Modification of Polyester Fibers by Grafting with Poly(acrylic acid)

JADWIGA BUCHEÑSKA

Man-Made Fibers Department, Technical University of Łódz, 90–543 Łódz, Żeromskiego 116, Poland

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ABSTRACT: The grafting of acrylic acid on PET using benzoyl peroxide has been investigated. The influence of the main parameters of grafting, the effect of additives on the degree of grafting, and the amount of homopolymer formed during the process have been determined. Futhermore, the values of apparent activation energy have been calculated. Also, the influence of the degree of grafting on the moisture sorption and swelling of modified fibers have been determined. By an additional treatment of the grafted fibers with antibiotics it is possible to provide the fibers with antibacterial properties. Liberation of antibiotics from fibers into solutions has been examined and mathematically described.
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Key words: graft copolymerization; biocide poly(ethylene terephtalate) fibers; acrylic acid

INTRODUCTION

Several approaches to employing the graft copolymerization of vinyl monomers to modify synthetic fibers have appeared in the literature of the recent 15 years. The reported methods mainly involve modifications of polyamide fibers. Some investigations into changes of polyester fiber (PET) properties after grafting vinyl monomers are also known[1–11]; however, the number of these articles is much less than those related to other types of fibres. Most of the literature reports dealing with grafting on polyester fibers come from Japanese and Indian authors and refer to grafting initiated by radiation. The use of this method to initiate the graft copolymerization on PET fibers is imposed by the fact that these fibers show a high resistance to chemical activators. Nevertheless, some articles on vinyl monomer grafting by means of chemical[9,11,12–21] and thermal[22,23] initiation have been reported recently. Most of the experiments were focused on changes in physical and mechanical properties of grafted PET fibers.

Due to their specific properties, polyester fibers have found practical applications in the manufacture of various implants. And, it should be stressed that, the product has acquired a good reputation among surgeons. The desire to obtain materials biocompatible with blood for medical purposes has induced further interest on grafted copolymers. These biopolymers are composed in such a manner that hydrophobic polymer is used as a matrix, while a polymer (grafted) with hydrophilic sites is fixed to this matrix.[24,25] This is due to the significant influence of their microphase structure and negative charge of the grafted polymer to contribute to the athrombogene properties of biopolymer.

The best results have been achieved so far with polyurethane elastomer superficially grafted with dimethylsilane–Avcothane 51 and PET fibers grafted with poly(acrylic acid) PAA,[25] which have already found practical applications. It should be noted, however, that despite good experimental results, neither PET fibers grafted with PAA nor

Correspondence to: Dr. J. Buchenska.
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other biopolymers (PU grafted) have not been used for the manufacture of implants on a large scale. The most important reason for undertaking the subject in the present case is that surgical yarns made from PET fibers cause only a slight tissue reaction within a living organism, even slighter when compared with other fibers. Particular attention should be paid here to the fact that the tissue reaction is usually caused by physiological fluids that do not permeate through, and become a good culture for bacteria. This, in turn, can cause chronic local infections[27–34] in wound healing, and result in a longer period for the patients' recovery. Therefore, research aimed at the improvement of those yarns, to provide them with antibacterial properties is ongoing. Such fibers are expected to be effective in healing wounds even in a not fully aseptic environment.

It is then highly recomended to use yarns containing bacteriostatic agents[34–37] or antibiotics.[34,38–41] Several attemps to immobilize antibiotics in PET fibers by impregnating them with biocide solutions have so far not led to their practical utilization, as such substances are easily and quickly washed out from the treated fibers. Furthermore, attempts to combine antibacterial agents with PET fibers through chemical bonding have also failed due to the absence of suitable functional groups that could form a chemical bond with a biocide compound. This explains the need for introducing into PET fibers proper functional groups, which in turn, would be able to combine an appropriate antibacterial agent. There are some ways, already presented in the literature, for attaching antibiotics with alkaline properties to PET fibers. The methods consist of preliminary sulphonation followed by treating the fibers with an appropriate antibiotic.[38,39] The major defect of this method, along with rather a complicated procedure of sulphonation, is, first of all, the decrease in the strength of fibers. These disadvantages can be eliminated by employing another method to modify PET fibers. Such a process as that used in this study consists of introducing into fibers, instead of sulphonic, carboxylic groups by PAA or poly(metacrylic acid) grafting,[17,21–23,42] which in turn, by a chemical bond, can be attached to alkaline antibacterial substances. In this case, grafting has been achieved in a heterogenous system in the presence of benzoyl peroxide as an activator. Afterwards, antibiotics such as crystalline penicillin, neomycin, and gentamycin will be combined with the PAA-grafted PET fibers.

EXPERIMENTAL

Materials

18 filament PET yarn of Elana S.A. (Toruñ) was used for the intended modification, prepared according to ref. 43. The following reagents were also used: (a) acrylic acid (AA) from FERAK (Berlin, Germany) stabilized with 0.05% hydroquino methylether b.p. 312, 5K/10 mmHg n_D^{20} = 1,421, purified by destillation under low-pressure, deoxigenated nitrogen in the presence of metallic copper; (b) benzoyl peroxide (BP), pure grade, of Argon (£ódz, Poland) crystallized from methanol–chloroform mixture and dried under vacuum over P_2O_5; (c) benzene, of POCh (Gliwice, Poland); pure grade; (d) dispersing agent NNO (a mixture of salts of multicore condensat aromatic sulphoacids) of ZPO-Rokita (Zgierz); (e) Diphenyl (DPh), of POCh-Gliwice, pure grade; (f) Nitrogene of Stilon S.A. (Gorzów Wlk.); (g) crystalline potasium penicillin (Pe), neomycin (Ne) as a mixture of B and C types, gentamycin (Ge) as gentamycin sulphate—all of them of Polfa (Tarchomin), pure grades.

Methods

Grafting of Acrylic Acid on PET Fibers

Samples of fibers (2 g ± 0.1 mg) as previously prepared[43] were impregnated with 5% benzene solution of BP. Then, the excess of peroxide solution was removed by pressing, and the fibers were put into a 250 cm^3 reactor equiped with a mechanical stirrer, a thermometer, a reflux condenser, and nitrogen supply. Grafting was carried out in acrylic acid solution containing DPh and/or NNO. The fiber to grafting bath ratio was 1 : 50 in all the experiments.

The degree of polymer grafting on fibers and the quantity of homopolymer formed during the process were calculated gravimertically as in article.[44] Grafting efficiency (E), extent of reaction (K) and grafting ratio (R) were calculated as before.[45]

Physical, Chemical, and Mechanical Properties of Grafted PET Fibers

The Hydrophilic properties of the grafted fibers were examined by water sorption within 24 and 48 h by means of the exsiccator method in 65 and 100% relative humudity, according to PN-71P-04635. The fibers were conditioned according to

PN-P-04602, and their hygroscopicity was calculated, using the equation:

$$H = (m_F - m_0)/m_0 \cdot 100\% \text{ by wt.} \quad (1)$$

Swelling of modified fibers in water was determined by the centrifugal method.[46] The fibers were plunged into water and allowed to stand for 3 h. The fiber to bath ratio was 1 : 50, rotation speed 4000 rpm, centrifugation time—10 min, and the distance of samples from the centrifuge axis—70 mm. The degree of swelling (P) was calculated by means of the following equation:

$$P = (m_F - m_0)m_0 \cdot 100\% \text{ by wt.} \quad (2)$$

where m_0 = initial weight of dry fibers before moisture sorption or swelling in (g); m_F = final weight of fibers after sorption or swelling and centrifugation (g).

Further Modifications of Grafted Fibers

PET fibers with different degrees of PAA grafting were impregnated with solutions of antibiotics at 313 K for a period of 1 h. The extent of impregnation with the antibiotics was determined by the gravimetric method.

Liberation of Biocides from the Modified Fibers

The amount of antibiotic liberated from the modified fibers into water was determined by use of the gravimetric method.[47,48]

Antibacterial Properties of the Modified PET Fibers

The antibacterial effects of the fibers were evaluated by the direct and disc-diffusion methods described previously.[47–49] Three test organisms considered representative for hospital environment[50] were used: Gram-positive bacteria *Staphyloccocus aureus* (Sa) NCTC 4163, Gram-negative *Escherichia coli* (E.c.) NCTC 8196, and *Pseudomonas aeruginosa* (P.ae) NCTC 6749.

RESULTS AND DISCUSSION

The Influence of the Reaction Parameters on the Degree of PAA Grafting on PET Fibers

The grafting of AA on PET fibers consisted in creating active centers on fibers before grafting by

Table I The Values of Degree of Grafting (X), the Amount of Homopolymer (Y), Grafting Efficiency (E), Extent of Reaction (K), and Grafting Ratio (R) for Reactions Conducted with Different Concentrations of DF and NNO, T = 368 K, C_{AA} = 7.5% wt., τ = 1 h

	Concentration, % by wt		X	Y	E	K	R
No.	DF	NNO			% by wt		
1	0.0	0.0	0.24	99.93	0.06	100.00	0.06
2	0.0	0.1	5.50	76.91	1.29	78.21	1.65
3	0.0	0.2	6.79	69.14	1.80	70.94	2.54
4	0.0	0.3	8.08	46.63	2.16	47.28	4.56
5	0.0	0.4	10.15	45.13	2.71	49.34	5.49
6	0.0	0.5	9.31	46.72	2.49	49.20	5.05
7	0.0	0.6	9.53	46.76	2.54	49.29	5.16
8	0.1	0.0	8.20	93.94	2.19	96.13	2.28
9	0.2	0.0	8.72	91.73	2.33	94.05	2.47
10	0.3	0.0	10.70	85.65	2.85	88.51	3.22
11	0.4	0.0	12.89	68.19	3.44	71.63	4.81
12	0.5	0.0	10.91	76.25	2.91	79.18	3.68
13	0.6	0.0	11.19	79.89	2.99	82.88	3.60
14	0.0	0.4	10.15	46.63	2.71	49.34	5.49
15	0.1	0.4	16.08	27.69	4.05	31.77	12.78
16	0.2	0.4	22.34	19.43	5.92	26.34	22.46
17	0.3	0.4	24.98	9.88	6.61	16.99	38.87
18	0.4	0.4	35.96	7.25	9.59	16.84	56.95
19	0.5	0.4	30.30	6.59	8.04	14.62	55.01
20	0.6	0.4	21.94	9.71	5.82	15.55	37.43

treating them with 5% benzene solution of BP at elevated temperature. After impregnation the excess of BP solution was removed under pressure and the solvent was evaporated at elevated temperature. The pretreated fibers were put into a bath containing acrylic acid, dispersing agent, and/or activator. However, the initiation process is rather complex; it allows easy and even BP penetration into the entire cross-section of fibers. It is important to press the excessive BP solution off, and consequently to remove BP from the fiber surface, to prevent the formation of homopolymer in the grafting bath. Subjecting the fibers to heat at 353 K during the initiation process facilitates the formation of oxybenzoyl and phenyl radicals. It can also result in the formation of peroxide and hydroperoxide groups on PET fibers. They can additionaly influence the formation of active centers able to initiate graft copolymerization. It is expected then, to obtain high degrees of PAA grafting on PET fibers and to minimize the homopolymerization reaction in the system.

It is worth mentioning that the decomposition of BP and hydroperoxide groups highly depends on the temperature of grafting, while, the process of grafting is affected by the presence of DPh activator and NNO dispersing agent in the grafting bath, facilitating quick vinyl monomer penetration and fiber swelling. Therefore, the following parameters and their influence on the degree of PAA grafting on PET fibers (X % by wt), and the amount of homopolymer formed during the process (Y % by wt) were examined: the amount of additives (activator and dispersing agent) in grafting bath, temperature, time, and AA concentration. All results obtained are presented in Tables I–IV. Table I shows the values of X, Y, and E, K, R in relation to the amount of DPh or NNO in grafting bath. The absence of these additives results in excessive homopolymer formation from the very beginning of the process. This, in turn, leads to increase in viscosity of the grafting bath that hinders AA penetration into fibers. Consequently, fibers with a very low degree of grafting are obtained, whereas almost the whole amount of monomer is turned into PAA homopolymer. The addition of DPh and NNO to the grafting bath brings about an increase in the degree of PAA grafting on PET fibers, and simultaneously reduces the amount of homopolymer formed during the process. The best results are obtained with 0.4% by wt of DPh and NNO in the grafting bath. It is also confirmed by E, K, and R values given in Table I.

The amounts of homopolymer given in Table I represent the total amount of homopolymer (Y) formed in the grafting bath (Y_B), and the amount of homopolymer remaining on fibers (Y_F), while $Y_B \gg Y_F$. As the results obtained from the gravimetric method are by 3% higher when compared

Table II The Values of Degree of Grafting (X), the Amount of Homopolymer (Y), Grafting Efficiency (E), Extent of Reaction (K), Grafting Ratio (R), Rate of Grafting (V), Preexponential Constant (A) from Arhenius Equation and Activation Energy (E_a) of the Grafting of PAA on PAN

No.	Temp. K	$1/K \times 10^{-3}$	X	Y	E	K	R	$V \times 10^{-7}$	log$V$	A	E kJ/mol
	7.5% KA										
1	333	3.00	0.02	0.00	0.01	0.01	100.00	0.01	−9.14		
2	343	2.92	0.48	0.10	0.13	0.23	56.20	0.19	−7.73	946.71	181.05
3	353	2.83	3.03	0.85	0.80	1.65	48.51	1.17	−6.93		
4	358	2.79	9.53	1.18	2.26	3.67	69.51	3.67	−6.17		
5	363	2.75	25.22	7.38	6.75	14.80	45.64	9.72	−6.01		
6	368	2.72	35.96	7.25	9.59	16.84	56.95	13.86	−5.86		
7	373	2.68	30.30	10.30	8.09	18.39	43.99	11.68	−5.92		
	10% KA										
8	333	3.00	0.01	0.00	0.01	0.01	100.00	0.00	−9.27		
9	343	2.93	0.51	0.19	0.10	0.20	36.22	0.20	−7.71	945.75	180.86
10	353	2.83	3.41	2.77	0.69	0.96	71.22	1.31	−6.88		
11	358	2.79	13.19	6.61	2.64	9.25	28.50	5.09	−6.29		
12	363	2.75	27.85	12.97	5.57	18.57	29.99	10.73	−5.97		
13	368	2.72	37.80	14.95	7.56	23.36	32.37	14.57	−5.84		
14	373	2.68	24.09	18.59	4.82	24.26	19.87	9.28	−6.03		

(τ = 1 h, NN) and DF 0.4% by wt each.

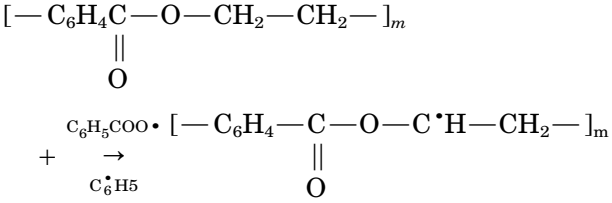
with those from the analytical method, the actual quantity of the homopolymer formed during the process is at minimum, which indicates that this type of initiation is very effective and efficient. Moreover, the grafting bath can be reused after acrylic acid and activators are replenished.

Next, the temperature and time of grafting were examined. In the first series of tests, temperature was changed within 333–373 K, while the reaction time was t = 1 h and constant. All tests were carried out with acrylic acid concentrations C_{AA} = 7.5% and 10% by wt. Table II presents the degrees of PAA grafting (X) on PET fibers and the total amount of homopolymer (Y) formed during the process. Table II also includes the calculated values of E, K, and R, reaction rate (V), and the values of apparent activation energy for grafting. From these data it follows that a high degree of grafting is obtained at 368 K with AA concentration of 7.5% in grafting bath (X > 30% by wt), with the quantity of homopolymer being very low. With an AA concentration of 10% in the grafting bath the degree of grafting on PET fibers is only a bit higher, whereas the amount of homopolymer obtained as a by-product is much higher.

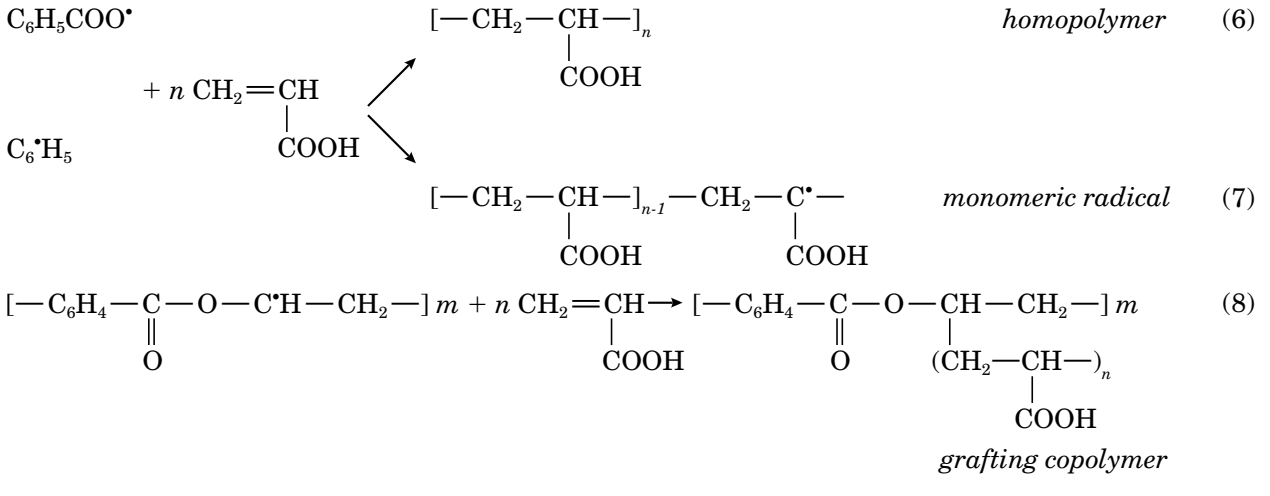
Considering the data in Table II, it can be concluded that if the grafting process is conducted at temperatures below 358 K the degree of grafting on PET fibers is rather low. But when the temperature exceeds the glass transition point of PET, there is a considerable increase in the degree of grafting, which is associated with the molecular dynamics of the fiber matrix,[51] as well as with the formation of radicals due to the decomposition of BP and hydroperoxide groups. These radicals can detach hydrogen atoms from the PET macromolecule. They also can react with the monomer to form a growing monomeric radical,[15] which is able to convey its radical character to the PET chain, and to induce AA graft copolymerization as well as homopolymerization. Presumably, with BP used as initiator, the active centers on PET are created due to the detachment of a hydrogen atom in a position to a carboxylic group. The graft copolymerization takes place as a result of the kinetic chain transfer to the polymer according to the reaction (3)–(8):

$$(C_6H_5COO)_2 \rightarrow 2C_6H_5COO^{\bullet} \qquad (3)$$

$$C_6H_5COO \rightarrow C_6^{\bullet}H_5 + CO_2 \qquad (4)$$



(5)



As has been mentioned above, the thermal initiation method can also be applied. In this case, active centers are also formed in a position to carboxylic groups, as in (5), but AA is fixed through an oxygen atom. The highest degree of PAA grafting is obtained at 368 K. The comparison of E and R values for AA concentrations of 7.5 and 10% (lines 6 and 13, Table II) indicates that the values of E and R for 7.5% by weight of AA in the bath are higher than for 10% of the acrylic acid. This

Table III The Values of Grafting (X), the Amount of Homopolymer (Y), Grafting Efficiency (E), Extent of Reaction (K), and Grafting Ratio (R) for Different Amounts of Acrylic Acid in Grafting Bath

	C_{KA}	X	Y	E	K	R
No.			% by wt			
1	1.0	1.40	0.00	2.37	2.37	100.00
2	2.5	9.62	0.00	7.54	7.54	100.00
3	5.0	19.76	1.51	7.56	9.07	83.30
4	7.5	35.96	7.25	9.59	16.84	56.95
5	10.0	37.80	14.95	7.56	23.36	32.37
6	15.0	29.34	31.85	2.58	34.43	7.50

T = 368 K, τ = 1 h, DF and NNO 0.4% by wt each.

means that the grafting at 368 K with the AA concentration of 7.5% by wt is more effective when compared with 10% solution of the acid in question. Hence, all further experiments were done with 7.5% concentration of AA in the grafting bath at the above-stated temperature.

In the next series of tests the reaction time was changed from 15 to 120 min while the temperature was 368 K and remained constant. The concentration of AA was 7.5% by wt. All results obtained are shown in Table III. It can be seen that the time extension over 1 h is virtually ineffective, which has been also confirmed by the values of E and R given in Table III.

The Influence of Temperature on the Rate of Grafting

The rate of grafting (V) is expressed as a ratio of the degree of grafting (X_1) to the time of grafting.[52] The results calculated on the basis of this formula and their logarithms are presented in Table II. If the relationship between the reaction rate and temperature is known, it is possible to calculate the value of apparent activation energy (E_a) for grafting by means of Arrhenius formula.

To verify whether the reactions in question fit to the Arrhenius formula, the dependence log $V = f(1/T)$ has been determined (Table II, Fig. 1). The calculated data show that the values of the apparent E_a for AA concentrations of 7.5% by weight and 10% by weight are almost equal and amount to about 180 kJ/mol. These values, however, should be treated as approximate, for the grafitng reaction runs in a heterogenous system.

Properties of the Modified PET Fibers

It is well known from the literature that the introduction of different polymer as a side branch into the main polymer chain of a given fiber can result in certain changes in its physical and chemical properties, such as moisture sorption and swelling. Having this in mind, the author decided to examine the hygroscopicity and swelling of the grafted PET fibers. The results of the experiments

Table IV The Values of Degrees of Grafting (X), the Amount of Homopolymer (Y), Grafting Efficiency (E), Extent of Reaction (K), and Grafting Ratio (R) for Grafting Conducted in Different Amounts of Times (τ)

		X	Y	E	K	R
No.	τ min			% by wt		
1	15	3.50	4.08	2.28	6.57	28.20
2	30	10.31	7.38	4.85	12.61	25.88
3	60	35.96	7.25	9.59	16.84	40.11
4	90	36.01	10.02	9.06	19.08	29.41
5	120	36.94	13.46	9.32	22.78	18.12

T = 368 K, C_{AA} = 7.5%, DF and NNO 0.4% by wt each.

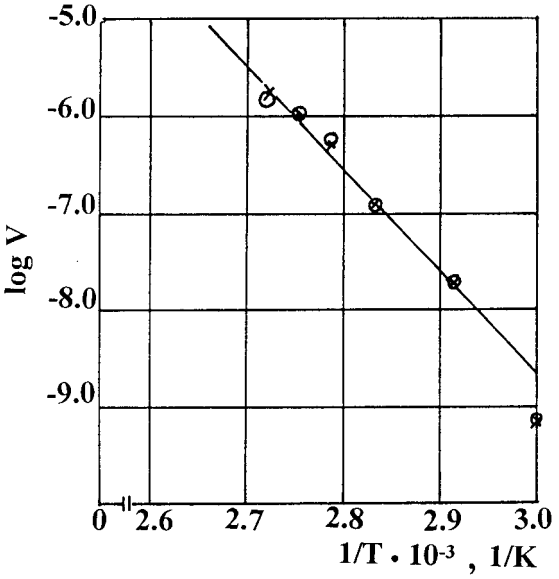


Figure 1 The dependence $-\log V = f(1/T)$ for PET fibers grafted with poly(acrylic acid) Marks (°) refer to grafting with $C_{AA} = 7.5\%$ by weight; (x) refer to grafting with $C_{AA} = 10\%$ by weight.

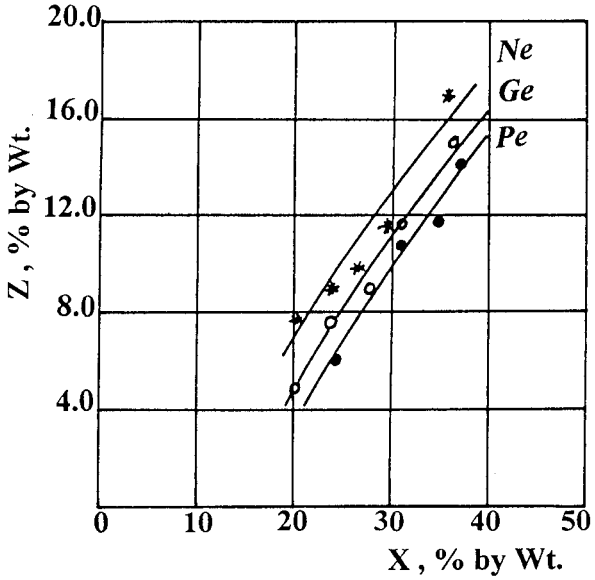


Figure 2 The dependence of the degree of treatment with antibiotic (Z) on the degree of PAA grafting (X) at $T = 313$ K, within $t = 1$ h, bath ratio 1 : 20, concetration of antibiotic in bath 20%.

are presented in Table V. It is seen that the introduction of carboxylic groups into PET fibers results in a significant increase in their hygroscopicity at 65 and 100% relative humidity, as well as in an increase in their swelling in water.

The quality of the implants is evaluated with reference to the tissue reaction they cause after being incorporated into a living organism. It is known from the literature that surgical polyester threads bring about a tissue reaction to a lesser extent than the natural catgut. It is also known that monofilament yarns are better in that respect than multifilament threads, which are connected with their hygroscopicity and capillarity. Thus, in the case of traditional surgical threads, these factors should be as low as possible, but with the synthetic surgical sutures and dressing materials showing antibacterial properties, their capillarity and absorbability may play a beneficial part. Figure 2 shows the dependence of the degree of treatment with antibiotics (Z) on the degree of grafting (X). The values Z for ungrafted PET fibers are given on the ordinate. It is seen from this figure that the ungrafted fibers contain a minute quantity of antibiotic (below 1.0%) in their structure under similar conditions (0.8% Pe; 0.5% Ne, and 0.21% Ge). On the other hand, PET fibers grafted with PAA are much more effective in fixing antibi-

Table V Swelling in Water and Moisture Sorption for PET Fibers Taken at an Equilibrium State at 65 and 100% Relative Humidity

		Hygroscopicity in % by wt at			
		65% RH	100% RH		
No.	Degree of Grafting % by wt	After 24 h	After 24 h	After 48 h	Swelling of Fibers % by wt
PET	untreated	0.28	0.61	0.65	5.82
1	8.50	0.88	4.11	4.20	13.42
2	10.31	1.55	8.27	8.86	22.37
3	27.21	1.99	11.29	12.87	31.55
4	33.69	2.16	14.12	15.43	49.64
5	36.51	2.29	14.62	17.00	52.76

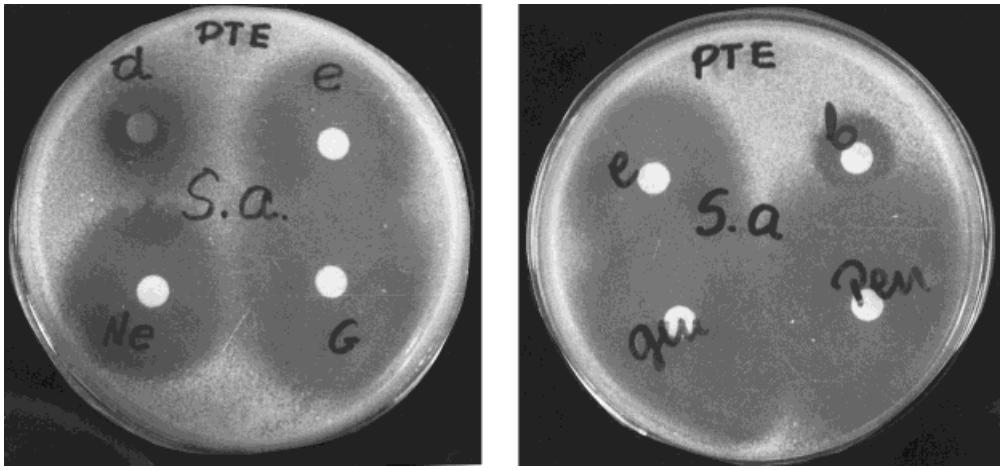


Photo 1 Antibacterial activity of PET modified fibers towards S.a strain determined with circle-diffusive method after 11 days of incubation. Symbols—b: PET–PAA–Pe (14.7%); d: PET–PAA–Ne (12.6%); e: PET– PAA–Ge (12.2%). Standard solution of: *Pen P* ↔ **Pe,** *GenG* ↔ **Ge, Ne.**

otics into their structure and show antibacterial properties. Photographs 1–3 illustrate some antibacterial effects of the fibers on certain bacterial strains representative for a hospital environment.[50] More details on the subject and inhibition zones of bacteria growths for fibers with individual antibiotics are given in other articles.[53]

Liberation of Biocide

The amount of biocides liberated into water was determined by the gravimetric method. The procedure and mathemathic models are given in refs. 35 and 48. The results of the experiments are given in Table VI and Figure 3. In the case of unmodified fibers, the whole amount of antibiotics added is thouroughly released from them after several hours. It is also true for other types of fibers.[35,48] On the other hand, antibiotics fixed to the fibers previosly grafted with PAA remain on the fibers for quite a long period of time, which is illustrated in Figure 3. After 400 h of additional hydrolysis the weight of fibers containing Ge or Ne did not change, and it was calculated that the

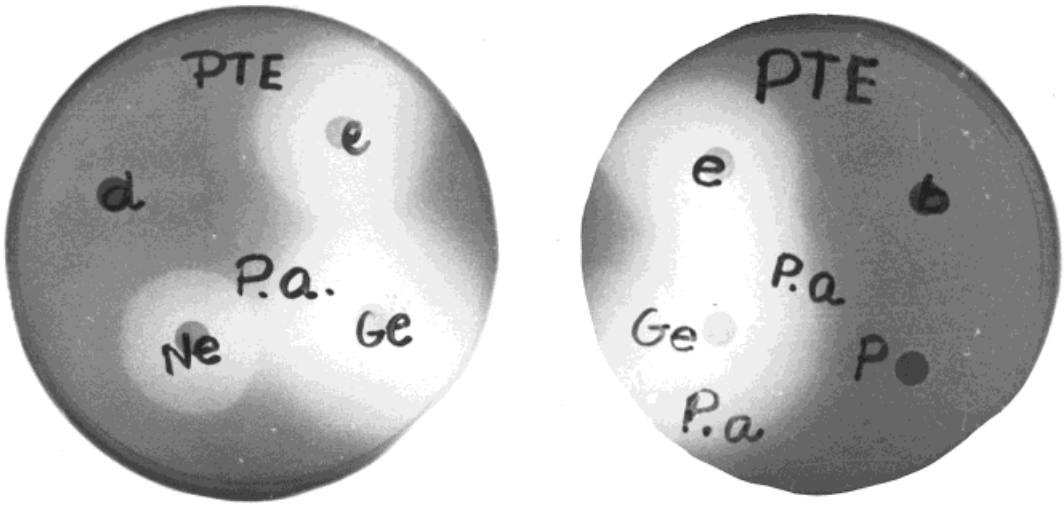


Photo 2 Antibacterial activity of PET modified fibers towards P.ae strain, determined with circle-diffusive method after 11 days of incubation. Symbols: b, d, e—as above for Photo 1.

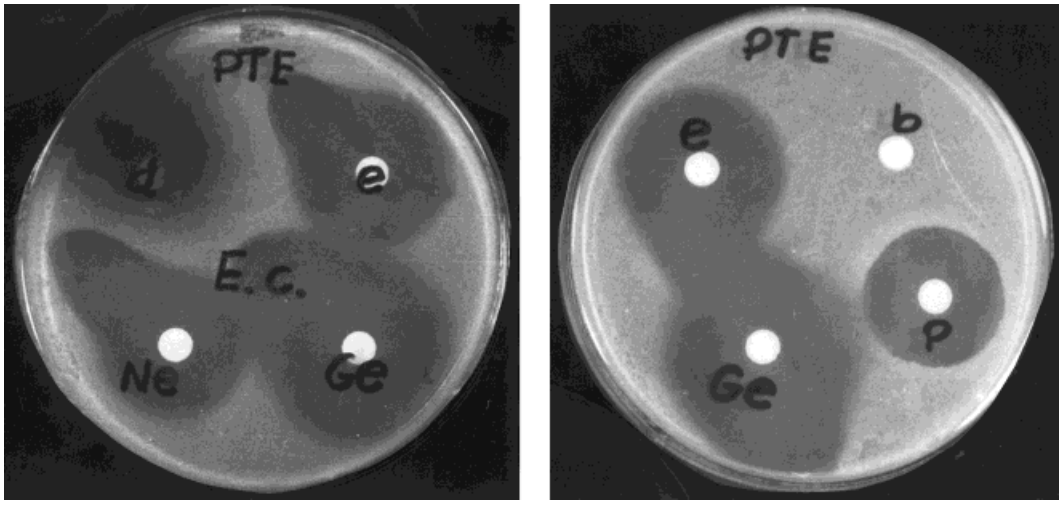


Photo 3 Antibacterial activity of PET modified fibers towards E.c. strain determined with circle-diffusive method after 11 days of incubation. Symbols: b, d, e—as above for Photo 1.

fibers still contained about 40% Ne and 50% Ge fixed when referred to the initial amount of antibiotics.

In the case of Pe, its hydrolysis from PET fibers runs faster when compared with other biocides. After 290 h of the process Pe is almost entirely removed from the fibers, the residue being only about 10–20%. Table VI shows the values of rate constants **K, b**—describing the system, and correlation coefficient κ indicated in the regression equations. The values of **K, b, n,** and κ were calculated on the basis of a computer program. The data shown in Table VI allow one to assume that the liberation of antibiotics from PET fibers into solution can be quite correctly described by the equation $C = C_\infty \cdot \sqrt{t} + b$. These results have been additionally proved by the highest value of the correlation coefficient κ.

CONCLUSIONS

The modification of PET yarn by PAA grafting with benzoyl peroxide is made more effective by the use of an activator and auxilliary substances

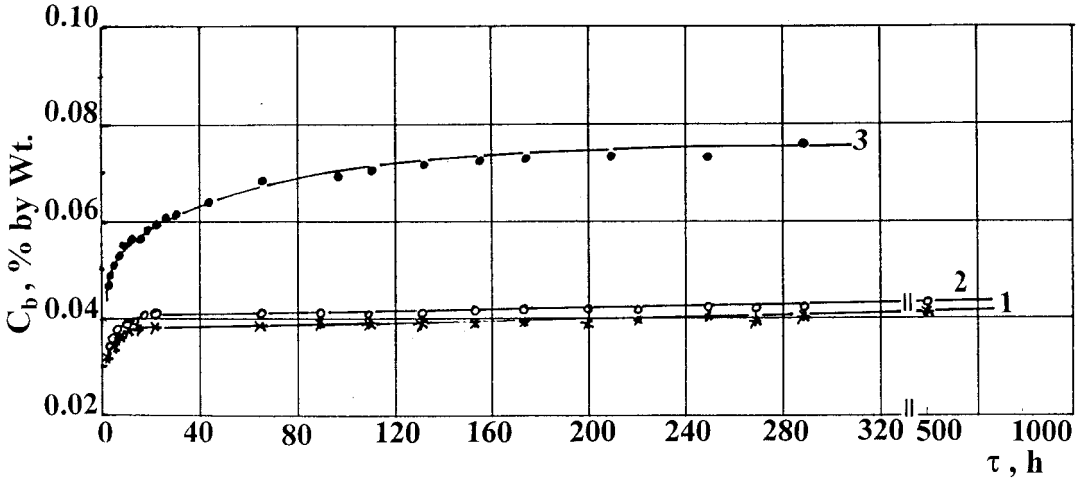


Figure 3 The dependence of antibiotic concentration C_{AA} on the time of liberation $\square t$ from modified fibers. Curve 1 PET–PAA–Pe Z = 13.02% by wt; Curve 2 PET–PAA–Ne Z = 11.04% by wt; Curve 3 PET–PAA–Ge, Z = 14.05% by weight.

Table VI Liberation of Antibiotics from Modified PET Fibers into Water; Correlation Coefficient κ, Constants K, b, n for Exponential Equations: (1), (2), (3)

	Equation								
	(1) $C = C_\infty \cdot [1 - e^{-k \cdot t + b}]$			(2) $C = C_\infty \cdot k \cdot t$			(3) $C = C \cdot \sqrt{t} + b$		
Samples	k	b	κ	k	n	κ	k	b	κ
PET-PKA-Pe $x = 30.03\%$ $z = 12.02\%$	0.01199	−1.12689	0.9222	0.63604	0.07576	0.9729	0.00149	0.05191	0.9735
PET-PKA-Ne $x = 30.03\%$ $z = 11.04\%$	0.00481	−0.95261	0.7800	0.61005	0.05821	0.9036	0.00055	0.02737	0.9367
PET-LPKA-Ge $X = 30.03\%$ $Z = 11.09\%$	0.00447	−0.84926	0.8075	0.55164	0.07051	0.9111	0.00055	0.02110	0.9623

facilitating the process. The grafting process used allows one to prepare a product with a high degree of PAA grafting and very low amount of homopolymer.

This type of modification makes it possible to introduce antibiotics into fibers that provide antibacterial properties. The liberation of biocides from the modified fibers into solutions can be described quite precisely by the eponential equation $C = C_\infty \cdot \sqrt{t} + b$. The liberation of biocide from the fibers into solutions lasts for quite a long period of time, after which certain amount of antibiotics still remains on the fibers.

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