

A New Generation of Fibers from Alginic Acid for Dressing Materials

Teresa Mikołajczyk, Dorota Wołowska-Czapnik, Maciej Boguń

Department of Man-Made Fibres, Faculty of Textile Engineering and Marketing Technical University of Lodz, 90-924 Lodz, Poland

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ABSTRACT: We developed and elaborated manufacturing conditions for the production of alginic acid fibers with high sorption properties. The fibers' tenacity obtained at a level of 16 cN/tex is suitable for textile processing these fibers, and will make it possible to produce a new generation of highly absorptive dressing materials. The presence of acid groups in the fiber-forming material

allows us to use them for the addition of new generation antibiotics, which makes it possible to extend the antibacterial effects of these fibers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1670–1677, 2008

Key words: alginate fibers; antibacterial; absorption; dressing material

INTRODUCTION

Alginate fibers find increasing use for the manufacture of modern dressing materials which can be adapted to the type of the wound and the stage of its healing. They show many therapeutical advantages without parallel in traditional dressing materials. Their high sorption properties facilitate the absorption of large amounts of secretion from wounds. Fibers from sodium alginate have the capability totally to gelatinize.¹

Different progresses of gelatinization of the currently produced dressings made from calcium alginate depend on the content of groups derived from the mannuric or guluronic acids in the fiber-forming material.^{2,3} Because of these properties, a dressing may be in a close contact with the wound even in hard to reach places. The wound surface remains elastic, the dressing is permeable to gases, and its replacement is painless.

Fibers made from zinc and copper alginates, beside its high moisture absorption, are characterized by antibacterial properties and modified electric properties expressed by the change of electric conductance to an extent dependent on the relative humidity of air. Thus, their application is extended from dressings designed for wounds being in advanced stages of healing (zinc alginate fibers) to

compression bandages that reduce pain, and hospital linen (mainly copper alginate fibers). The capability of these fibers to generate negative static charges in contact with human skin should facilitate their analgesic effects.⁴ Such effects have been confirmed by clinic examinations carried out with fabrics made from other fiber-forming polymers.⁵

The use of acid groups in alginic acid fibers in order to attach an appropriate antibiotic makes it possible to obtain a new generation of highly absorptive dressing materials, which would demonstrate bactericidal activity. They should be capable of gradually releasing the antibiotic combined with the fibers and consequently show specific remedial properties.

The aim of this study was to determine the effect of fiber spinning parameters such as the as-spun draw ratio and the deformation during the drawing stage related to them on the porous structure, moisture absorption, and tensile strength (tenacity) of fibers made from alginic acid.

The investigations carried out by us were the basis for selecting optimum conditions of manufacturing such fibers. The use of a computer-aided experiment system in order to optimize the maximum sorption properties allowed us to select the manufacturing conditions for producing alginic acid fibers with high sorption properties, and a tensile strength suitable for their processing into dressing materials. Modern dressing materials should be characterized by the ability of absorption large amounts of secretion from wounds. Fibers with optimum sorption and tensile strength properties will be dedicated to attach antibiotics to their fiber-matter's acid groups. The

Correspondence to: T. Mikołajczyk (mikolter@mail.p.lodz.pl).

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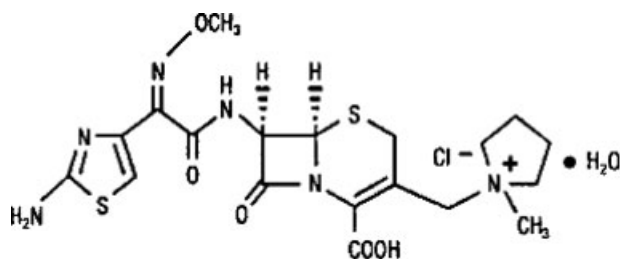


Figure 1 Cefepim (component of Maxipime).

Maxipime antibiotic preparation, which belongs to the cephalosporin group of the IV generation and which contains amid groups in its structure (Fig. 1) was selected for use in our investigations. Its step-wise release to the wound surroundings will enable a local healing effect of infected and long-healing wounds without the necessity to change often the dressing. This is caused by the high activity of a dressing such this prepared against the majority of aerobic bacteria Gram (+) and rod-shaped Gram (-) including *Pseudomonas aeruginosa*.⁶ Taking into consideration the significance of the antibiotic's activity, we tested the release kinetics of the antibiotic bounded to the fiber matter.

FIBRE SPINNING

The fibers were spun by the wet process from a solution with the use of a laboratory spinning machine whose construction allowed us to stabilize the technological parameters at a predetermined level under continuous control and monitoring. A 500-hole spinneret with hole diameter of 0.08 mm was used.

A 7% aqueous spinning solution of sodium alginate (Protonal LF 60/20 produced by FMC Biopolymer) was used. The content of blocks derived from guluronic acid predominates that of blocks derived from mannuric acid in this product. The intrinsic viscosity of sodium alginate of 4.91 dL/g was determined in a 0.2M NaCl solution at a temperature of 25°C. The polydispersity determined as the ratio of M_n/M_w was equal to 4.7. The rheological properties of the spinning solution were similar to those described in Ref. 7. The fibers were solidified in a bath containing a 2% HCl aqueous solution at a temperature of 25°C. The as-spun draw ratio was changed within the range of 20–140%. The fiber drawing was performed as one-stage in an aqueous plastification bath at a temperature of 65°C

TEST METHODS

The properties of the fibers obtained were assessed on the basis of the following methods:

The moisture absorption was determined at RH of 65 and 100% according to Polish standard PN-71/P-04653.

The water retention was measured by the centrifuge-method. Fiber samples were immersed in distilled water containing a surface-active agent (Rokafenol Rx-3 in an amount of 0.1%) for 24 h and then the water absorbed was centrifuged off for 10 min at an acceleration of 10,000 m/s.

The fibers' porosity was determined by the mercuric porosimetry method with the use of a Carlo-Erba porosimeter linked to a computer system, which enabled the determination of the total volume of pores, the percentage share of pores with dimensions within selected subranges from the total range of 5–7500 nm, as well as the total internal surface of pores.

The degree of crystallinity and the size of crystallites were determined by means of the wide angle X-ray diffraction (WAXS) method. Diffraction patterns were recorded in the symmetrical reflection mode using URD-6 Seifert diffractometer and a copper-target X-ray tube ($\lambda = 1.54 \text{ \AA}$) operated at 40 kV and 30 mA. The Cu K α radiation was monochromized with a Ni filter. WAXS curves were recorded within the range of 4–60°, with a step of 0.1°.

The X-ray radiographic examination was carried out at the Department of Textile Engineering of the University of Bielsko-Biala, Poland.

The analysis of the cross-sections of fibers were performed using JOEL 5400 SEM. The SEM measurements were carried out at the Institute of Fibre Physics, Technical University of Lodz, Poland.

The strength properties were determined with the use of an INSTRON tensile tester working with the IX series software according to standard PN-EN ISO 5079 : 1999.

The content of acid groups (COOH) in the fiber-matter was determined by the analytical method following the procedure: a weighted portion of alginate fibers dried to a constant weight was added to a solution containing 100 cm³ of saturated KCl and 90 cm³ of a 0.025N KOH solution free from carbonates and 10 cm³ of H₂O. The sample was kept in this solution for about 60 min under constant stirring. Next, 100 cm³ of the filtrate was titrated with a 0.1N HCl solution from a microburette in the presence of an indicator (the following mixture of alcohol solutions: 1 part by wt of 0.1 % thymol blue and 3 parts by wt of 0.1% phenolphthalein). A blank test was made at the same time.

Impregnating the alginic acid fibers with a Maxipime antibiotic solution

The fibers were padded by the Maxipime solution at a constant bath module of 1 : 15 and various antibiotic

TABLE I
Properties of Alginic Acid Fibers Obtained Under Various Forming Conditions

Sample symbol	As-spun draw ratio (%)	Total draw ratio (%)	Moisture absorption at 100% (%)	Moisture absorption at 65% (%)	Water retention (%)	Tenacity (cN/tex)	Elongation (%)	Young's modulus (cN/tex)
K1	20	7	21.95	15.7	151	11.62	10.42	420.7
K2	40	18.94	22.25	15.65	154	13.98	9.51	502
K3 ^a	40	18.9	21.1	15.55	166	13.26	10.29	479.9
K4	60	18.64	20.75	15.8	152	13.86	8.79	541.8
K5	80	21.3	23.05	15.6	148	14.15	7.95	590.9
K6	100	18.71	22.15	15.6	134	15.33	7.92	620.6
K7	120	17.72	20.15	18.53	165	16.05	7.64	623
K8 ^a	120	17.3	22.30	15.55	162	15.60	8.23	621.2
K9	140	16.2	20.50	15.05	151	19.32	5.38	878.7

^a The samples K3 and K8 were drawn by a two-stage drawing process.

concentrations of 5, 10, and 15% for 60 min at a temperature of 24°C. After rinsing, the impregnated fibers were dried to a constant weight at 54°C.

The kinetics of antibiotic release was determined by spectrophotometric investigations using a V-530 JASCO UV/VIS spectrophotometer (made in Japan) within a wavelength range of $\lambda = 190\text{--}1100$ nm. The measurements were made in a sodium chloride solution of pH 7 as reference.

The antibacterial effects of the fibers obtained were tested according to standard SN 198920 : 1994

DISCUSSION OF RESULTS

The solidification of fibers made from alginic acid takes place because of chemical reactions, during which the water-soluble sodium alginate is transformed into water-insoluble alginic acid fibers. The course of this process depends on the diffusion of hydrogen ions from the coagulation bath, which contains hydrochloric acid, into the solidifying stream and a partial diffusion of Na^+ ions into the coagulation bath accompanied by NaCl formation. The structure created and the properties of fibers being dependent on their structure are affected by HCl in the solidifying bath, as well as depend on the basic parameters of the spinning process, such as the as-spun draw ratio and the related to it deformation during the drawing stage. However, the rigid structure of alginic acid macromolecules limits the fibers' susceptibility to deformation. Thus, an important part is played by the orientation of macromolecules, which takes place in the still liquid stream. It depends on the value of the longitudinal velocity gradient which is directly connected with the value of the as-spun draw ratio.

Generally, the increase in the as-spun draw ratio leads to small changes in the moisture absorption of alginic acid fibers, whereas to an extreme course of changes in the retention (Table I). The moisture sorp-

tion at 100% RH was the highest (at a level of 23%) for an as-spun draw ratio applied of 80%, whereas by the highest moisture sorption at 65% RH was characterized the sample K7 spun at an as-spun draw ratio of 120%.

The sorption properties of fibers, depend on the hydrophilic character of the fiber matter and the mechanism of bounding water via hydrogen bonds, and as it is reported are connected with the fibers' porous structure.⁸

However, when the total pore volume is low, amounting to $58.73 \text{ mm}^3/\text{g}$, and the internal surface is $3.88 \text{ m}^2/\text{g}$ with a relatively low content of small pores at a level of 19% (Fig. 2, Table II), we may assume that the sorption properties of alginic acid fibers are dependent on the hydrophilic character of alginic acid. Despite the fact that the content of small pores responsible for moisture absorption through capillary condensation is twice as high, the values of moisture absorption of alginic acid fibers at 100% RH are lower or comparable with those of the fibers from copper or zinc alginate.⁷

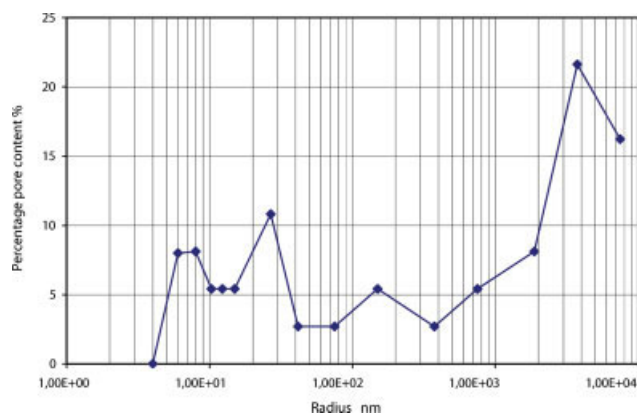


Figure 2 Dependency of the percentage shares of pores as a function of their radius for alginic acid fibers (sample K7).

TABLE II
Percentage Shares of Pores in Alginic Acid Fibers (Sample K7)

Sample symbol	Total pore volume (mm ³ /g)	Internal surface (m ² /g)	Percent contents of pores (%)			
			Small pores 4–12.3 (nm)	Medium pores 12.3–75 (nm)	Large pores 75–750 (nm)	Very large pores 750–7500 (nm)
K 7	58.73	3.88	18.93	21.62	13.52	45.92

On the other hand, the water retention of alginic acid fibers amounts a value twice as high as the value of fibers from divalent metal alginates, and can reach even 165%. At the same time, the character of changes in this property as a function of both the process parameters (the as-spun draw ratio and the drawing degree) also show an extreme course similarly as in the case of fibers from copper and zinc alginates (Fig. 3),⁷ while the highest retention is shown by fibers spun with high positive values of the as-spun draw ratio at a level of 120%. The very high values of the retention of alginic acid fibers confirm the quoted by us interpretation⁷ according to which the formation of polymolecular ordered associates of water, the so-called clusters,⁹ makes it possible to hold them in very large pores of 750–7500 nm. Such pores in a hydrophobic material are not capable of holding water after its mechanical removal. Considering the possibility of creating large amounts of hydrogen bonds in alginic acid fibers, the attachment of the formed associates to the internal capillary surface seems to be very stable. The formation of a considerable number of such bonds and their stability are confirmed by the fact that with a similar pore distribution, the retention of alginic acid fibers is twice as high as that of fibers from alginates

substituted with divalent metals, despite the lower by 10% content of large and very large pores.⁷

The kind of the porous structure formed is also visible on the SEM photos. Although regarding the very low total volume of pores, understandable is the uniform character of the fiber's cross-section (Fig. 4) and the lack of visible distinctive radial positioned very great pores of dimensions beyond the range of the mercury porosimeter.

Alginic acid fibers, similarly as other types of alginate fibers (Zn, Ca, Cu) demonstrate an upward trend in their tenacity with increasing the as-spun draw ratio and the deformation during the drawing stage (Fig. 5, Table I). The highest tenacity at a level of 19.3 cN/tex we stated by the fibers spun with an as-spun draw ratio of 140%. This confirms the fact that in the case of a rigid macromolecule structure of the fiber matter's macromolecules it is beneficial to use high positive values of the as-spun draw ratio.

The value of elongation at break of the fibers from alginic acid, which was within the range of 8–10% (Table I), is suitable for textile processing.

Similarly as in other types of alginate fibers,⁴ an opposing trend of changes in the sorption and strength properties, we observed as a function of the as-spun draw ratio and deformation during the

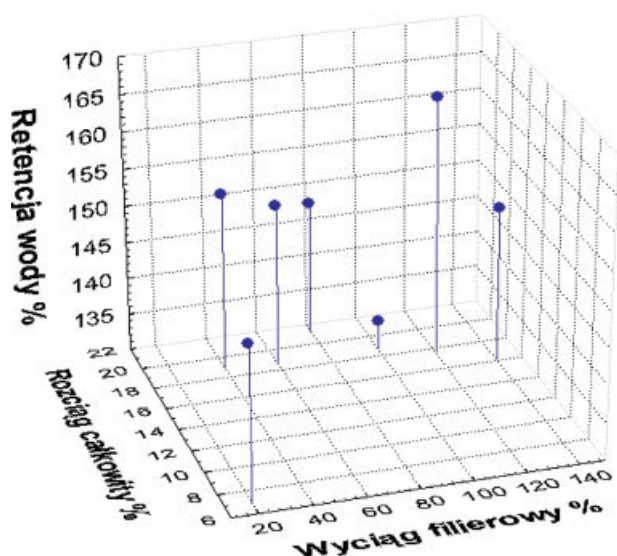


Figure 3 Dependence of the water retention on the as-spun draw ratio and the total draw ratio for acid alginate fibers.

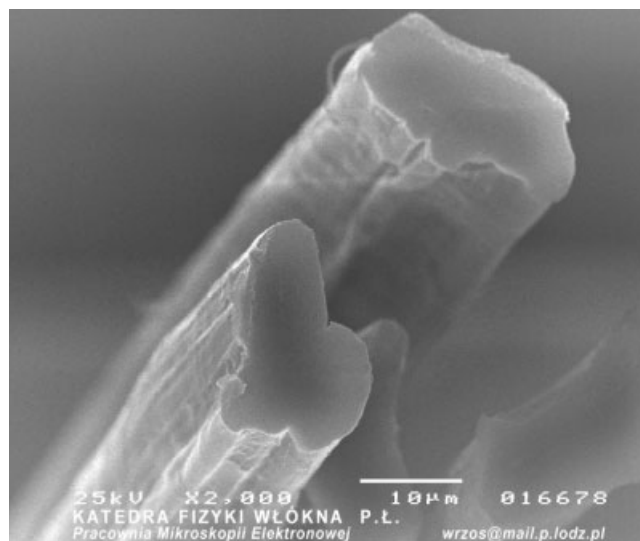


Figure 4 Cross section of alginic acid fibers.

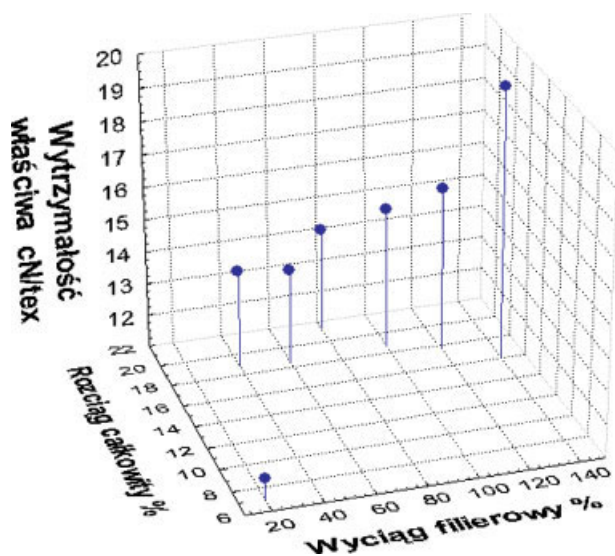


Figure 5 Dependence of the tenacity on the as-spun draw ratio and the total draw ratio for acid alginate fibers

drawing stage. In this connection, the spinning conditions were selected so as to obtain alginic acid fibers with high sorption properties, with the fibers' strength and elongation at break being at a level suitable for fiber processing into dressing materials (sample K7).

High sorption properties and, in particular, the very high water retention of fibers formed under optimum conditions guarantee good absorption of wound secretion by a dressing made from such fibers. Good absorption of physiological fluids by this type of materials seems to be confirmed also by the value of fiber swelling assessed on the basis of changes in the crosswise dimensions of fibers: after 60 s the value of swelling was about 100%.

The value of thermal shrinkage at a level of 1.2% of the fibers heated without tension at a temperature of 125°C for 120 min is beneficial with respect to the required sterilization of dressing materials.

An attempt was undertaken to increase the fibers' tensile strength properties by applying a two-stage drawing process with suitable distributions of the drawing degrees in the both stages. In the case of polymers with flexible chains such processing results in obtaining fibers with increased tensile properties¹⁰ whereas applying a two stage process for alginic

TABLE III
The Crystallinity Degree and Crystallite Dimensions

Sample index	Degree of crystallinity (%)	Angular position 2 θ (°)	Dimensions of crystallites (Å)	Bragg's distance (Å)
K 7	27.0	13.4	44	6.58
K 8	22.6	13.3	45	6.60

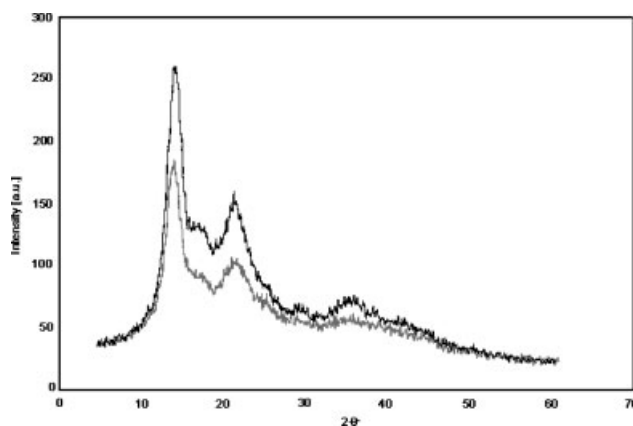


Figure 6 WAXS pattern of acid alginate fibers: line black (sample K 7), line grey (sample K 8).

acid fibers do not cause an increase in the fibers' tenacity (sample K8). The second drawing stage was performed in a preheated steam at a temperature of 135°C, and the total drawing degree was the same. The sorption properties were also at the same level as for sample K7.

The crystallinity degree and the crystallite dimensions of both fiber samples (K7 and K8) were determined by the WAXS method (Table III).

From the analysis of WAXS diffractograms (Fig. 6), it follows that the use of high positive values of the as-spun draw ratio facilitates the polymer crystallization. The crystallinity degree of alginic acid fibers reaches a considerably higher value (within the range of 22.6–27%) than that of fibers made from the alginates of divalent metals for which this parameter equals only 6–9.5%. With the "egg-box" type of the structure appearing in this case, greater distances between macromolecules are connected, which may cause low values of the crystallinity degree. On the other hand, the presence of OH groups in the macromolecules of alginic acid fibers makes it possible to form a considerable number of hydrogen bonds, which results in high values of crystallinity degree considering the high packing

TABLE IV
Content of Acid Groups in Alginic Acid Fibers

Sample symbol	As-spun draw ratio (%)	Total draw ratio (%)	Content of acid groups (mol/g) $\times 10^{-2}$
K1	20	7	2.150
K2	40	18.94	2.920
K4	60	18.64	3.955
K5	80	21.30	3.074
K6	100	18.71	4.006
K7 ^a	120	17.72	4.290
K9	140	16.20	3.782

^a Sample for attach new generation antibiotics.

TABLE V
Percent Content of Antibiotics and Acid Group Content in Alginic Acid Fibers (Sample K7)

Antibiotic concentration in the padding bath (%)	Percent content of antibiotic (%) ^a	Antibiotic contents (g) ^b	Number of acid groups after padding (mol/g) ^c	Number of acid groups after releasing the antibiotic (mol/g) ^c
<i>Maxipine</i>				
0	–	–	2.49×10^{-2}	2.49×10^{-2}
5	17.35	0.173	7.74×10^{-3}	8.03×10^{-3}
10	26.07	0.261	3.11×10^{-3}	5.05×10^{-3}
15	23.00	0.230	2.39×10^{-3}	4.90×10^{-3}

^a Percent content of antibiotic in relation to the initial weight of fiber sample.

^b Antibiotic contents per 1 g of fibers.

^c The quantity of acid groups per 1 g of fibers.

density of macromolecules. The crystallite dimensions (Table III) also were nearly twice as high as for fibers from divalent metal alginates (16–23 Å).

By the highest content of acid groups were characterized fibers formed with an as-spun draw ratio at the level of 120%, which is connected with the thickness change of elementary fibers, and easier sodium ions exchange following the formation of a greater number of acid groups. However, the increase in the as-spun draw ratio is accompanied with a decrease in the period by which the fibers are processed in the coagulation bath, and as a result of this the dependency has an extremal character (Table IV).

Alginic acid fibers spun under optimum conditions (sample K7) were treated with an antibiotic preparation named Maxipine. The Maxipine preparation includes cefepim, an antibiotic of the IV generation from the cefalosporine group, characterized by a wide spectrum of bactericidal activity, which consists on restraining the synthesis of peptidoglykane, the main component of the bacteria's cell wall. This specific demonstrates high activity to the majority of *Enterobacteriaceae*, and higher activity than other cefalosporines to *Enterobacter* spp. strains including the majority strains resistant to aminoglycosides and III generation cefalosporines.¹¹ The chem-

ical structure and the kind of activity predispose Maxipine to healing infected wounds resistant to healing by antibiotics.

To make that fibers from alginic acid gain antibacterial properties, the fibers were padded by a solution of Maxipine in accordance with conditions described in the "Test methods." The percentage content of the antibiotic and the acid groups in alginic acid fibers processed under different conditions are presented in Table V.

On the basis of an analysis of the results obtained, we can state that the greatest amount of the antibiotic is released to the physiological salt solution over the first hour independently on its concentration in the padding bath. By the highest amount of the antibiotic released after this time period, at the level of 25%, are characterized the fibers padded in a bath with concentration of 5%. For all the remaining concentrations of the antibiotic in the bath, the content of the released antibiotic is only within the range of 12–18%. In all the cases, the amount of the antibiotic released increases successively with the increase in

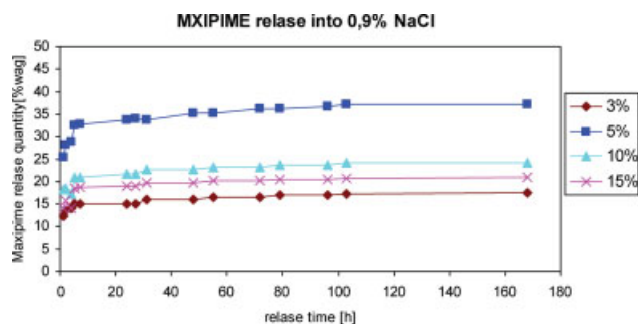


Figure 7 Dependence of the quantity of released maxipine on the time of its releasing from the modified fibers into 0.9% NaCl solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

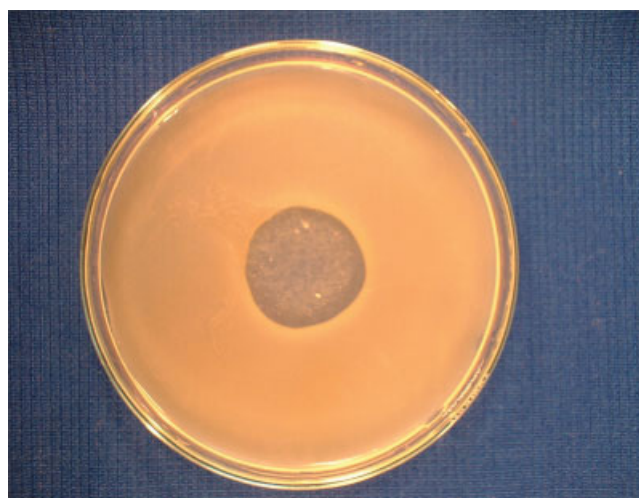


Figure 8 Inhibition zone on *Staphylococcus aureus* for acid alginate fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

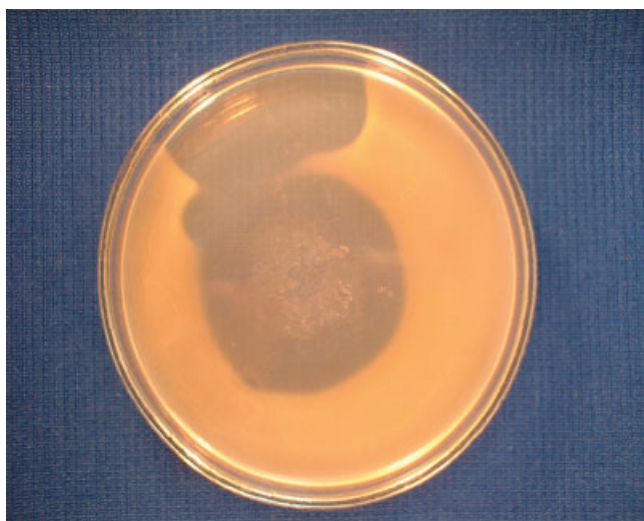


Figure 9 Inhibition zone on *Staphylococcus aureus* for acid alginate fibers + 5%Maxipime. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the releasing time period. But this increase is significantly slower, and the releasing curve shown in Figure 7 has a relative flat curve.

The rapid release of the antibiotic over the first hour can be explained by the disconnection of the antibiotic part included in the fiber structure and at the same time of that part which is chemically bonded with the fiber matter. The slower process of releasing over the second period is probably connected mainly with the hydrolysis of amide bonds and releasing the antibiotic part chemically bonded with the acid groups of the fiber matter.

The releasing of the chemically bonded antibiotic over this period was confirmed by assessing the number of acid groups in the fibers after the releasing stage. This number increases after the releasing process and is higher when compared with their content in the fiber matter after the padding process (Table V). In all cases, even after 7 days, significant amounts of the antibiotic remained in the fibers.

While comparing the antibiotic amounts that are released after 168 h, it results that the greatest amounts, at the level of 37%, are released in the case of padding the fibers by a 5% antibiotic solution. For the remaining antibiotic concentrations in the padding bath, the amount of the antibiotic released over the

same time from the fibers is lower, within the range of 17–24%. Thus, we may assume that in this case discussed, the appropriate concentration of the Maxipime antibiotic in the padding bath is 5%. A confirmation of the correctly chosen antibiotic content in the padding bath was a test series of the padded fibers' antibacterial properties under selected conditions.

To determine the fibers' antibacterial properties, the alginate acid fibers padded by the Maxipime antibiotic were tested by microbiological tests *in vitro* (Fig. 8). For comparison, the alginate acid fibers without antibiotic and a cotton woven fabric were used as blanc tests (Fig. 9). Antibacterial tests of the fibers obtained by the quality method were carried out against the *Staphylococcus aureus* Gram (+) bacteria. From the analysis of the results obtained (Table VI), it follows that the impregnation with a solution of the Maxipime antibiotic made it possible to obtain fibers with antibacterial activity. The bacteria growth depression zone for alginate acid fibers impregnated with a 5% solution of Maxipime was about 12 mm, which indicates that these fibers show a good resistance to the action of *Staphylococcus aureus* bacteria, while the alginate acid fibers containing no antibiotic are inactive in relation to the same bacteria.

CONCLUSIONS

1. The sorption properties of alginate acid fibers are principally dependent on the hydrophilic character of alginate acid. The influence of the as-spun draw ratio and the total draw ratio on these parameters is limited. The process parameters considerably affect the water retention and tensile strength (tenacity) of the fibers under investigation.
2. The use of highly positive values of the as-spun draw ratio results in good tensile strength properties of alginate acid fibers.
3. The presence of acid groups in the fiber forming matter of alginate acid fibers makes it possible to attach new generation antibiotics, such as the Maxipime preparation, being capable of gradual releasing into the solution of physiological salt.
4. We developed and elaborated technological conditions for manufacturing alginate acid fibers with

TABLE VI
Results of Testing Antibacterial Properties of Alginate Fibers (Sample K7)

Sample index	Growth inhibition zone	Growth	Discription	Result
Standard cotton	0	Full	No growth inhibition zone, growth no disturb	Insufficient activity
Acid alginate fiber	0	–	No growth inhibition zone	Insufficient activity
Acid alginate fiber + 5% Maxipime	12	–	Growth inhibition zone >1 mm	Good activity

an antibiotic of new generation belonging to the cefalosporine group attached. The fibers combine high sorption properties and the ability to absorb fluids with good antibacterial properties against *Staphylococcus aureus* Gram (+) bacteria.

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