Polyamide Fibers (PA6) with Antibacterial Properties

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SYNOPSIS

The graft polymerization of acrylic acid (AA) on PA6 yarn was examined. Prior to the grafting process, the fibers were activated with a benzene solution of benzoyl peroxide. The effects of the main process parameters and auxiliary additives on the degree of grafting, quantity of the homopolymer formed during grafting, effectiveness of grafting, extent of conversion, and grafting ratio were determined. The resultant fibers, containing carboxylic groups in their structure, were additionatly modified with penicillin, neomycin, or gentamycin to obtain antibacterial fibers in relation to Gram-positive and Gram-negative microorganisms (*Staphylococcus aureus, Escherichia coli,* and *Pseudomonas aeruginosa*). This was confirmed *in vitro* by measuring the stunted growth zones of the above-mentioned bacteria. The modified fibers show different activities in relation to the microorganisms, being dependent on the type and quantity of the added biocide. The kinetics of antibiotic release into water was examined and described by means of a mathematical equation. The release of antibiotics into solution proceeds for quite a long time after which there is still enough antibiotic on the fibers to provide them with antibacterial properties. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, scientific reports on synthetic fibers have revealed a continuously growing interest in polymers and fibers suitable for medical applications. To provide synthetic fibers with bioactive properties, many authors have appropriately modified polyamide fibers (PA6). Antibacterial properties of these fibers were obtained by modifying them with the derivatives of 8-hydroxyquinoline, furane, imidazole, benzoimidazole, thiazole, and other heterocyclic compounds containing $-NO_2$ and $-SO_3$ groups, etc.

The manufacture of bioactive polyamide fibers can be accomplished by the modification of ready-made fibers followed by their treatment with bactericidal agents[1-11] or by addition of bactericides to polyamide chips before fiber formation.[12,13] Antibacterial fibers find their application mainly in surgery as surgical sutures,[14] while woven fabrics made of them can be used for protective clothing. Synthetic antibacterial threads are used in general surgery, chest and alimentary canal surgery, orthopedics, urology, laryngology, gynecology, etc.

Medical reports show that frequent, long-lasting local infections are often brought about by surgical sutures incorporated into tissues and then soaked with liquids being potential culture media. Not infrequent are also the cases of seriously complicated healing of wounds which have been developed in nonaseptic media and wounds coming from secondary infections. In these situations, surgical sutures with antibacterial properties seem to be indispensable. Hence, studies have long been conducted to perfect the fibers designed for surgical sutures[7,11,15-19] and to reduce the reaction at the tissue anastomosis locus and, consequently, to maximize the possibility of beneficial surgical results which often determine human health or the extent of disablement.

It has been particularly recommended to use threads which contain bacteriostatic agents[7-9,15,16] or antibiotics.[7,10,11,17] They include among others the surgical threads named "Letilan" with antibacterial properties obtained by the modification with 5-nitrofurfural or 5-nitrofurylacrolein[18] as well as polyamide fibers modified in a similar way.[7,8,10,16]

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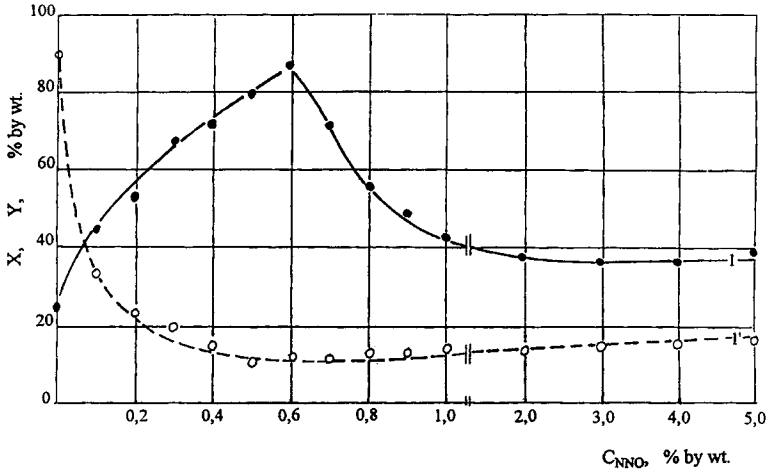

Figure 1 Dependence of degree of grafting of PAA onto PA6 fibers (X, curve 1) and homopolymer content (Y, curve 1') on NNO concentration (C_{NNO}) in grafting solution. Grafting temperature T = 353 K; grafting time τ = 1 h; concentration (C_{AA}) 7.5% by wt, C_{DPh} = 0.

Another approach to imparting bioactive features to synthetic fibers consists of incorporating antibiotics. Such modification should result in bactericidal and bacteriostatic effects on a wider spectrum of Gram-positive and Gram-negative bacteria than in the case of modifying fibers with furane derivatives. According to the reports on the subject in question, this type of modification requires functional groups, such as sulfonic groups, to be added to fibers prior to the treatment with appropriate antibiotics or anesthetic.[17,20-23] Polypropylene fibers modified in this way have recently been used in Russian oncological hospitals with patients showing immune deficiency.[17] The sulfonation of fibers is carried out at elevated temperatures with oleum, concentrated sulfuric acid, or its anhydride,[24] the latter requiring a high vacuum.[25] Such severe reaction conditions bring about a considerable decrease in the initial tensile strength of fibers and some authors have therefore proposed to graft the fibers with polystyrene prior to sulfonation.[26]

This complicated sulfonation procedure and the resultant fiber degradation can be avoided by adding carboxylic groups instead of sulfonic ones for the subsequent chemical binding of antibiotics.[11,27] Further advantages of such an approach include in-

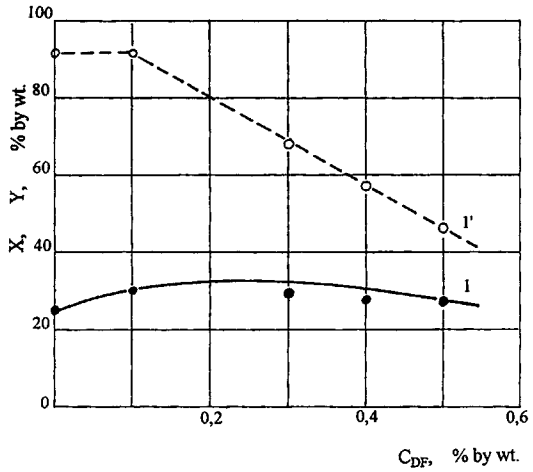

Figure 2 Dependence of degree of grafting of PAA on PA6 fibers (X, curve 1) and homopolymer content (Y, curve 1') on DPh concentration (C_{DPh}) in grafting solution. T = 353 K; τ = 1 h; C_{AA} = 7.5% by wt; C_{NNO} = 0.

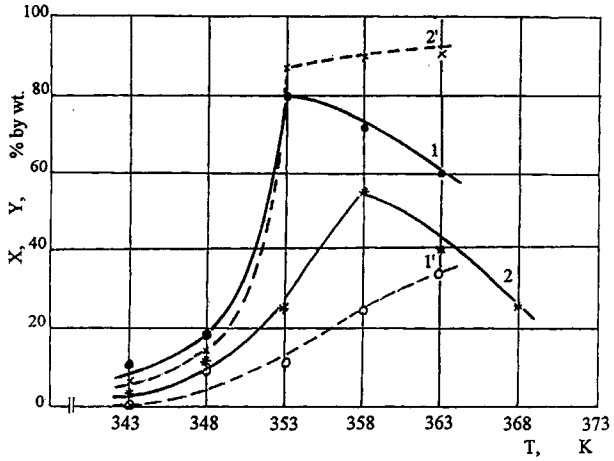

Figure 3 Dependence of degree of grafting of PAA on PA6 fibers (X, curves 1 and 2) and homopolymer content (Y, curves 1' and 2') on grafting temperature (T). τ = 1 h; C_{AA}, 7.5% by wt. (Curves 1, 1') with NNO in grafting solution; (curves 2, 2') no NNO in grafting solution.

creased stabilities and effectiveness of these medicines (their slow release into the organism within a given time), their reduced concentration in the organism, and, consequently, their toxicity or noxious effects as well as their increased resistance to enzymes.

Carboxylic groups can be incorporated in polyamide fibers by grafting acrylic acid initiated chemically. If graft copolymerization is to be effective and suitable for commercial implementation, it should be characterized by the minimum quantity of homopolymer formed during the process or even better by its absence, short grafting times, and a wasteless technology to avoid environmetal pollution and to provide safe work conditions.

These requirements, however, have not been met yet in our laboratory or in other research centers. The main problem consisted of the formation of a byproduct (homopolymer) in considerable quantities, which resulted in process difficulties such as the increase of grafting bath viscosity, slowing-down penetration of a free monomer into fibers, and, consequently, limited degrees of grafting and monomer utilization. In addition, it was necessary to remove the troublesome homopolymer by a time-consuming extraction.

The aim of the present study was to develop such conditions for the modification of PA6 fibers (grafting acrylic acid and posttreatment with antibiotics) which would be suitable for implementing on a larger laboratory or commercial scale. Thus, short grafting times and as low as possible but effective reagent concentrations should be used for ecological reasons. Antibacterial properties of the modified PA6 fibers will be verified by testing *in vitro* with strains of appropriate microorganisms.

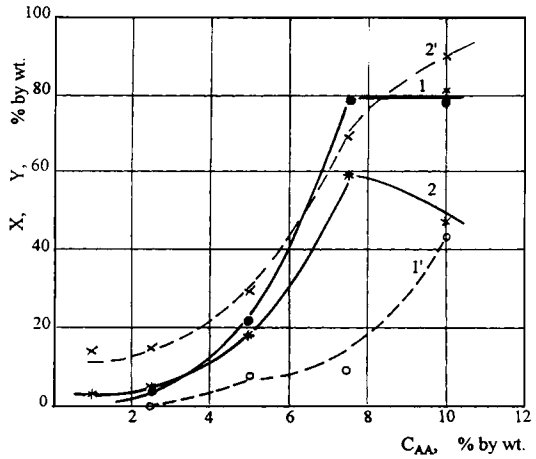

Figure 5 Dependence of degree of grafting on PA6 fibers (X, curves 1, 2) and homopolymer content (Y, curves 1', 2') on concentration AA (C_{AA}) in grafting solution. T = 353 K; τ = 1 h. (curves 1, 1') with NNO in grafting solution; (curves 2, 2') no NNO in grafting solution.

EXPERIMENTAL

Materials

A polyamide monofilament yarn of STILON S.A. (Gorzów Wlkp.), prepared according to Ref. 28, was used in the experiment. For grafting and further modification, the following reagents were used:

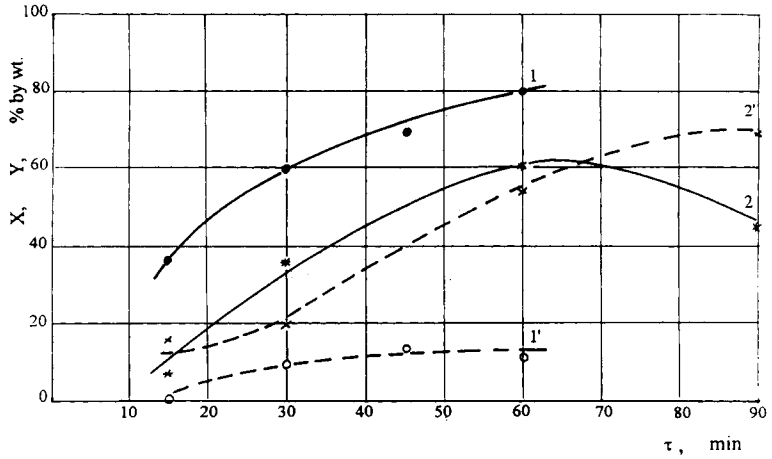

Figure 4 Dependence of degree of grafting of PAA on PA6 fibers (X, curves 1, 2) and homopolymer content (Y, curves 1', 2') on time of grafting (τ). T = 353 K; C_{AA} = 7.5% by wt. (Curves 1, 1') with NNO in grafting solution; (curves 2, 2') no NNO in grafting solution.

- Acrylic acid (AA) of FERAK (Berlin), pure grade, stabilized with 0.05% hydroquinomethyl ether, bp 312,5 K/10 mmHg, $n_D^{20} = 1.421$; it was purified by distillation under vacuum in the atmosphere of deoxidized nitrogen in the presence of metallic copper;
- Benzoyl peroxide (B_2O_2) of ARGON (Łódź), pure grade;
- Benzene of POCh (Gliwice), pure grade;
- Dispersing agent NNO (mixture of salts of condensated aromatic sulfoacids) of ZPO-ROKITA (Zgierz);
- Diphenyl (DPh) of POCh (Gliwice), pure grade;
- Nitrogen of STILON S.A. (Gorzów Wlkp.);
- Crystalline potassium penicillin (Pe), neomycin (Ne) in the form of a mixture of neomycins B and C, and gentamycin (Ge) as gentamycin sulfate—all of them of POLFA (Tarchomin), pure grades.

EXPERIMENTAL

Graft Polymerization on PA6 Fibers

Prior to the graft polymerization of AA on PA6 fibers, the latter were impregnated with a 5% benzene solution of B_2O_2 at 323 K to form active centers on the fibers. Next, excess of the peroxide solution was pressed off and the fibers were heated at 353 K for 15 min to evaporate the solvent. The fibers were then treated with a grafting bath containing AA, the dispersing agent, and/or activator under prescribed conditions in the atmosphere of nitrogen. The fiber-to-bath ratio was 1 : 30 in all the experiments.

The degree of polymer grafting on fibers and the quantity of the homopolymer were calculated gravimetrically according to Ref. 29. Grafting efficiency

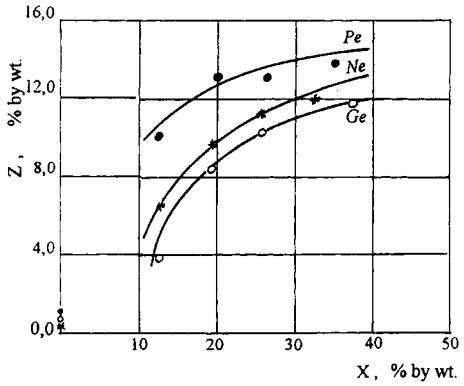

Figure 6 Dependence of absorption of antibiotics (Z) on degree of grafting of PAA on PA6 fibers (X). T = 313 K; τ = 1 h; ratio of modification solution, 1 : 20; C_b = 20% by wt.

Table I Efficiency (E), Extent of Reaction (K) and Ratio of Grafting (R)

	Concentration							
No.	NNO % by Wt	DF % by Wt	X % by Wt	Y % by Wt	E % by Wt	K % by Wt	R % by Wt	R-K % by Wt
1	0.0	0.0	25.79	88.53	11.46	100.00	11.46	−88.54
2	0.1	0.0	44.95	33.96	19.96	53.92	37.02	−16.90
3	0.2	0.0	53.55	23.97	23.81	47.78	49.83	2.05
4	0.3	0.0	69.75	20.00	30.28	50.28	60.22	9.91
5	0.4	0.0	71.82	15.86	31.97	47.84	66.83	18.99
6	0.5	0.0	80.72	11.35	35.82	47.16	75.96	28.80
7	0.6	0.0	85.99	12.00	38.32	50.32	76.15	25.83
8	0.7	0.0	70.46	12.59	31.33	43.93	71.33	27.40
9	0.8	0.0	56.35	13.06	25.10	38.11	65.87	27.76
10	0.9	0.0	48.41	13.49	21.57	35.07	61.52	26.45
11	1.0	0.0	43.89	14.43	19.56	34.00	57.55	23.55
12	2.0	0.0	38.40	14.54	17.09	31.64	54.02	22.38
13	3.0	0.0	36.90	14.99	16.40	31.40	52.24	20.84
14	4.0	0.0	35.99	15.50	16.00	31.50	50.80	19.30
15	0.0	0.1	30.76	86.32	13.67	100.00	13.67	−86.33
16	0.0	0.3	28.88	65.10	12.85	77.96	16.48	61.48
17	0.0	0.4	26.91	58.01	12.38	70.40	17.59	−52.81
18	0.0	0.5	27.54	46.97	12.27	59.25	20.72	−38.53

Table II Antibiotic Release from Untreated Fibers in Time τ

Sample	Weight of Modified Fibers with Biocides (Biocides Weight on the Fiber)		
	0	1 h	2 h
PA6–Pe	1.0436	1.0353	1.0322
$x = 0$, $z = 1.10\%$[a]	(0.0114)	(0.0031)	(0.0000)
PA6–Ne	1.0166	1.0145	1.0136
$x = 0$, $z = 0.29\%$[a]	(0.0030)	(0.0009)	(0.0000)
PA6–Ge	1.0028	1.0012	0.9960
$x = 0$, $z = 0.68\%$[a]	(0.0068)	(0.0052)	(0.0000)

[a] The real quantity of —COOH groups in the investigated untreated PA6 fibers were about $6.26 \cdot 10^{-5}$ mol/g Pa; the groups were measured with analytical methods [40].

E, extent of reaction K, and grafting ratio R were calculated according to Ref. 30.

Posttreatment of Grafted Fibers

Fibers with various degrees of grafting were impregnated with solutions of antibiotics *Pe, Ne,* and *Ge* under various conditions of concentration, time, and temperature. The extent of reaction between these antibiotics and grafted fibers was determined also by the gravimetric method.

Antibiotic Release from Modified Fibers

The release of antibiotics from fibers into water was determined gravimetrically because the attempts to find absorption maxima for the references of the above-mentioned antibiotics on a PU 8700 UV Philips spectrophotometer within the wavelength range 190–900 nm ended in failure.

The samples of modified fibers containing a given antibiotic were placed in 150 cm^3 weighing bottles and 100 cm^3 of distilled water was added to each, and the bottles were closed with grind-in covers. At the appropriate intervals, the solution was stirred with a glass rod, and then the samples were taken out, slightly pressed off, and dried at 313 K for 1.5 h to a constant weight. The weighed samples were immersed in the water, which had been changed everyday. The measurements were repeated several times for each sample.

The quantity of released antibiotic (B_τ) in time τ was calculated from the difference:

$$B_\tau = m_a - m_\tau, \tag{1}$$

where m_a is the initial weight of fiber with added antibiotic (g), and m_τ, the weight of fiber with added antibiotic after releasing it into water for time τ (g). The released quantity of the antibiotic calculated as

Table III Antibotics Release from Modified Fibers into Water; Correlation Coefficient κ, Constants k, b, and n, Concerning (3)–(5) Equations

	Equations								
	$C = C_\infty \cdot [1 - e^{-k \cdot t + b}]$			$C = C_\infty \cdot k \cdot t^n$			$C = k \cdot \sqrt{t} + b$		
Sample	k	b	χ	k	n	χ	k	b	χ
PA6–PAA–Pe $x = 12.72\%$ $z = 10.16\%$	0.0121	−2.2108	0.0869	0.0832	0.0334	0.9029	0.0008	0.0797	0.8049
PA6–PAA–Ne $x = 33.16\%$ $z = 9.92\%$	0.0124	−1.0737	0.7828	0.5882	0.0881	0.9051	0.0014	0.4675	0.8445
PA6–PAA–Ge $x = 25.79\%$ $z = 8.64\%$	0.0120	−1.5355	0.8104	0.6882	0.0668	0.8549	0.0012	0.0539	0.7634

Table IV Antibacterial Effect of Antibiotic Standard Solution (diameter ϕ of the Zone Inhibition in mm)

Tested Bacteria	Inhibitions Zones of Bacteria Growths for Individual Antibiotic Solutions, ϕ mm		
	Ge	*Ne*	*Pe*
Staphylococcus aureus	38.0	30.0	45.5
Escherichia coli	32.0	28.5	22.0
Pseudomonas aeruginosa	39.5	24.5	0.0

above constitutes, at the same time, the approximate concentration of the given antibiotic (% by wt) in water.

Antibacterial Properties of the Modified Fibers

The samples of modified PA6 fibers designed for bacteriological testing were packed with a double plastic film, tightly sealed, and then sterilized by radiation at the Institute of Radiation Techniques (Technical University of Łódź) (25 kGy dose). Antibacterial effects of the modified fibers were tested by[31,32]

- A direct method consisting of placing the fibers on an agar support containing the test bacterial strain, and after incubation, measuring the zones of stunted bacterial growth around the tested fibers;
- A disc-diffusion method, using 6 mm paper discs impregnated with the solutions in which modified fibers were soaked, placing the discs on support plates and incubating the samples at 310 K for 18–20 h.

Antibacterial activity was determined in length units (mm), measuring the stunted zones of the test organism growth around the disc or fiber in the direct method. In diffusing from the fiber or disk into the support, the antibiotic stunted the growth of the reference bacteria, forming stunted zones, then was subjected to measurement. All the tests were repeated two to three times and the result obtained is an average of the measurements.

Three test organisms, recognized to be representative for a hospital environment, were used in the investigation[33]: Gram-positive bacteria *Staphylococcus aureus (S.a.),* NCTC 4163, and Gram-negative bacteria *Escherichia coli (E.c.),* NCTC 8196, and *Pseudomonas aeruginosa (P.ae.),* NCTC 6749, were provided by the State Hygiene Institute (Warsaw).

The sensibility of the above-mentioned bacteria to the antibiotics added to fibers was evaluated by comparing the zone sizes with standard solutions of the antibiotics under investigation, their concentrations being found on the basis of biocide release curves prepared previously. The antibacterial effects of the antibiotics added to the fibers were tested in aqueous solutions obtained by soaking the modified fibers in sterilized water with pH 6 in the proportion 1 : 5 by wt. Fibers with neomycin were soaked in a sterilized buffer with pH 8 to ensure the stability of this antibiotic during testing. After 1, 5, 7, and 11 day intervals of storing the samples in water or buffer at 310 K (protected from evaporation), the antibacterial activity of the solutions was examined by the disc-diffusion method.

The antibacterial activity of the standards of *Ge, Ne,* and *Pe* was tested by the same disc-diffusion method under the same conditions as with modified fibers, using the *S.a.* strain. The tests were carried out both before and after irradiation, finding the same size of the stunted growth zones after incubation, which confirmed the fact that the radiation dose used had no effect on the activity of the antibiotics under investigation.

RESULTS AND DISCUSSION

The Effect of Reaction Conditions on the Degree of PAA Grafting on PA6 Fibers

The effect of particular parameters such as the dispersing agent NNO and activator DPh levels, temperature and time of grafting, and the concentration of AA on the degree of poly(acrylic acid) (PAA) grafting on PA6 fibers and on the quantity of homopolymer formed during the process were examined to optimize the grafting conditions. The results obtained are illustrated in Figures 1–5 and listed in Table I.

From Figure 1, which illustrates the dependence of the grafting degree and the homopolymer quantity on the concentration of NNO, it follows that the addition of this particular dispersing agent to the reaction bath facilitates the grafting process, i.e., the degree of PAA grafting increases as the concentration of NNO grows and, at the same time, a decrease in the quantity of the homopolymer formed during the process can be observed. The best results are obtained with 0.5–0.6% by wt. of NNO. Exceeding this concentration results in a decreased grafting degree and an increased homopolymer quantity.

Table V Antibacterial Activity of Modified Fibers PA6 Tested with Direct Method (Diameter ϕ of Zone Inhibition in mm)

	Inhibition Zones of Growth, ϕ mm			
Tested Bacteria	Untreated; No Antibiotics	PA6–PAA–Pe	PA6–PAA–Ne	PA6–PAA–Ge
Staphylococcus aureus	0.0	39.0	10.0	6.5
Escherichia coli	0.0	16.0	5.0	6.0
Pseudomonas aeruginosa	0.0	0.0	6.5	3.0

On the other hand, the degree of PAA grafting was not affected by the DPh activator added in various quantities, but the quantity of the homopolymer was gradually decreased as the concentration of DPh increased in the reaction system (Fig. 2). This decrease is, however, lower than in the case of NNO. Therefore, the latter was selected for further PAA grafting on PA6 fibers.

The quantity of the homopolymer was determined gravimetrically. Taking into account the fact that this method gives the results overestimated by about 3% by wt in relation to the analytical method,[29] the actual quantity of the homopolymer should be very low and easily removable from the fiber surface in a short time. This feature well confirms the efficiency and effectiveness of the process. Moreover, the grafting bath can be reused after making up AA and the dispersing agent.

In the next series of experiments, the effect of temperature was examined. With a constant time of the process (1 h), its temperature was changed from 343 to 363 K using a monomer concentration of 7.5% by wt. The results obtained are illustrated in Figure 3. It can be seen that the best result was obtained at 353 K with the addition of NNO to reduce the homopolymer formation.

Examining the effect of the reaction time, the temperature of grafting was maintained constant (353 K) and the time ranged from 15 to 90 min. The results are shown in Figure 4. It is seen that 60 min is an optimum duration of the grafting and it is of no use prolonging it. The results of evaluating the effect of AA concentration illustrated in Figure 5 show that the optimum concentration of this monomer is 7.5% by wt, and applying a higher concentration of AA is useless from the point of view of the grafting degree and the quantity of the homopolymer.

Since the curves shown in the presented figures are not fully sufficient to assess whether the selected parameters are in proper relation to the obtained effect, Table I gives the values of the efficiency E,

Table VI Antibacterial Activity of PA6 Fibers Tested with Disc-diffusion Method

		Inhibitions Zone of Growth (mm) Test Days				
Tested Bacteria	Test	1	2	5	7	11
Staphylococcus aureus	PA6 unt.	0.0	0.0	0.0	0.0	0.0
	PA6–PAA–Pe	72.0	70.0	65.5	52.5	50.0
	PA6–PAA–Ne	29.0	31.5	17.5	—	—
	PA6–PAA–Ge	31.5	31.5	34.0	31.0	32.0
Escherichia coli	PA6 unit.	0.0	0.0	0.0	0.0	0.0
	PA6–PAA–Pe	—	—	34.0	23.5	—
	PA6–PAA–Ne	9.0	15.0	13.5	11.0	14.5
	PA6–PAA–Ge	27.5	29.0	29.0	27.0	29.0
Pseudomonas aeruginosa	PA6 unt.	0.0	0.0	0.0	0.0	0.0
	PA6–PAA–Pe	0.0	0.0	0.0	0.0	0.0
	PA6–PAA–Ne	8.0	12.0	11.5	13.0	9.0
	PA6–PAA–Ge	33.0	35.5	32.0	34.0	29.0

—, not tested; 0, missing zone; unt., untreated PA6 fibers.

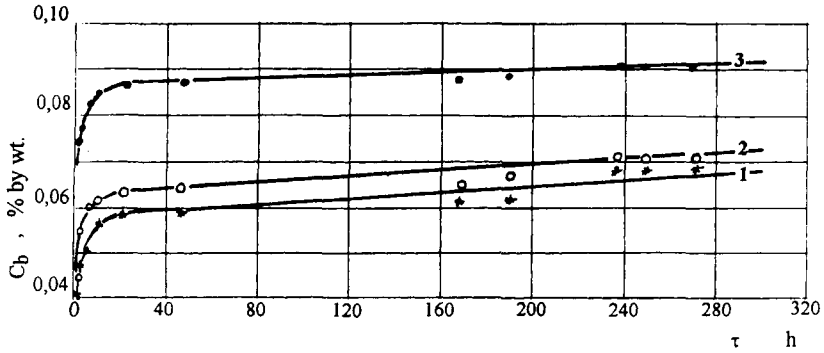

Figure 7 Dependence of concentration of biocides (C_b) on time of release (τ) from modification PA6 fibers: (curve 1) for PA6 fibers contains 9.92% *Ne;* (curve 2) for PA6 fibers contains 8.64% *Ge;* (curve 3) for PA6 fibers contains 10.16% *Pe.*

the extent of reaction K, and the grafting ratio R[29,30] for the reactions shown in Figures 1 and 2. It follows from these data that the highest grafting efficiency is shown by the systems containing 0.5–0.6% by wt of NNO. It is also accompanied by the highest grafting ratios. To precisely select the proper value, an additional parameter was introduced to the analysis of results, namely, the difference between R and K. The highest difference between these values is shown by the system containing 0.5% by wt of NNO and it is this concentration which was selected. K and R depend on the quantity of the homopolymer: R should be as high as possible, and K, as low as possible. It is clear that the selected NNO concentration was revelant.

The Assessment of Antibiotic Addition

The degree of antibiotic addition to the modified fibers can be affected by various conditions, particularly by the degree of grafting PAA onto PA6 fibers. Figure 6 illustrates the results of the dependence of antibiotic addition (Z) on the degree of PAA grafting (X). It can be seen that the initial PA6 fibers (grafting degree 0, ordinate axis) have only a slight quantity of the antibiotic added, which is due to the fact that PA6 fibers contain only very small quantities of carboxylic groups (PA6 end groups). Therefore, the grafted fibers containing numerous carboxylic groups tend to combine an antibiotic much more effectively, provided that the antibiotic involved has appropriate base groups. It is thus assumed that the addition of *Ge* or *Ne* can proceed according to the following reaction:

$$P\text{—}COOH + H_2N - An \rightarrow P\text{—}COO^-[H_3N^+ - An] \quad (2)$$

where P is the remainder of the polymer, and *An*, an appropriate remainder of *Ge* or *Ne*. The addition of *Pe* to the grafted fibers containing carboxylic groups is more complex. Potassium penicillin G used in this study contains in its composition two functional groups: —COOK and —NHCO—, which can participate in the formation of a chemical bond with the grafted fiber. It is assumed that this antibiotic can be added through a covalent bond[34] via an amine group or through an ionic bond.[35]

If a biocide added to fibers is to perform its function properly, it should be released into its surroundings in due time. Thus, controlled releases of *Pe, Ne,* and *Ge* from fibers into water were performed, using the gravimetric measurement method.

As follows from the literature data,[36–39] precise kinetic equations of biocide release, based on the analysis of diffusion, are very complex and, in many cases, have the character of exponential functions. The results were interpreted by means of eqs. (3)–(5):

$$C = C_\infty \cdot [1 - e^{-(\mathbf{k}t - \mathbf{b})}] \quad (3)$$

$$C = C_\infty \cdot \mathbf{k} \cdot t^{\mathbf{n}} \quad (4)$$

$$C = \mathbf{k} \cdot \sqrt{t} = \mathbf{b} \quad (5)$$

where C is the biocide concentration in solution after time t; C_∞, the biocide concentration under equilibrium; $\mathbf{k}$ and $\mathbf{b}$, constants, characterizing the system; and $\mathbf{n}$, an exponent.

It results from the data in Table II that in the case of unmodified fibers containing low quantities of antibiotics the whole amount of them is released as soon as after 2 h. The release of the antibiotic added to PAA-grafted fibers proceeds in two stages: The first stage, lasting 1 day, is characterized by a rapid release, which can be accounted for by the fact

that there are two modes of addition: absorption and chemical bonding. In the second stage (slow release), antibiotics are released by hydrolysis. After 12 days of release, there still remain 15–65% of the antibiotics on the fibers. The release is continued as confirmed by testing *in vitro* with Gram-positive and Gram-negative microorganisms.

Table III contains the values of rate constants **k** and **b** and the correlation coefficient κ concerning regression eqs. (3)–(5), calculated on the basis of a computer program. Based on the results given in Table III, it can be assumed that the release of antibiotics from modified fibers into solution can be described by eq. (4): $C = C_\infty \cdot \mathbf{k} \cdot t^n$, which is confirmed by the highest value of correlation coefficient κ.

Antibacterial Properties of Modified PA6 Fibers

Antibacterial effects of modified PA6 fibers with added antibiotics (*Pe, Ne,* and *Ge*) initial unmodified fibers, and standards of the above-mentioned antibiotics were tested *in vitro*. The results obtained are given in Tables IV–VI. It is seen from these data that the antibiotics used are characterized by quite strong biocide effects on the Gram-positive microorganism *S.a.* and the Gram-negative *E.c.* This is demonstrated by quite large zones of stunted microorganism growth. *Ge* and *Ne* show also such effects on *P.ae.*, while penicillin fails to do so, which means that these bacteria are not sensitive to this biocide. With regard to PA6 fibers containing the discussed biocides, similar behavior can be expected.

Similarly, *Ge* and *Ne* added to the grafted fibers show antibacterial effects on *S.a., E.c.,* and *P.ae.*, while *Pe* added to the fibers does not stunt the growth of *P.ae.* The unmodified fibers have no effects on both Gram-positive and Gram-negative microorganisms such as *S.a., E.c.,* and *P.ae.*

It is evident from the results obtained that antibacterial effects on Gram-positive and Gram-negative bacteria are maintained for quite a long time, i.e., over 11 days. So, it should be long enough for the wounds to be healed if the modified fibers in question are used as surgical sutures.

CONCLUSIONS

An effective process has been developed for grafting acrylic acid onto PA6 fibers (high degree of grafting, low quantities of homopolymer, short duration of grafting).

- The modification of PA6 fibers by adding to their structure carboxylic groups and then combining them with antibiotics makes it possible to provide fibers with biocide properties.
- The release of antibiotics from fibers into solutions can be approximately described by the exponential equation: $C = C \cdot \mathbf{k} \cdot t^n$.
- The antibiotic release into solution takes quite a long time after which there is still some quantity of antibiotic on the fibers, being high enough to provide the fibers with antibacterial effects on Gram-positive and Gram-negative microorganisms.
- Modified PA6 fibers with added antibiotics show different effects on Gram-positive and Gram-negative bacteria typical of hospital conditions, depending on the type and quantity of the added antibiotic.

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