifies degradation of both the surface and the inner sections of the fiber.

Table 2. PCA-fiber damaging by bacteria *

Type of culture	Exposure time, days	Damage coefficient by classes:			Biodegradation index K, unit
		A $\overline{x}_1$	B $\overline{x}_2$	C $\overline{x}_3$	
Microflora of active sludges:	7	4.7	0	0	0.009
5 nylon 2	21	5.9	0	0	0.012
5 nylon 5	7	7.9	1.5	0	0.053
	21	24.2	5.4	0	0.183
5 nylon 6	7	15.5	1.3	0	0.064
	21	53.1	4.5	0	0.219
Spontaneous microflora of nylon:	7	22.4	2.4	0	0.105
6a	21	47.9	5.7	0	0.519
62a	7	5.3	0	0	0.011
	21	9.1	0	0	0.018
63a	7	5.4	0	0	0.011
	21	8.3	0	0	0.017
64a	7	27.9	0	0	0.056
	21	64.2	0	0	0.128
	21	73.7	0	0	0.199

*Developed by the authors

Table 3. Degree of biodegradation of nonwoven polycaproamide material fibers of different surface density by the culture of the bacterium *Bacillus subtilis k1**

Sample	Exposure time, days	Damage coefficient by classes:			Total number of damages, N, units	Biodegradation index, K, units
		A($\overline{x}_1$), unit	B($\overline{x}_2$), unit	C($\overline{x}_3$), unit		
Original	–	0	0	0	0	0
No. 1	30	34.3	10.7	1.3	46.3	0.67
No. 2	30	61.3	6.3	1.3	68.9	0.63
No. 1	90	48.6	15.3	4.2	68.1	1.5
No. 2	90	83.5	16.4	5.6	105.5	2.01
No. 1	180	76.3	19.4	7.1	102.8	2.45
No. 2	180	115.1	28.3	10.2	153.6	3.54
No. 1	270	89.4	25.7	12.4	127.5	3.98
No. 2	270	122.3	33.5	17.1	172.9	5.44
No. 1	360	110.5	39.3	15.7	165.5	5.2
No. 2	360	155.7	49.9	23.3	228.9	7.5

*Developed by the authors

The purpose of further research was to identify the bacterial strain that degrades PCA fibers, which can be used to develop an express method for assessing the bacteriological resistance of textile materials containing polycaproamide fibers. According to Bergey's Manual, the resulting strain 6a was identified as a strain of the species *Bacillus subtilis* [11].

The degree of PCA biodegradation of fibrous materials was assessed by Yermilova's method after inoculation of textile nonwoven PCA materials with the bacterial strain *Bacillus subtilis k1* [1].

Table 3 shows the results of changes in the degree of damage to polyamide nonwoven fabrics No. 1 and No. 2 under the impact of the bacterium *Bacillus subtilis k1* for 360 days. Control (initial) samples of nonwoven materials that are not damaged.

The nature and degree of bacterial degradation of polycaproamide fibrous materials was studied on nonwoven needle-punched polyamide fabrics with surface density of 535 g/m^2 and fiber fineness of

0.7 tex (No. 1), surface density of 250 g/m^2 and fiber fineness of 0.3 tex (No. 2) using *Bacillus subtilis k1*, the most active of bacteria-biodegraders strain.

Nonwoven fabric No. 1 had a biodegradation index of K = 067, and nonwoven fabric No. 2 had K = 0.63 30 days after inoculation with a pure culture of *Bacillus subtilis k1* that indicates damage on both the surface and in the inner sections of the fibers. At the same time, a large amount of Class A damage of the biomass fouling type was observed in nonwoven fabric No. 2. Fibers of nonwoven fabric No. 1 showed almost 2 times less fouling and, at the same time, stronger structural changes, such as damage to the fiber walls, were observed.

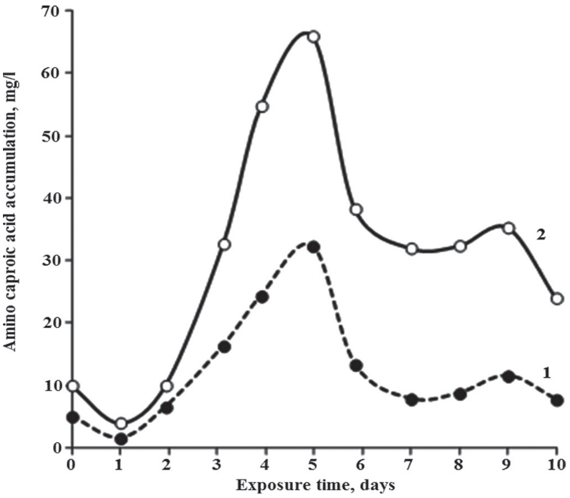

Figure 1. Change in α-amino caproic acid concentration during *Bacillus subtilis k1* development on PCA material fibers: 1 – 0.7 tex; 2 – 0.3 tex. * Developed by the authors.

After 360 days, the index of fiber biodegradation in nonwoven fabric No. 2 was 1.4 times higher than that in fibers of material No. 1, and this dependence was observed throughout the entire study. This is apparently due to the fact that, firstly, the nonwoven fabric No. 2 fiber fineness is almost 2 times less than that of the nonwoven fabric No. 1. (No. 1 – 7 tex, No. 2 – 0.3 tex), This is related to the fact that thinner fibers have a more developed porous structure and adsorb a larger number of microorganisms, and, therefore, are more intensively damaged. Secondly, the surface density of the nonwoven material No. 2 itself creates favorable conditions for the contact of fibers with microorganisms, since its total surface of interaction with microorganisms is 2 times greater.

To study the effect of microorganisms on the chemical structure of PCA fibers and elucidate the mechanism of degradation, the possibility of accumulation of ε-aminocaproic acid by *Bacillus subtilis k1* culture was investigated. The control was a mineral medium without carbon sources inoculated with bacteria; a mineral medium with carbon sources in the form of polycaproamide nonwoven materials, but without inoculation; and a mineral medium with a carbon source in the form of ε-aminocaproic acid (10 mg/l). In a mineral medium with ε-aminocaproic acid, it was not detected after one day.

Figure 1 shows the results obtained. As follows from the data obtained, the maximum amount of ε-aminocaproic acid affected by *Bacillus subtilis k1* strain on PCA fibrous materials is released on the fifth day: 32 mg/l, 66mg/l. Therefore, the proposed *Bacillus subtilis k1* strain causes degradation of polycaproamide fibrous materials with the formation of ε-aminocaproic acid.

Thus, basing of the data obtained inference should be drawn that PCA fibers of 0.3 tex are more accessible to microorganisms, which is confirmed by the data of microscopic studies. The results obtained also indicate the possibility of using *Bacillus subtilis k1* strain for the disposal of polycaproamide fibrous materials in order to obtain ε-aminocaproic acid as a secondary raw material and in order to protect the environment against pollution by over-age polyamide materials. The mechanism of PCA fibrous materials degradation releasing ε-aminocaproic acid was established. Apparently, when the amide bond is broken, terminal amino and carboxyl groups are formed. Based on this assumption, an attempt was made to prove the increase in the number of active terminal carboxyl and amino groups by the sorption capacity method.

Analysis of the results obtained indicates (Table 4) that as PCA fiber is exposed to *Bacillus subtilis k1* bacterium, the sorption capacity increases. Bacteria impacting a weak amide bond in the macromolecular chain of nylon break it and release ε-aminocaproic acid. This translates to an increase of active terminal carboxyl and amino groups. In this case, cationic and anionic sorption capacities increase. It should be emphasized that after 12 months of exposure, the anionic sorption capacity increased 2.0 times for 0.7 tex PCA fibers, while the cationic capacity of 0.7 tex fibers increased 1.2 times and for 0.3 tex fibers it increased 1.4 times. Therefore, the sorption capacity of 0.3 tex fibers increases more intensively, which is confirmed by data on the degradation level of nonwoven materials.

Table 4. Variation in static exchange capacity of PCA fibers impacted by *Bacillus subtilis k1* culture (in mol/g)*

Time of infection, days	End group content		Exposure time, days	End group content	
	–COOH	$-NH_2$		–COOH	$-NH_2$
30	2.76	1.06	270	3.30	1.49
90	2.95	1.37	360	3.50	1.53
180	3.14	1.41	Original	2.47	0.61

Note: the relative precision ranged from 3 to 5%. *Developed by the authors.

This method can be used to study dynamics of the biological damage and to identify the ability of microorganisms to affect the polymer.

CONCLUSION

As determined by the studies, the culture of the bacterium *Bacillus subtilis k1* affects polycaproamide fibers, both the structure of fibers at the supramolecular level and the chemical structure of the fibers at the molecular level.

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