Modified Polyacrylonitrile (PAN) Fibers

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ABSTRACT: An effective two-stage method for obtaining polyacrylonitrile fibers with antibacterial properties has been developed. The method consists of the incorporation of carboxylic groups into fibers by PAA grafting polymerization followed by fiber impregnation with gentamycin, neomycin, or penicillin solutions. The modified fibers show effective biocide liberation into water and antibacterial activity towards Gram-positive and Gram-negative microorganisms (*Staphylococuus aureus, Escherichia coli,* and *Pseudomonas aeruginosa*). The presence of antibiotics combined with the modified fibers though chemical bonds has been proved by IR and ^{1}H-NMR investigations.
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Key words: graft copolymerization; modified polyacrylonitrile fibers; poly(acrylic acid); biocide polyacrylonitrile fibers; modification of fibers

INTRODUCTION

A successful wound healing by primary adhesion requires the use of surgical sutures that would not cause any serious tissue response within the joined parts of wounded tissues. Conventional catguts used to that end are nonuniform and difficult both to make and to sterilize.

On the other hand, synthetic threads due to their high chemical and mechanical resistance, formability, easy-to-perform manufacturing, and sterilization processes have been gradually replacing traditional catguts obtained from natural sources.

The manufacture of synthetic surgical threads and other implants mainly involves polyester, polyamide, polypropylene, and polyacrylonitrile fibers.[1–6] Implants obtained from synthetic fibres, however, show some unquestionably good qualities and can also cause long-lasting perithread infections within living organism tissues. These tissue reactions are still substantialy slighter than the ones caused by threads of natural origin.

Among materials biocompatible with blood, grafted copolymers have been considered interesting and practicable, especially for their athrombogene properties. The latter are dependent on a proper biopolymer microstructure adequate to the proportion of hydrophobic polymer used as a matrix to hydrophilic polymer fixed to the matrix. In spite of some encouraging results of experiments, only a few biopolymers of this class have found practical applications in the manufacture of implants and other medical adaptations.[7]

The grafting of a hydrophilic polymer such as polyacrylic acid not only provides fibers with athrombogene properties but also allows for developing antibacterial properties. The process consists of introducing an appropriate antibiotic in the form of cation into previously added carboxylic groups. Fibers modified in this way show a biocide effect on Gram-positive and Gram-negative bacteria.[8–14]

The present case involves the modification of PAN fibers to provide them with antibacterial properties, including the examination of a modification mechanism. In the experiment crystalline potassium penicillin, neomycin, and gentamycin will be used as biocides. The above-mentioned therapeutic agents should be fixed to a fiber with chemical or absorption bonds.

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As PAN fibers do not contain appropriate functional groups able to bond antibiotics, the author first intended to add carboxylic groups by the graft polimerization of acrylic acid (AA), then to incorporate the above-mentioned therapeutic agents into fibers. Carboxylic groups can also be created within PAN fibers by hydrolysis of —CN to —COOH groups. This method, however, is apparently more troublesome in practice than it has been suggested in the literature.[15–18]

Antibacterial effects of modified fibers will be verified by microbiological examination *in vitro* by measuring the stunted zones of growth for the tested microorganisms. All the tests will involve bacterial strains *Staphylococcus aureus* (Sa), *Escherichia coli* (Ec), and *Pseudomonas aeruginosa* (Pae),[19] which have been considered representative for hospital environment.

The mechanism of the modification in question will be explained on the basis of the IR and ^{1}H-NMR spectroscopy.

EXPERIMENTAL

Materials

The subject of the experiment was PAN–Anilana fiber of the Chemitex-Anilana Works (Łódź, Poland), a copolymer consisting of 92.0% of acrylonitrile, 6.3% methyl acrylate, and 1.7% of itaconic acid. The fibers were freed from the spin finish before the experiment.[20] For grafting and further modification the reagents were used according to ref. 14.

In the ^{1}H-NMR investigation dimethylsulfoxide (DMSO) was used as a solvent for initial and modified fibers and tetramethylsilane (TMS) as an internal standard.

Methods

The process of basic hydrolysis of PAN fibers has been described previously.[12] As the results of the basic hydrolysis were not satisfactory, in this study carboxylic groups were added to PAN–Anilana fibers by graft polymerization of AA in a heterogeneous system[12] containing an activator (diphenyl, DF) and a dispersing agent (NNO) as in the early studies.[8,10,14,21] The grafting method consisted in creating active centers on fibers by impregnation at elevated temperature (323 K) with 5% benzoyl peroxide (BzO_2) followed by pressing off the excess of BzO_2 and heating the fibers at 353 K within 15 min to evaporate the solvent.

The fibers initiated in this way were then treated with the grafting bath containing AA, dispersing agent, and/or activator under prescribed conditions in the atmosphere of nitrogen.[8,12] The fiber-to-bath ratio was 1 : 50 in all the experiments. The degree of polymer grafting on fibers was calculated gravimetrically.[12] The grafted fibers were used for further stages of the experiment.

Further Modifications of Grafted Fibers

PAN–Anilana fibers with different degrees of grafting were impregnated with 20% (by weight in bath) solutions of antibiotics (An): penicillin, neomycin, and gentamycin at 313 K within τ = 1 h.

Liberation of Biocides from Modified Fibers

The amount of an antibiotic liberated from modified fibers into water was determined by the gravimetric method.[10,14]

Antibacterial Properties of Modified Fibers

Antibacterial properties of modified fibers were tested on the basis of direct and disc-diffusion methods earlier described.[10,12,14] Three test organisms considered representative for hospital environment[19] were used in the experiment: Gram-positive bacteria *Staphylococcus aureus* (Sa) NCTC 4163, Gram-negative bacteria *Escherichia coli* (Ec) NCTC 8196, and *Pseudomonas aeruginosa* (Pae) NCTC 6749. All the bacteriological tests were carried out at the Institute of Fermentation Technology and Microbiology (Technical University of £ódŸ, Poland).

Infrared (IR) Spectrophotometric Measurements

IR measurements were conducted by use of a FT–IR MATSON 1000 spectrophotometer within the range of frequency between 4000 and 500 cm^{-1}. The following samples were tested: initial PAN–Anilana fibers without free from spin finish, PAN–Anilana fibers grafted with PAA (x = 18.6% by weight), PAA grafted fibers (x = 18.6% by weight) with Ge fixed with the fibers (z = 6.5% by weight), PAA grafted fibers (x = 18.6% by weight) with Ne fixed with the fibers (z = 18.2% by weight), PAA grafted fibers (x = 18.6% by weight) with Pe fixed with the fibers (z = 11.0% by

weight). Samples of fibers cut with a microtom were prepared in the form of tablets. KBr was used as a standard reference.

^{1}H-NMR Measurements of Modified Fibers

^{1}H-NMR mesurements were conducted by means of a TESLA impuls spectrometer (Brno) with a basic frequency of 80 MHz and resolving power 0.1 Hz. All the ^{1}H-NMR spectra were taken at room temperature and frequency of 1000 Hz. The temperature of the sounder was 310 K.

The following samples of PAN–Anilana fibers were selected for the investigation: (1) initial untreated PAN fibers with active centers (created by impregnation with 5% solution of benzoyl peroxide at 323 K within 30 min, and heating at 353 K within 15 min; (2) PAN fibers grafted with PAA (x = 13.6% by weight)[12]; fibers grafted with PAA and with fixed penicillin.

The solution to be measured contains 10 mg of the given fiber sample or a suitable standard of antibiotic, dissolved in 0.7 mL DMSO (PAN fibers grafted with PAA with fixed Ne or Ge were insoluble in DMSO).

RESULTS and DISCUSSION

The samples of PAN–Anilana fibers with the degree of grafting x = 4.70–36.00% (by weight PAA) after extraction (without homopolymer) were selected for further investigations. Grafted PAN–Anilana fibers containing carboxylic groups within their structure are able to fix combine with appropriate antibiotics through chemical or absorption bonds.

Before the selection of antibiotics detailed analysis of the bacteria sensitivness to each type of biocide was carried out. The results of the analysis indicate that microorganisms show different sensitivness to the antibiotics in question. It is then expected that fibers with fixed biocides will also have antibacterial properties. Therefore, PAN–Anilana fibers with different degrees of grafting were impregnated with aqueous solutions of antibiotics (Ge, Ne, Pe) under indentical conditions. The results of these experiments are given in Table I. The data show that initial ungrafted PAN fibers perform quite a limited ability to fix antibiotics, which is determined by a very few carboxylic groups from itaconic acid in their structure (about 1.7% by weight).

On the other hand, fibers grafted with PAA containing much more of carboxylic groups are more effective in fixing with antibiotics. Thus, it is clear that if a basic type antibiotic is to be fixed with fibers through covalent[24] or ionic[25] bonds, the latter should have an adequate number of acid groups in their structure.

Antibiotic Liberation from Modified Fibers

If an antibiotic incorporated into fibers is to perform its function it has to be liberated into its

Table I The Results of Impregnating Modified PAN-Anilana Fibers with Antibiotics

No.	Degree of Grafting x (%)	Antibiotic	Degree of Impregnation with Antibiotic z (%)
1	Ungrafted fibers		0.25Ge, 0.20Ne, 2.19Pe
2	13.63		6.53
3	18.60		7.21
4	25.30		9.92
5	36.02	Gentamycin (Ge)	10.95
6	13.63		8.27
7	18.60		18.22
8	25.30		26.81
9	36.00	Neomycin (Ne)	40.11
10	13.63		7.82
11	15.00		8.10
12	19.80		11.02
13	24.80	Penicillin (Pe)	12.85

Table II Antibiotic Release from Untreated Fibers in Time τ

Sample	Weight of Modified Fibers with Biocides (Biocides Weight on the Fiber)		
	0	2	4
PAN–Gen	0.3690	0.3949	0.3949
$x = 0, z = 0.25\%$	(0.0011)	(0)	(0)
PAN–Ne	0.4025	0.4014	0.4014
$x = 0, z = 0.24\%$	(0.0011)	(0)	(0)
PAN–Pe	0.5026	0.4950	0.4918
$x = 0, z = 2.1\%$	(0.0108)	(0.0076)	(0)

surrounding in due time. Therefore, controlled liberation of antibiotics from PAN–PAA–An-modified fibers into water was conducted, and the amount of biocides liberated into water was determined by the gravimetric method.[10,14] The procedure and mathematic models[26–29] have been detailed previously.[10,14] The results of the experiments are presented in Table II and Figure 1.

The data presented in Table II and in Figure 1 show that in the case of ungrafted fibers containing low quantities of antibiotic the whole amount of it is thoroughly released as soon as after 2–4 h. The evaluation of the results obtained for grafted fibers with fixed antibiotics is rather difficult, as samples with different degrees of treatment with antibiotics were investigated. It is especially true for the fibers fixed with neomycin. However, even the given results show that the fastes liberation of the antibiotics is observed after 70 h of exposure, then it slows down. After 600 h of exposure the fibers still contain certain amount of antibiotics, namely about 50% Ge, 55% Pe, and over 60% Ne. The initial fast liberation of antibiotics (within the period of up to 70 h) is due to the fact the absorbed An is released first and then the chemically bonded An to some extent. Later on, only the chemically bonded antibiotics are released by hydrolysis.

Table III shows the values of rate constants k and b, describing the system and correlation coefficient κ indicated in regression eqs. (1)–(3):

$$c = c_\infty \cdot [1 - e^{-(kt-b)}]; \quad (1)$$

$$c = c_\infty \cdot k \cdot t^n; \quad (2)$$

$$c = c_\infty \cdot \sqrt{t} + b; \quad (3)$$

where c is the biocide concentration in solution after time t; c_∞ is the biocide concentration under

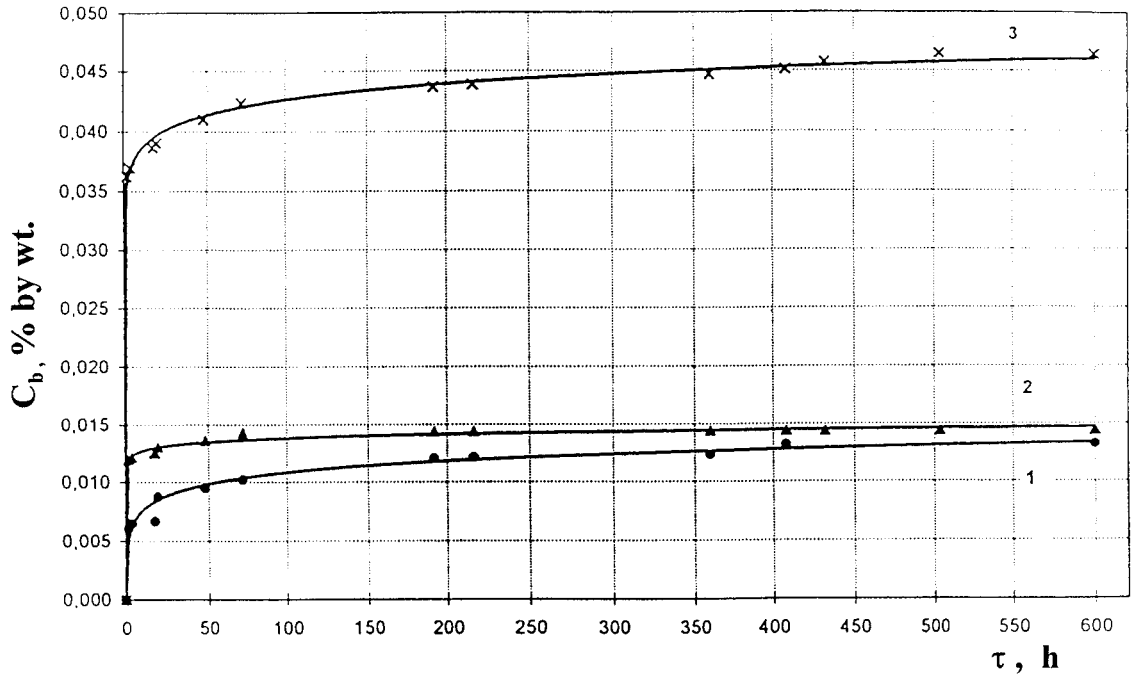


Figure 1 Dependence of concentration of biocides (C_b) on the time of release (τ) from modified PAN–Anilana fibers into water: (1) fibers containing 5.5% Pe; (2) fibers containing 6.5% Ge; (3) fibers containing 18.2% Ne.

Table III Antibiotic Release from Modified Fibers into Water; Correlation Coefficient κ, Constants k, b, and n, Concerning Eqs. (1)–(3)

	Equations								
	$c = c_\infty [1 - e^{-(k \cdot t - b)}]$			$c = c_\infty \cdot k \cdot t^n$			$c = k \cdot \sqrt{t} + b$		
Sample	k	b	κ	k	n	κ	k	b	κ
PAN–PAA–Ge x = 18.6% z = 6.5%	0.01419	−1.91543	0.9057	0.7777	0.04633	0.9608	0.00022	0.01182	0.9295
PAN–PAA–Ne x = 36.0% z = 40.0%	0.00640	−1.61140	0.9194	0.74326	0.04495	0.9919	0.00044	0.03693	0.9683
PAN–PAA–Pe x = 19.8% z = 5.5%	0.00810	−0.71396	0.9343	0.32297	0.15167	0.9687	0.00037	0.00626	0.9545

equilibrium; k and b are constants, characterizing the system; and n is an exponent.

The values of k, b, and n, were calculated on the basis of a computer program. From the data shown in Table III it results that the liberation of antibiotics from the fibers into solution can be quite correctly described by eq. (2), as confirmed by the highest value of correlation coefficient.

Investigation of the *In Vitro* Antibacterial Effect of Modified PAN–Anilana Fibers

Investigations were carried out for the following modified fibers: initial unmodified fibers; grafted with PAA with fixed Ge (x = 25.3% by weight, z = 6.92% by weight); grafted with PAA with fixed Ne (x = 25.3% by weight, z = 26.81% by weight); grafted with PAA with fixed Pe (x = 25.3% by weight, z = 12.85% by weight); and standard samples of Ge, Ne, and Pe. The results of all the experiments are shown in Tables IV–VI. The data given in Table IV indicate that the antibiotics used for impregnation are able to deteriorate microorganisms or to inhibit their develompent. This ability was especially true for Ge and Ne. The penicillin standard is active towards Sa and Ec and not effective towards Pae. It is then expected that the fibers fixed with penicillin will not show their effect in the case of blue pus bacterium.

From the results presented in Table V it is seen that the initial PAN–Anilana fibers have no antibacterial properties, i.e., they show no stuned zones of bacteria growth. The antibacterial activity of modified PAN–Anilana containing antibiotics in their structure, verified by the use of the direct method, show various activities dependent on the type of the antibiotic and bacteria strains (Table V). The widest range of activity was observed in the case of the fibers impregnated with gentamycin, which effectively inhibited the increase in bacteria population of all the tested strains. The effect of penicillin compared with gentamycin was stronger towards Sa, whereas its effect on Ec was substantially slighter. Penicillin was completely ineffective towards Pae, which was also true for the standard sample of this bio-

Table IV Antibacterial Effects of Antibiotic Standard Solution (Diameter ϕ of the Zone Inhibition in Millimeters)

	Inhibitions Zones of Bacteria Growths for Individual Antibiotic Solutions (ϕ mm)		
Tested Bacteria	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

Table V Antibacterial Activity of Modified PAN Fibers Tested by the Direct Method

Tested Bacteria	Inhibition Zones of Growth (ϕ mm)			
	Untreated; No Antibiotics	PAN–PAA–Ge	PAN–PAA–Ne	PAN–PAA–Pe
Staphylococcus aureus	0	31	27	50
Escherichia coli	0	22	23	23
Pseudomonas aeruginosa	0	24.5	21	0

cide. The fibers modified with neomycin showed similar antibacterial activity towards all three types of microorganisms.

The antibacterial activity of extracts taken from fibers retained in water at 310 K within 14 days is presented in Table VI. The results obtained by applying the direct method are similar to the above and they also show that Ge is the most effective one. Ge antibacterial activity increases with time, which is also proved by its amount liberated into water. Neomycin showes slighter biocide effect, especially on Pae, which is also true for the standard sample of the antibiotic. The extracts from the fibers containing penicillin are effective towards Sa only, and their activity decreases with the time, probably due to the biocide liberation rate or its hydrolysis in water solution, diminishing the biocide effect towards the tested bacteria strains. The effect of these extracts on Ec is substantially slighter, and in the case of Pae practically insufficient. The same is true for the standard samples of penicillin (Table IV).

IR Spectrophotometric Measurements

The chemical modification of PAN–Anilana fibers due to the grafting of PAA followed by the addition of An has been examined by IR spectrophotometry. The absorption spectrum of the initial unmodified PAN–Anilana fibers [Fig. 2(a)] show absorption bands at the following wave numbers: 3544 cm^{-1}, a band that corresponds to OH group vibration; 1454 and 1362 cm^{-1}, bands due to CH_2 vibration; 2243 cm^{-1}, a band due to the presence of C≡N groups; 1733 and 1627 cm^{-1}, bands due to the presence of C=O groups of itaconic acid and methyl acrylate (comonomers of PAN–Anilana fibers); 2940 and 1249 cm^{-1}, those corresponding to COOH; and at 1074 cm^{-1}, a band due to C—H vibration.

Table VI Antibacterial Activity of Modified Fibers Tested by the Disc-Diffusion Method

Tested Bacteria	Test	Inhibitions Zone of Growth (mm)				
		Test Days				
		1	5	7	12	14
Staphylococcus aureus	PAN untreat.	0.0	0.0	0.0	0.0	0.0
	PAN–PAA–Ge	21.5	26.0	24.0	28.5	29.5
	PAN–PAA–Ne	12.0	14.5	14.0	19.0	15.0
	PAN–PAA–Pe	30.0	15.0	12.0	13.5	14.5
Escherichia coli	PAN untreat	0.0	0.0	0.0	0.0	0.0
	PAN–PAA–Ge	17.0	25.0	25.0	24.5	26.0
	PAN–PAA–Ne	10.0	14.0	12.0	16.5	9.5
	PAN–PAA–Pe	16.0	0.0	0.0	0.0	0.0
Pseudomonas aeruginosa	PAN untreat.	0.0	0.0	0.0	0.0	0.0
	PAN–PAA–Ge	19.5	24.0	27.0	26.5	30.0
	PAN–PAA–Ne	0.0	0.0	0.0	9.0	0.0
	PAN–PAA–Pe	0.0	0.0	0.0	0.0	0.0

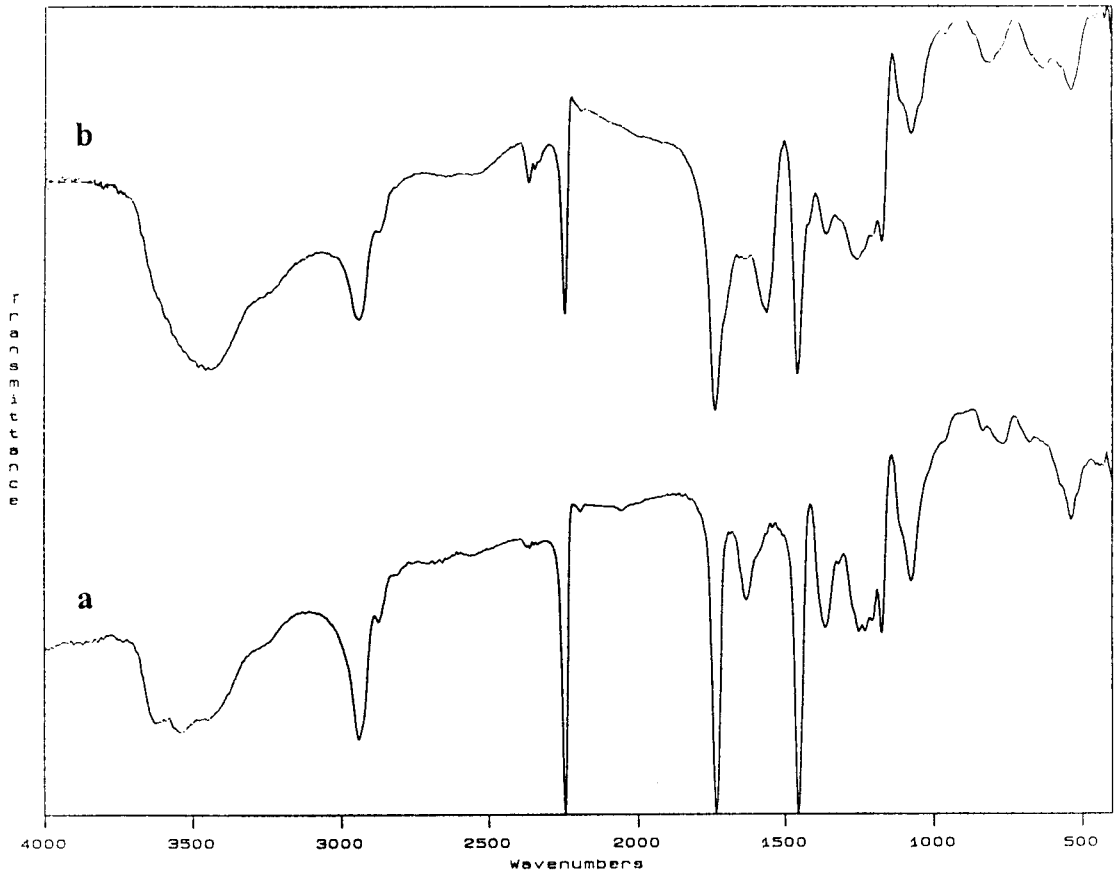


Figure 2 IR spectra for (a) initial PAN–Anilana fibers and (b) PAN–Anilana fibers grafted with PAA (x = 18.6% by weight).

The spectrum of the PAN–Anilana fibers grafted with PAA [Fig. 2(b)] shows higher absorption bands at the wave numbers 1737 and 1253 cm^{-1} corresponding to C—O and COOH vibrations, respectively, which testifies to the increase in the carboxylic group content in the fibres due to the grafted PAA.

Figure 3 shows the IR spectra of PAA grafted and Ge impregnated fibers (c) and Ge standard (d). The following absorption bands can be distinguished in the Ge spectrum: at the wave number 3436 cm^{-1} a characteristic band of OH and NH groups included in the structure of this antibiotic; at γ = 1632 cm^{-1} and γ = 1537 cm^{-1} bands corresponding to the vibration of cyclic rings; at γ = 1057 cm^{-1} a characteristic band of C—O—C groups, and at γ = 616 cm^{-1} a band corresponding to C—H group vibration.

The spectrum shown in Figure 3(c) contains absorption bands that mainly correspond to the PAA grafted PAN–Anilana fibers, which results from the high proportion of the grafted fiber material to a low quantity of the added Ge (z = 6.5% by weight). However, the changes in the spectrum brought about by grafting and Ge addition are noticeable. The absorption bands at γ = 1627 and 1537 cm^{-1} correspond to the vibration of Ge cyclic rings. There is a change seen in the band at 3436 cm^{-1} corresponding to the OH group vibration. The absorption is distinctly increased, which is brought about by the increased number of OH groups derived from Ge. New bands are observed at γ = 1627 and 1562 cm^{-1}, which can correspond to the carboxylic ions of the new bond PAN–PAA–Ge. At the same time, broad bands are observed at γ = 2700–2200 cm^{-1} and 1482 cm^{-1}, which can be ascribed to ammonium ions. The mentioned bands are not observed in the spectral characteristics of the initial PAN and the spectrogram of PAN–PAA. Neither can they be found in the spectrogram of PAN–PAA–Pe.

Figure 4 shows the IR spectra of the PAA grafted and Ne impregnated fibers (e) and Ne standard (f). The spectrum of Ne standard shows

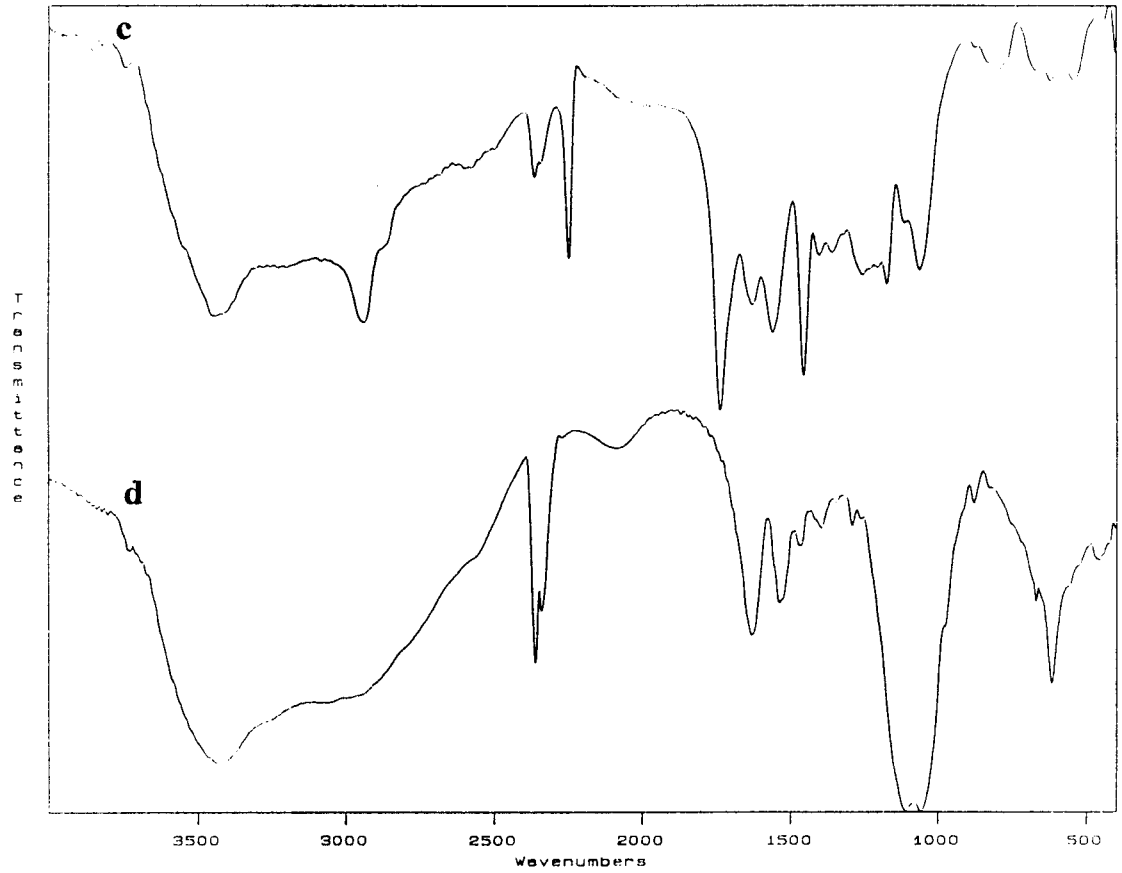


Figure 3 IR spectra for (c) grafted PAN–Anilana fibers containing Ge (x = 18.6%, z = 6.5%) and (d) standard sample of Ge.

characteristic absorption bands corresponding to OH and NH vibrations within the wave number range 3420–2920 cm^{-1}, characteristic bands of NH_2 groups present in the Ne rings at 1633–1537 cm^{-1}, a band derived from C—O—C groups at γ = 1051 cm^{-1} and that corresponding to C—H group vibration at γ = 611 cm^{-1}.

The spectrum of the PAA grafted and Ne impregnated fibers [Fig. 4(e)] contains absorption bands derived both from Ne and from the PAA-grafted fibers. The bands at wave numbers: 2939 cm^{-1}, 2243 cm^{-1}, and 1736 cm^{-1} brought about by the vibration of COOH, CN, and C= groups are derived from the PAA grafted PAN–Anilana fibers. The increased content of OH and NH groups derived from the antibiotic is confirmed by the distinctly higher absorption band at γ = 3418 cm^{-1}, while the changes in the bands at γ = 1169 cm^{-1} and γ = 1042 cm^{-1} are likely to be due to the vibration of C—O—C of neomycin. The appearance of a new band at γ = 1560 cm^{-1} and at γ = 1042 cm^{-1} can testify to the presence of carboxylate ions of the new fiber–An bond. A similar band at the same wave numbers is also observed in the spectrum of the grafted PAN fibers containing Ge. The spectrograms of PAN–PAA–Ne show also a new band at γ = 1620 cm^{-1}, which can be ascribed to the ammonium ion.

The presence of the bands corresponding to both ammonium and carboxylate ions [Figs. 3(c) and 4(e)] can testify to a ionic character of the new bond formed due to the addition of gentamycin or neomycin to the PAN fibers modified with PAA.

Based on the above discussed results, it can be suggested with a high probability that the addition of Ge or Ne can proceed according to the following reaction:

$$\text{P–COOH} + \text{H}_2\text{N–An} \rightarrow \text{P–COO}^-[\text{H}_3\text{N}^+\text{–An}] \quad (4)$$

where P–PAN–PAA is a grafted polymer and An is an appropriate radical of Ge or Ne.

Figure 5 shows the spectra of the PAA-grafted

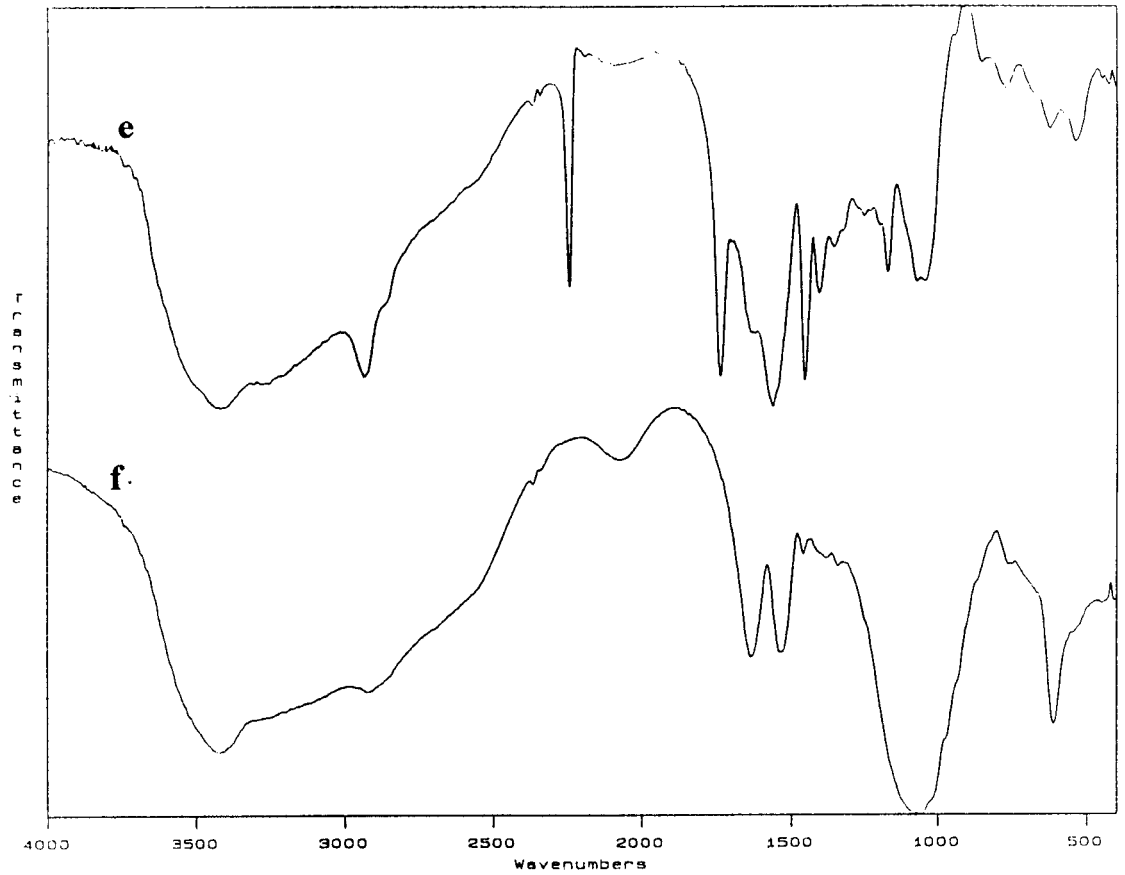
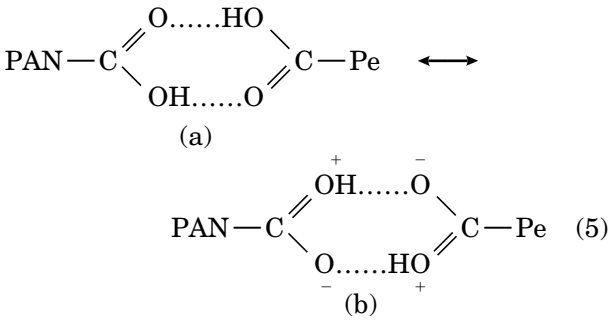


Figure 4 IR spectra for (e) grafted PAN–Anilana fibers containing Ne (x = 18.6%, z = 18.2%), (f) standard sample of Ne.

and Pe-impregnated fibers (g) and Pe standard (h). The spectrum of Pe is quite a complicated one and shows the following absorption bands: at γ = 3369 cm^{-1} and γ = 1639 cm^{-1}, bands corresponding to the vibration of characteristic CONH group of penicillin; at γ = 2963 cm^{-1}, a band derived from the presence of CH_2; at γ = 1612 cm^{-1} and at γ = 1419 cm^{-1}, bands derived from the vibration of the aromatic ring; at γ = 1332 cm^{-1}, a band derived from the amide group —C—N—; within the range from 759 to 665 cm^{-1}, bands brought about by the vibration of the neighboring five hydrogen atoms in the aromatic ring and monosubstituted benzene derivative; at γ = 573 cm^{-1}, a band derived from the presence of C—S. The spectrum of the PAA-grafted and Pe-impregnated fibers [Fig. 5(g)] shows first of all the bands derived from PAN fibers; only at γ = 2940 cm^{-1} a change in absorption is noticeable, indicating that some COOH groups of the grafted fibers have been transformed into carboxylate ions. Also, the numerical value of the band corresponding to the C=O groups in the β-lactam system has been reduced from 1766 cm^{-1} to 1733 cm^{-1}, which can be brought about by the dimerization of COOH groups of penicillin and the grafted PAN fibers according to the following scheme:



(5)

The interpretation of these spectra is made difficult by the superimposing of absorption bands derived from both the grafted polymer and penicillin over one another.

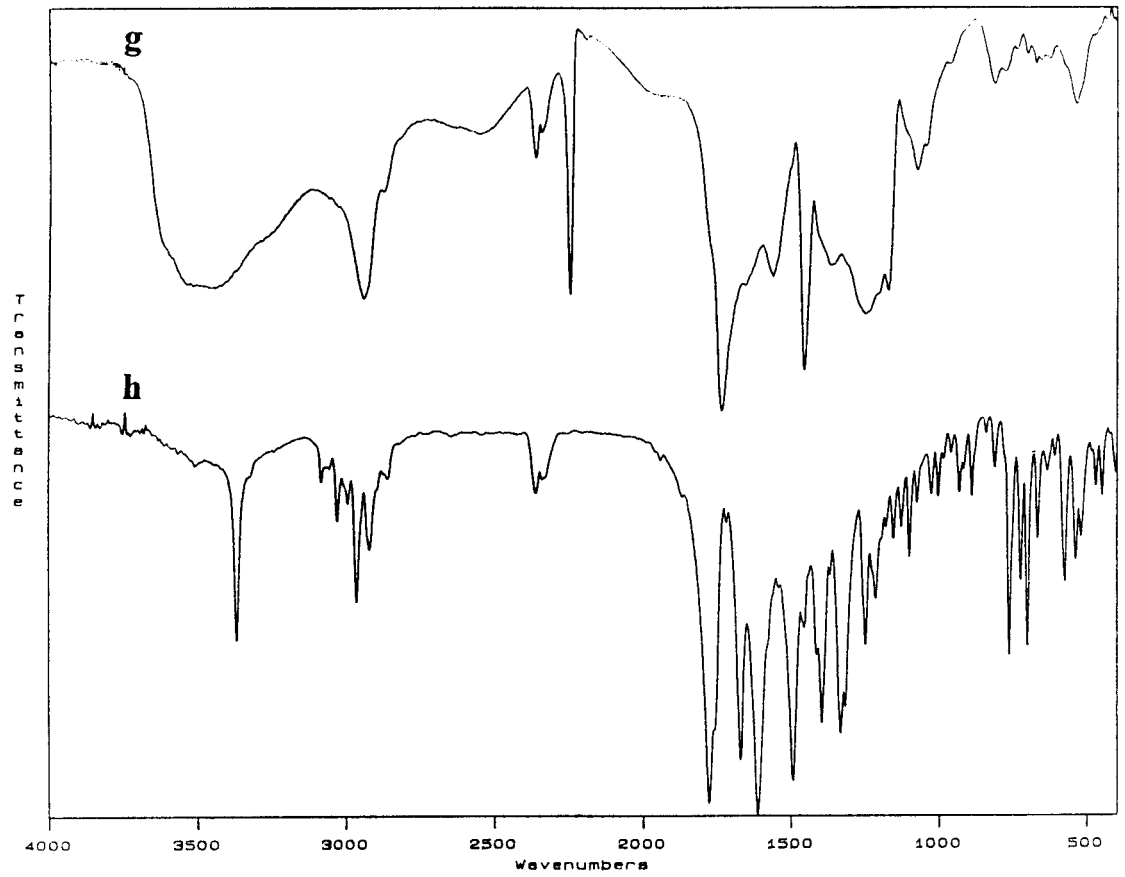


Figure 5 IR spectra for (g) grafted PAN–Anilana fibers containing Pe (x = 18.6%, z = 11.0%), (h) standard sample of Pe.

^{1}H-NMR Measurements

Figure 6 shows the ^{1}H-NMR spectrogram of the PAA-grafted and Pe-added fibers (b) and Pe standard (a). The bands at the shifts δ 2.545 ppm are derived from DMSO (solvent). The broad bands at the shifts δ 2.50, δ 3.58, and δ 3.70 ppm are derived from the protons belonging to the initial PAN and the PAA-grafted PAN. On the other hand, the bands at the shifts δ: 1.45, 1.55, 3.35, 3.5, 3.84, and 5.35 ppm correspond to the bi-cyclic system formed by the two condensed rings in penicillin : thiazolidyne and β-lactam. The band at the shift δ 7.26 ppm corresponds to the side benzene ring of penicillin. Their presence has been also confirmed in the spectrogram of Pe standard [Fig. 6(a)].

The band at δ 8.68–8.55 ppm corresponds to the protons of the carboxylic group in penicillin resulted from the dissociation under the influence of water present in DMSO (the band corresponding to the protons of water present in this solvent appears at the chemical shift δ 3.32 ppm). The band at δ 8.68–8.55 ppm is not observed in the spectrograms of PAN, PAN–PAA, and PAN–PAA–Pe. The absence of this band in the spectrogram of the modified fibers containing penicillin can indicate that penicillin is combined with the PAA-grafted PAN fibers according to reaction (5).

From the performed experiments it follows that after the liberation of biocides into water for a period of 600 h (Fig. 1), there is still 50% of antibiotics left on the fibers, which might be combined with stronger bonds than those under discussion. Thus, taking this fact into consideration, one cannot exclude that some amount of the antibiotics is attached to fibers by means of chemical bonds of different type and stronger than the discussed ones; therefore, it is more difficult for them to be released from the fibers.

CONCLUSIONS

The modification of PAN fibers by introducing carboxylic groups into their structure by grafting

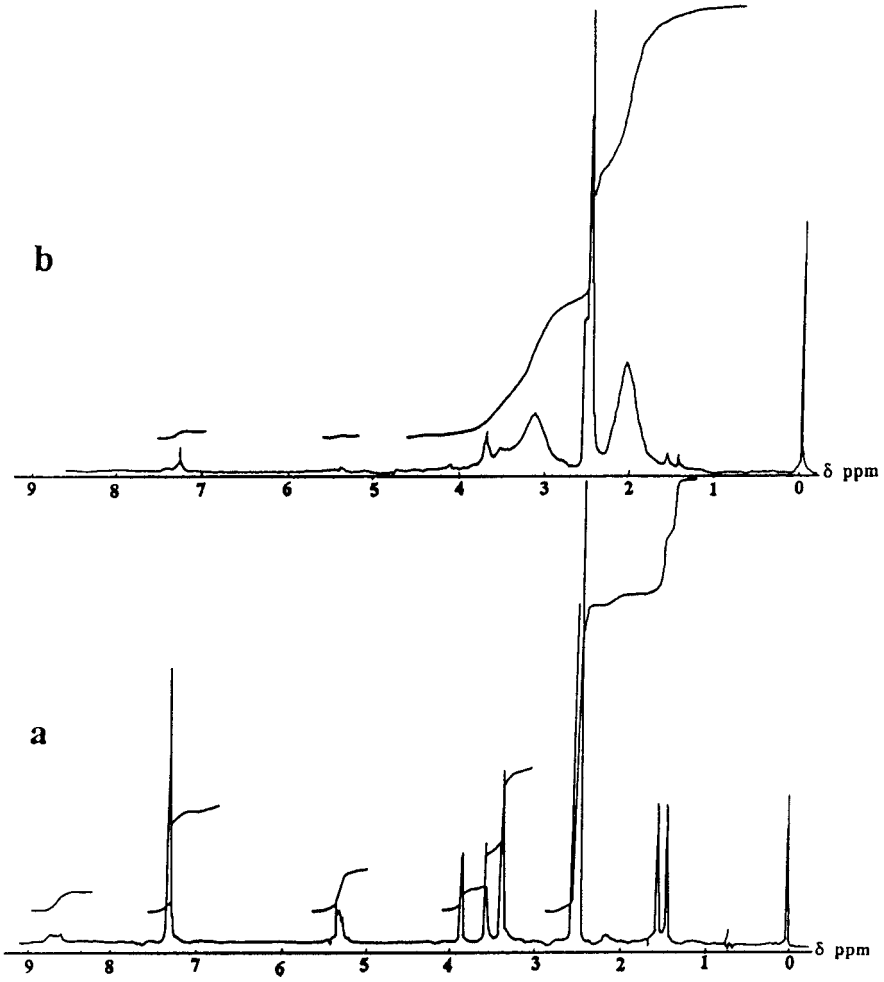


Figure 6 ^{1}H-NMR spectra for modified PAN–Anilana fibers containing Pe. (a) Spectrum for standard sample of Pe; (b) spectrum for PAN–PAA–Pe fibers.

PAA and then treating them with gentamycin, neomycin, or penicillin solutions makes it possible to produce fibers with biocide properties active towards wide Gram-positive and Gram-negative bacteria spectrum.

The liberation of biocides from fibers into water can be described quite precisely by the exponential equation $C = C\ kt^n$.

The liberation of antibiotics from fibers into solution is a long-lasting process, and after a considerably long period of liberation there is still some amount of antibiotic left in the modified fibers preserving their bioactive properties.

The modified fibers show different effects on Gram-positive and Gram-negative bacteria, which depends on the type of the fixed antibiotic.

IR spectrometry and ^{1}H-NMR measurements confirm the presence of antibiotics combined with fibers through chemical bonds.

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