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# Fibrous Products with Keratin Content

## Abstract

*A method of manufacturing fibrous composite materials by wet spinning is presented. We used natural polymers, namely sodium alginate and keratin obtained from chicken feathers. Spinning solutions were prepared from these polymers, and after filtration and aeration they were used for fibre and fibril formation. The investigations included preparing alginate-keratin spinning solutions of different keratin content, estimating the influences of formation speed and drawing on the fibre properties, and estimating the sorption properties of the composites obtained. The alginate-keratin fibres obtained are characterised by better sorption properties, higher hygroscopicity and smaller wetting angle, than those of alginate fibres. The introducing of keratin into alginate fibres lowered their mechanical properties, but they are further on a level which enables applying these fibres for manufacturing composite fibrous materials. The alginate-keratin fibrils are also characterised by better sorption properties than those of alginate fibrils.*

**Key words:** keratin, alginate, composite fibres, fibrils, sorption properties.

## ■ Introduction

Natural polymers and their derivatives are valuable raw materials used in the production of fibres, films, sponges, and fibrils [1, 2]. Fibrils and fibres manufactured from natural polymers, such as alginate, chitosan, and cellulose, have found broad practical application in the textile and cosmetic industries, in medicine and environmental protection, with regard to their special properties, sorption capability among others [3 – 6]. The increasing interest in obtaining modern alginate-keratin fibrous forms results from their unique properties. Fibrils are characterised by a significantly developed surface, which principally depends on their small dimensions, and they are therefore suitable for manufacturing different kinds of fibres including the composite types. Presently, fibrils with a developed surface of about 20 m<sup>2</sup>/g and diameters within the range of 0.5 μm to 5 μm and manufactured of cellulose acetate [5] are used not only as filtration materials but also for wastewater purification and binding of proteins [7, 8]. Fibres from natural polymers are also widely used as dressing materials, as they are characterised, like fibrils, by great specific surface, softness, high moisture absorptivity, and simple technologies allowing different products to be obtained easily. Dressings obtained on the basis of alginate are very popular among different types of fibrous products. Such dressings are characterised by haemostatic features, but principally by their very good sorption properties [9].

The applications best known and described in literature are numerous applications of keratin preparations in the cosmetic industry, but possibilities have also arisen of using this interesting protein in

other areas, for example as a component of different composites and component of biodegradable nonwovens [10 – 13].

The interest in using keratin for manufacturing fibres and other fibrous products is continuing to rise. The first reports connected with using keratin for the production of unique fibres and fibrous forms, which can compete with cellulose fibres in such product groups as children's diapers, personal hygiene products, and towels appeared in 1996 [10]. McCurry and other American researchers [14 - 16] developed a well-known method of transforming chicken feathers into a fibrous form containing keratin.

Feathers are made up of keratin to nearly 90%. As they are a troublesome by-product of the poultry industry, and at the same time a cheap raw material for obtaining protein, they have become a valuable source. It should also be emphasised here that these proteins have unique features. Considering their hydrophilic properties, it seems reasonable to obtain keratin for manufacturing fibres with increased sorption properties, which could be applied in numerous branches of the textile industry, in sanitary and medical applications, and as a sorptive material in technique. Such applications of keratin obtained from feathers are innovative directions of use.

On the basis of data from literature, and of research carried out in the Institute of Biopolymer and Chemical Fibres (IBWCh) connected with developing new, alternative methods of manufacturing fibrils and fibres of natural polymers [17 - 19], research was commenced into obtaining biopolymers with keratin content dedicated to hygienic materials [20].

The aim of our research work was to obtain different fibrous forms, such as fibres and fibrils with a content of keratin gained from chicken feathers. We chose alginate already used to manufacture biocomposites for medical applications as the second component. An assumption was made that by using the hydrophilic properties of keratin, the application of this biopolymer should result in the manufacture of fibrous composite materials with increased sorption properties.

The process of manufacturing alginate fibrils and fibres both including keratin was investigated. The investigations included:

- preparing alginate-keratin spinning solutions with different keratin contents,
- estimating the influence of the formation speed and the drawing on the fibre properties, and
- estimating the sorption properties of the composites obtained.

## ■ Materials

### Keratin

The method of obtaining keratin from chicken feathers has been described in [21], whereas the properties of keratin we used in this research are presented in Table 1.

### Sodium alginate

Protanal LF 10/60 LS sodium alginate from FMC Biopolymers (Norway) dedicated to manufacturing alginate fibres for medical applications was used in our investigations. The basic properties of this alginate are listed in Table 2.

The chemical agents used to tests were analytically pure reagents.

## ■ Research methods

### Preparing sodium alginate spinning solutions

The dissolution process of sodium alginate was performed at a temperature of 20 °C for 180 min in a mixer equipped with a high-speed agitator. Glycerol was added in an amount of 10% in relation to sodium alginate. The aqueous solution of sodium alginate obtained was filtered through a filter cloth, which prevented contaminations of dimensions above 3 µm from flowing through. The concentrations of sodium alginate in the spinning solutions were set at 5.56% and 6.47%.

### Preparing sodium alginate-keratin spinning solutions

The alginate-keratin solutions were prepared by mixing the filtered and aerated aqueous 6.47% alginate solutions with an aqueous keratin suspension. In order to obtain it, an aqueous keratin suspension with concentrations of 10%wt to 25%wt were prepared and added stepwise to the sodium alginate solution, which was stirred by a low-speed agitator of 60 rpm for 30 min at a temperature of 20 °C.

### Forming alginate-keratin fibres

The alginate-keratin fibres were manufactured using a laboratory spinning machine for wet spinning. The aqueous solution containing a mixture of alginate and keratin was placed in a pressure container, and next fed to the spinning head with a gear pump of 3 ml/min yield. The polymer solution was introduced into the coagulation bath with a yield of 18.6 cm<sup>3</sup>/min through the spinning head equipped with a 300-hole platinum-rhodium spinneret, with hole diameters of 80 µm. The fibres were spun into the coagulation bath containing CaCl<sub>2</sub>, with a concentration of 25 g/l, at pH of 4.0 – 4.8, and at a temperature of 28–30 °C. The fibres were spun at a speed within the range of 15.5 to 20.0 m/min, at a drawing degree from 18% to 50% in air, or hot water at a temperature of 80 – 85 °C. The fibres after conducting through a washing bath were taken up in the shape of a hank, and then processed by introducing a preparation containing Tween 20/Span 20 (1:2) with a concentration of 9 g/l in 50% wt of EtOH. The fibres were next dried in a free state at room temperature. The spinning speeds and drawing conditions of the alginate-keratin fibres are presented in Table 3.

**Table 1.** The basic properties of keratin; WRV – water retention value; A – lyophilised keratine, K VIII – spatter-dried keratin; the keratin designation according to [18].

Property	Keratine type	
	A **	K VIII *
Nitrogen content, %	15.23	15.09
Sulphur content, %	2.30	2.07
Moisture content, %	5.9	4.2
WRV, %	138.5	155.5
Sorption factor, %	160.0	188.5
Mw, kDa	144.4	86.2
Mw/Mn	6.5	2.6
Colour, shape	White powder	White powder

**Table 2.** Selected properties of sodium alginate used.

Property	Protanal LF 10/60 LS
Shape	powder
Colour	from white to bright yellow
Content of guluron acid, %	40 - 45
manuron acid, %	55 - 60
Moisture content, %	10.0
Viscosity (1% concentration, at 20 °C), mPas	52
Particle dimension (60M BS), %	100.0
Calcium content, %	1.5
pH (1% concentration, at 20 °C)	6.5
non-soluble part content, %	0.01
Total amount of aerobic bacteria, cfu/g	125

**Table 3.** Spinning speeds and drawing conditions of the alginate-keratine fibres; Alg1 – control test – forming pure alginate fibres; AKn/m – alginate-keratin fibres, drawing in water at a temperature of 80 - 85 °C.

Fibre symbol	Spinning speed, m/min	Drawing conditions	
		Drawing, %	Medium
Alg1 1)	20.0	50	water 2)
AK 1/1	20.0	50	water
AK 1/2	20.0	50	air
AK 2/1	20.0	50	water
AK 2/2	20.0	38	air
AK 3	18.4	38	water
AK 4/1	15.5	18	air
AK 4/2	20.0	50	water

### Manufacturing alginate-keratin fibrils

In order to obtain fibrils at laboratory scale, we used a stand composed of a pressure container, a spinning head with a spinneret, an agitator and a container with coagulation bath. The aerated spinning solution was placed in the pressure container, from which it was fed to a gear pump with a yield of 0.6 cm<sup>3</sup>/rotation and 1.2 cm<sup>3</sup>/rotation; this ensured constant and regular feeding of the solution to the spinneret. A 600-hole spinneret with holes of 60 µm diameter was used. The polymer solution flows from the spinneret placed in the spinning head, into the coagulation bath. The agitator of the Turax-type homogenisation device with rotary speed of 4,000 rpm was positioned at a specified

distance above the spinneret in order to guarantee a speed of the coagulation bath flow which could force the breaking of the solidifying spinning solution stream. The fibrils obtained were separated from the coagulation bath, put into methyl alcohol for about 1 hour, and next after centrifuging it, washed several times in water and lyophilised. A coagulation bath containing 3 g/l CaCl<sub>2</sub> with an addition of HCl in order to maintain pH 4 of the solution, were used for manufacturing the alginate-keratin fibrils.

## ■ Analytical methods

### Microscope analysis of the spinning solutions

The solutions of sodium alginate, keratin, and alginate-keratin were assessed

**Table 4.** Properties of alginate-keratin spinning solutions used for fibre formation; Alg1 – sodium alginate spinning solution, AK1 ... 4 – alginate-keratin spinning solutions.

Symbol of spinning solutions	Total content of alginate and keratine, wt.%	Keratine content, wt.%	Brookfield viscosity, cPs
Alg1 <sup>1)</sup>	6.47	-	44 000
AK 1	5.79	0.90	28 000
AK 2	5.85	1.08	31 000
AK 3	6.59	3.45	-
AK 4	6.36	2.27	38 500

**Table 5.** Properties of alginate-keratin spinning solutions dedicated for fibrid manufacturing; Alg2 – sodium alginate spinning solution, FibAK1 ... 5 – alginate-keratin spinning solutions.

Symbol of spinning solutions	Total content of alginate and keratine, wt.%	Alginate content, wt.%	Keratine content, wt.%
Alg2 <sup>1)</sup>	5,56	5,56	-
FibAK 1	1,76	0,93	0,83
FibAK 2	1,60	0,93	0,67
FibAK 3	1,76	0,93	0,83
FibAK 4	1,60	0,93	0,67
FibAK 5	1,34	1,01	0,33

with the use of a Biolar-type polarisation microscope from ZPO Warsaw, with an adapter which enables photos of the observed images to be taken. A system of digital image analysis from IMAL was used to monitor the images.

#### Assessing the dynamic viscosity of solutions

The dynamic viscosity of the sodium alginate spinning solutions was assessed with the use of a LVF Brookfield viscometer.

#### Assessing the water retention value (WRV)

The water retention value was assessed according to the standard method [22].

#### Assessing the sorption coefficient

The sorption coefficient was assessed according to the standard method [23].

#### Testing the moisture absorption

Testing the moisture absorption was carried out on alginate and alginate-keratin samples placed in an exsiccator of 65% moisture (NH<sub>4</sub>NO<sub>3</sub>) at room temperature (20 - 21 °C). Assessing the sample mass as a function of time served to monitor the moisture sorption. After stabilising the sample mass at an approximate constant level, which means full saturation of the samples by moisture under the given conditions, the keratin samples were placed in an exsiccator with a relative humidity of 93% (KNO<sub>3</sub>) and the changes of the samples' masses over time were assessed. Next, after stabilising the

sample masses at an approximately constant level for the second time, they were again placed in the 65% moisture exsiccator, and the moisture desorption of the samples tested were determined.

#### Determining the content of sulphur and nitrogen

The nitrogen content was determined by the Kjejdahle method, whereas the sulphur content was determined by the Sheniger method [24, 25].

#### Evaluating the surface of the alginate-keratin composite materials with a scanning electron microscopy (SEM)

The SEM observations were carried out with the use of a Quanta 200 SEM from FEI at a magnification of 2,000x. Structural investigations were performed under a high vacuum, in a natural state, without gold sputtering. The area of the fibres' cross-section surface was measured with the use of the analySIS Docu software program from Soft Imaging System.

#### Assessing the fibre's wetting angle

The tests of the fibres' wetting angle were performed in relation to glycerol, whose polar properties and surface tension are similar to those of water. The wetting angle measurements were conducted after time 60 s since the deposition of the drop [23].

#### Determining the hygroscopicity of fibres

The hygroscopic properties of the fibres manufactured were determined at the

IBWCh, in the Analytical Laboratory which has the Good Laboratory Practice certificate GLP G016, in accordance with standard PN-80/P-04635:1981.

#### Estimating the fibres' mechanical properties

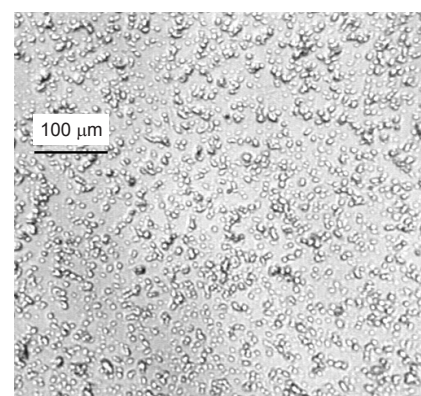
The mechanical properties of the fibres manufactured were determined at the IBWCh, in the Laboratory of Metrology which has the certificate Nr. AB 388 of the Polish Accreditation Centre (PCA), in accordance with the standards PN-ISO-1973:1997 and PN-EN ISO 5075:1999.

## Research results and discussion

#### Obtaining the alginate-keratin spinning solutions

The alginate-keratin spinning solutions with different keratin contents were prepared according to the procedure described on page 31. The properties of the solutions which were dedicated for fibre formation are presented in Table 4, whereas those of the alginate-keratin solutions which were applied for composite fibrid manufacture are shown in Table 5.

The keratin content influenced the properties of the spinning solutions in a different way. It should be stressed that irrespective of the keratin content introduced into the spinning solutions, the keratin particles did not dissolve, which is visible in the photo in Figure 1. Adding the aqueous keratin suspension to the spinning solution causes a distinct viscosity drop from 44,000 cPs of the alginate solution to 28,000-38,500 cPs of the alginate-keratin spinning solutions.



**Figure 1.** Microscopic photo of an alginate-keratin spinning solution with visible non-dissolved keratin particles.

**Table 6.** Mechanical properties of alginate and alginate-keratin fibres; the test symbols are related to the solution symbols shown in Table 4.

Parameter tested	Test symbol							
	Alg1	AK 1/1	AK 1/2	MAK 2	AK 3/1	AK 3/2	AK 4/1	AK 4/2
Linear density, dtex	3.25	3.19	4.68	6.20	7.47	3.32	9.78	3.95
Coefficient of variation of linear density, %	2.00	2.19	0.534	1.08	2.34	2.29	1.23	2.40
Breaking force of fibres in conditioned state, cN	8.62	4.79	7.33	8.31	8.38	2.38	10.3	4.44
Coefficient of variation of breaking force in conditioned state, %	17.4	14.8	23.7	16.1	27.7	27.0	13.3	10.4
Tenacity in conditioned state, cN/tex	18.9	15.0	15.7	13.4	11.2	7.15	10.5	11.2
Elongation at break in conditioned state, %	18	12	16	14	9	3	7	5
Coefficient of variation of elongation at break in conditioned state, %	10.0	40.6	22.0	37.1	56.1	42.8	23.6	22.9

**Table 7.** Hygroscopic properties of alginate and alginate-keratin fibres; AK 4 – formation conditions as AK 2, but after drawing additional processing ETOH.

Test symbol	Nitrogen content, %	Hygroscopicity, %	Wetting angle, deg
Alg1	-	60.3	28.5
AK 1/2	1.2	65.2	27.0
AK 2/2	1.6	68.8	26.3
AK 3	3.3	69.5	25.4
AK 4	2.6	67.8	-

### Microscopic analysis of alginate-keratin spinning solutions

Previous investigations proved that alginate solutions prepared for fibril formation should be characterised by a polymer concentration of about 0.93%. In order to estimate the quality of the alginate-keratin solutions prepared, they were all analysed with the use of an optical microscope (Figure 1). Aqueous keratin suspensions of different polymer concentrations were prepared, and in this way, the keratin in the shape of a suspension was introduced into the sodium alginate spinning solution in different proportions.

### Investigation into the process of alginate-keratin fibre formation

A laboratory spinning machine for wet spinning was used for manufacturing the alginate-keratin fibres according to the procedure described on page 31. The conditions for alginate-keratin fibre formation are presented in Table 3. Next the fibres obtained were tested, including assessing the mechanical properties, estimating the sorption properties by measuring their hygroscopicity and wetting angle, and evaluating these composite fibres by the SEM method.

The mechanical properties of alginate and alginate-keratin fibres are presented in Table 6. The process of alginate fibre formation was stable, and the fibres obtained were characterised by the following mechanical properties: tenacity of 18.9 cN/tex and elongation at break of 18%.

The process of alginate-keratin fibres was not so stable, compared to that of the alginate fibres: fibre breaks appeared periodically during the drawing process, as well as disturbances consisting of elementary fibre breaks within the spinneret range. With the increase in the keratin content in the spinning solution (the solutions from AK1 to AK4), we noted a worsening of the fibre formation process conditions, and also as a result a decrease in the tenacity and elongation at break, as well as a worsening of these parameters' coefficients of variation.

The increase in linear density in relation to the value assumed (3.0 dtex) in the case of some samples may be caused by choking a part of the spinneret holes during fibre spinning (we indicated a pressure increase of the spinning solution before the spinning nozzle), and by wors-

ening finish process conditions; we stated that parts of the monofilaments were difficult to separate. The drawing process of the alginate-keratin fibres was carried out in two variants, in hot water and in air, as we expected that the manner of conducting the drawing process may influence the mechanical properties of the fibres obtained, as well as the degree of retaining keratin in the fibres. From the data presented in Table 6, we can conclude that the fibres drawn in water and air have similar tenacity and elongation at break, but the fibres drawn in air have significantly greater linear densities, which may be the result of a higher tendency to mutual gluing of these fibres, caused by the greater difficulties in conducting the process of finishing them.

Summarising, it should be stated that the mechanical properties of the composite fibres were essentially worse in comparison to the properties of the non-modified alginate fibres. The alginate-keratin fibres manufactured were characterised by the following mechanical properties:

- linear density of 3-10 dtex,
- tenacity in conditioned state from 7 cN/tex to 15 cN/tex, and
- elongation at break from 5% to 16%.

On the basis of the results obtained (Table 7), we stated that the modification of alginate fibres evaluated on the basis of the nitrogen content, changes in hygroscopicity, and values of the wetting angle can be observed for all alginate-keratin fibres. The alginate-keratin fibres obtained are characterised by better sorption properties: higher hygroscopicity (69%) and smaller wetting degree (25 deg), compared with alginate fibres, for which the hygroscopicity is equal to 60% and the wetting angle is 28 deg. The property changes differ depending on the keratin content added. The greatest improvement in the sorption properties was noted for the AK 3 fibres, in which the keratin content was the greatest (25%).

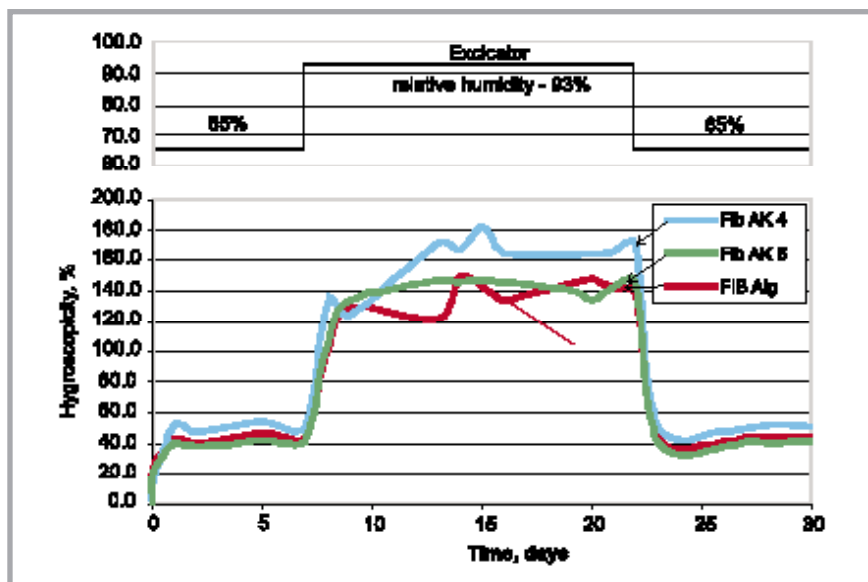
### Evaluation of the alginate-keratin fibrils

The properties of the alginate-keratin fibrils were evaluated by assessing the nitrogen content, estimating the sorption properties (Table 8), and by analysing SEM photos.

Depending on the keratin content in the ready-to-use spinning solution, the nitrogen content in the alginate-keratin fibrils varied within the range of 1.9% to 2.4%.

**Table 8.** Properties of alginate-keratin fibrids; the fibrid symbol is the same as the spinning solution symbol.

Test symbol	Nitrogen content, %	Sorption coefficient, %	WRV, %
Fib Alg2	-	175.0	170
Fib AK 1	1,9	194,4	179
Fib AK 2	2,0	198,2	180
Fib AK 4	2,4	200,5	188
Fib AK 5	2,1	195,2	184



**Figure 2.** Sorption and desorption curves of alginate and alginate-keratin fibrids.

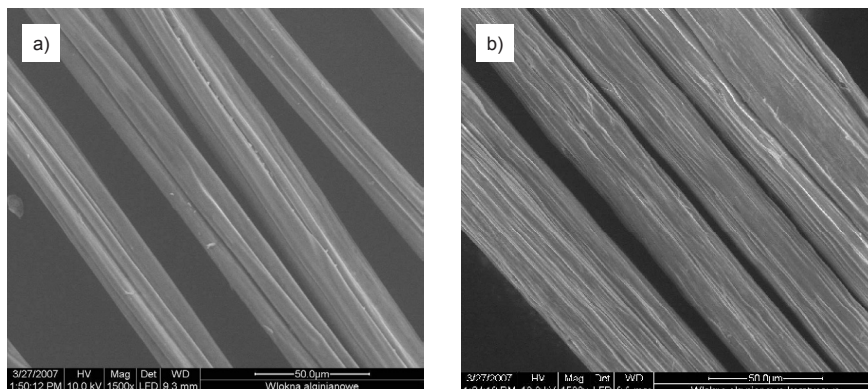
The sorption coefficient changed within 190% to 200%, whereas the WRV was equal to 180-188%. For comparison, the sorption coefficient of alginate fibrids is 170%, and the WRV is 150%.

A different method of evaluating the sorption properties is testing the moisture absorption. The kinetics of this process were tested for selected alginate-keratin fibrid samples, and for comparison with alginate fibrids. The sorption and desorption curves are presented in Figure 2.

#### Evaluating the alginate-keratin fibrous composite materials by the SEM method

In order to evaluate the surfaces and cross-sections of the alginate and alginate-keratin fibres and the general view of the fibrids obtained, microscopic observations were carried out by the SEM method. The photos are presented in Figures 3 to 5.

Numerous longitudinal grooves are visible on the surfaces of alginate fibres (Figure 3.b), at least some on each fibre.



**Figure 3.** SEM photos of the fibre surface; a) alginate fibres Alg1, b) alginate-keratin fibres AK3.

The character of these grooves on the cross-sections of alginate fibres is readily apparent (Figure 4.a). The average area of the fibres' cross-section is  $272 \mu\text{m}^2$ . Even more numerous (up to several dozens) are the grooves on the surfaces of the alginate-keratin fibres, but they are not as deep (Figure 3.b). On the other hand, a smaller amount of greater flat depressions is visible on the photo of the cross-section of alginate-keratin fibres (Figure 4.b), compared to the cross-section of alginate fibres (Figure 4.a). The average area of the fibre cross-sections of alginate-keratin fibres is  $424 \mu\text{m}^2$ . Nevertheless, it can be stated that the alginate-keratin fibres have a more developed surface than the alginate fibres. Spots darker than the background are visible (Figures 4.b and 4.c) on the surfaces of the cross-sections of alginate-keratin fibres. These spots are keratin which had been added to the spinning solution in the form of a suspension.

The differences between alginate and alginate-keratin fibrids are clearly visible on the photos presented in Figure 5. The alginate-keratin fibrids are thinner and shorter than alginate fibrids (see the numerous short and thin fibrids in Figure 5.b).

#### Summary

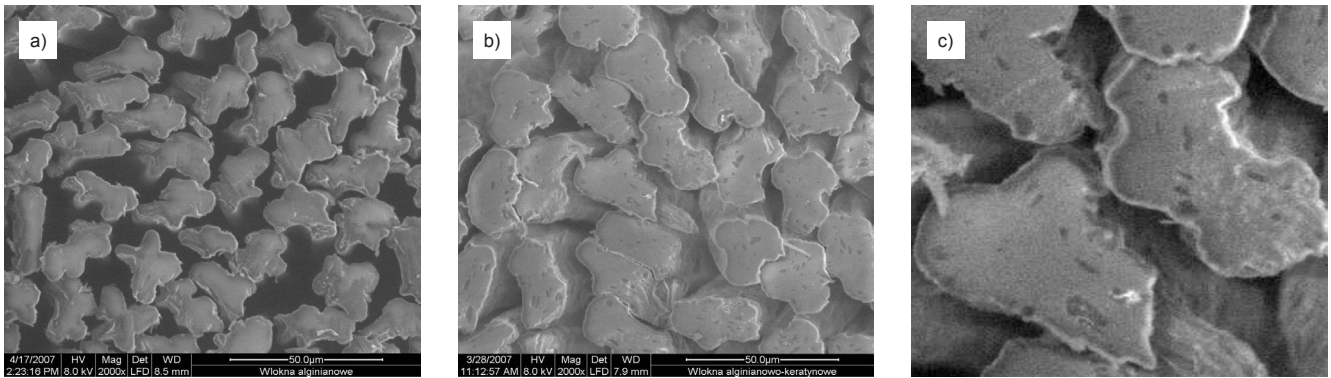
Alginate-keratin biocomposites in the shape of fibres and fibrids were obtained as the result of our investigations. It was demonstrated that adding keratin improves the hygroscopic properties.

The alginate-keratin fibres were characterised by the following mechanical properties:

- linear density of 3–10 dtex,
- tenacity in conditioned state from 7 cN/tex to 15 cN/tex, and
- elongation at break from 5% to 16%.

The modification of alginate fibres by adding keratin, evaluated on the basis of nitrogen content, the changes in hygroscopicity, and the value of the wetting angle, is evident for all alginate-keratin fibres. The alginate-keratin fibres obtained are characterised by better sorption properties: higher hygroscopicity (69%) and a smaller wetting angle (25 deg) than those of alginate fibres with hygroscopicity of 60% and a wetting angle of 28 deg.

Introducing keratin into alginate fibres lowered their mechanical properties; a decrease in tenacity of a factor of



**Figure 4.** SEM photos of the fibre cross-sections; a) alginate fibres Alg1, b) alginate-keratin fibres AK3, c) alginate-keratine fibres AK3, photo of greater magnification.

nearly two, and a significant decrease in elongation at break took place, but both parameters remained further on a level which enables these fibres to be used for manufacturing composite fibrous materials. However, a further increase in the keratin amount of the alginate spinning solution over the values used in this research work may essentially hinder the fibre formation process.

Depending on the keratin content in the ready-to-use spinning solution, the nitrogen content in the alginate-keratin fibrils varies within the range of 1.9% to 2.4%. The sorption coefficient changes from 190% to 200%, and the water retention

value equals 180 to 188%, compared to those of alginate fibres of 170% and 150% respectively.

Evaluating the view of the alginate-keratin fibrous composite materials by the SEM method, we noted that the alginate-keratin fibres have a more developed surface than that of the alginate fibres, whereas the alginate-keratin fibrils are thinner and shorter than the alginate fibrils. Improving the sorption properties of the biocomposites obtained creates opportunities to use them as hygienic fabrics.

### Acknowledgment

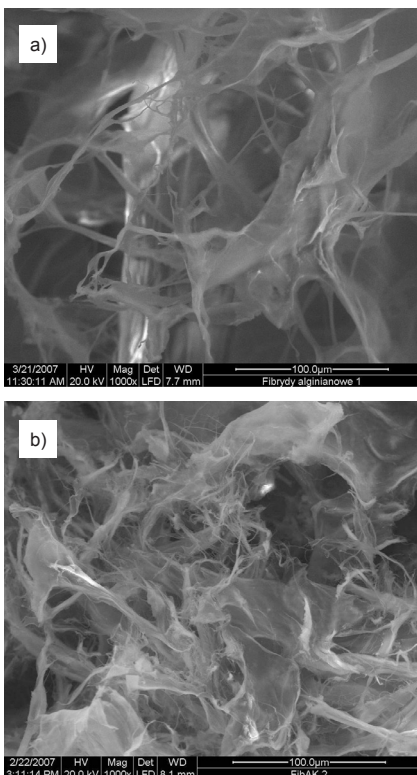
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### References

1. Pat US nr 5 316 705, (1994) 'Process for the production of cellulose ester fibres'.
2. S. Salmon, S. Hudson; *Fiber and Polymer Science Program, Box 8301, North Carolina State University, Raleigh, North Carolina 27695-8301.*
3. R. A. A. Muzzarelli, M. Matioli-Belmonte, A. Pugnali and G. Biagini, 'Biochemistry, histology and clinical uses of chitins and chitosans in wound healing, in: Chitin and Chitinases, P. Jolles and R. A. A. Muzzarelli (eds.) Birkhäuser verlag, Basel, 1999, pp.251-264.
4. G. Skjak-Braek, T. Espevik; *Carbohydrates in Europe, 19-25, 1996.*
5. Pat. US 20020017493 A1, (2002) 'Use of absorbent materials to separate water from lipophilic fluid'.
6. Pat PL 167776 (1995), Sposób wytwarzania włókna, folii i innych produktów z rozpuszczalnej celulozy'.
7. Pat. US V5 5 695 64, (1997), 'Methods of treating waster water.
8. Pat. US 4 274 914, (1981), 'Filter material'.

9. E. Rybicki, T. Stożek, 'Substancje pomocnicze w technologii postaci leku', PZWL, Warszawa, 1980.
10. Pat. US 6544548, 2003, 'Keratin-based powder and hydrogel for pharmaceutical applications'.
11. Schmidt W. F. 'Microcrystalline keratin: from feathers to composite products. MRS Symposium Proceedings, 2001, Boston, MA, 702; 25-29.
12. T. Toshizumi., Naoya O., Tachibana, A.; *Biomaterials, Vol:23 Issue:3, February, 2002, pp: 817-825.*
13. 'Novel approach to fabricate keratin sponge scaffolds with controlled pore size and porosity', *Biomaterials Volume: 25, Issue: 18, August, 2004, pp. 4255-4262.*
14. J. Mc Curry, 'Fibres, Yarns and Fabrics', *Textile World, 28, 1996.*
15. F. W. Schmidt, R. M. Waters, G. Gasner; *Chemical Eng., News, February, 23, 1998.*
16. US. Pat. 5, 705, 030.
17. J. Józwicka, D. Wawro, P. Starostka, H. Struszczyk, W. Mikołajczyk; *Fibres & Textiles in Eastern Europe, 2001, Vol. 9, No. 4(35) p. 28-32.*
18. D. Wawro, D. Ciechańska, W. Stęplewski, A. Bodek; *Fibres & Textiles in Eastern Europe, 2002, Vol. 10, No. 3(38) p.23-26.*
19. D. Wawro, H. Struszczyk, D. Ciechańska, A. Bodek; *Fibres & Textiles in Eastern Europe, 2006, Vol. 14, No. 3(57) p. 97-101.*
20. Pat PL 193736 (1998), 'Sposób wytwarzania włókien, folii, fibryd i innych form mikrokrystalicznych zawierających keratynę'.
18. K. Wrześniewska-Tosik, J. Adamiec; *Fibres & Textiles in Eastern Europe, January / March 2007, Vol. 15, No. 1 (60) p.106-112.*
19. R. Ferrus, P. Payes; *Cell. Chem. Techn. 11, p. 633 /1977/.*
20. 'Badanie możliwości wytwarzania nowych biomateriałów kompozytowych z udziałem keratyny', *Research report, IWCh, 2004.*
21. 'Ćwiczenia z biochemii', ed. Kłyszajko-Stefanowicz L., PWN, 1999.
22. Majewska J., 'Sulphur assessing methods in fibre-grade polymers and co-polymers' (in Polish): *Włókna Chemiczne, Chemia Analityczna, IWCh, vol.13, Nr.29, 1968.*
23. *Metrologia Włókiennicza, ed. W. Szmelter, vol. 4, chapter 2, p. 67, WNT, Warsaw, 1973.*

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**Figure 5.** SEM photos of the fibrils general view; a) alginate fibrils, b) alginate-keratin fibrils.