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Investigation of the Process for Obtaining Microfibrids from Natural Polymers

Abstract

The increase in the application of fibrids in the paper, cosmetic, and medical material industries, as well as in environmental protection, is based on their unique properties, principally their large developed surface. This was the ground to commence our investigation in the Institute of Chemical Fibres into obtaining and processing fibrids [1]. This paper is devoted to microfibrids, i.e. fibrids of a diameter smaller than 10 mm. The influence of the ratio of the spinning solution outflow velocity to the coagulation bath outflow velocity (existing over spinning) on the properties of microfibrids (principally on their dimensions) was tested. Test results of obtaining alginate, alginate-starch, and alginate mixed with keratin microfibrids by the wet method are presented, together with an estimation of their properties. The microscopical analysis carried out proved that the microfibrid diameters are in general below 10 μm.

Key words: *fibrids, microfibrids, alginate, starch, keratin, wet spinning.*

Introduction

Nowadays fibrids are applied more and more in the paper, cosmetic, and medical material industries, as well as in environmental protection [1]. The rising interest results from their unique properties, principally their large developed surface, which first of all depends on the fibrids' dimensions. The smaller the fibrids' diameter, the larger their specific surface. At present, fibrids with a developed surface of 20 m^2/g and a diameter from 0.5 μm to 5 μm are manufactured from cellulose acetate [2]. Modification of the fibrids' properties by the application of polymer solution mixtures is also possible. Nonwovens manufactured from fibrids obtained from chitosan and carboxymethylcellulose have bioactive properties, which create possibilities for medical applications [3]. Fibrids from cellulose acetate obtained by the wet method have a large developed surface which allow for their application not only as filtration material but also as waste water purification, in albumin binding, and as agents accelerating the sedimentation of contaminations [4]. Recently, available information in world literature [5] can be found concerning fibrid application of a much more developed surface (up to 50 m^2/g or even to 100 m^2/g). Fibrids from an acrylonitrile copolymer mixed with vinyl acetate of a surface of 70 m^2/g have been used for leukocyte filtration.

Fibrids of diameters below 10 μm are usually known as microfibrids. To manufacture fibrids (and especially microfibrids) special devices are necessary which allow us to obtain high shearing tensions in the polymer coagulation zone [6]. High shearing tensions force great drawing of the coagulated fibrids in the surrounding solution of the coagulation bath, which in turn results in a decrease in their diameter.

The aim of the presented work was to develop manufacturing methods for microfibrids obtained from natural polymers. In a previous investigation [1], manufacturing methods of cellulose-starch fibrids were developed, but the fibrids obtained were characterised by irregular dimensions and diameters of not less than about 10 μm. However one of those methods (based on spinneret wet spinning) also enabled the manufacture of fibrids with a diameter of about 1 μm, i.e. microfibrids. The experience achieved by those investigations was used in the work which is the subject of this article. The investigation results of the manufacturing process of microfibrids from alginate, alginate-starch, and alginate mixed with keratin conducted by the method of spinneret wet spinning are discussed, and the microfibrids' properties are presented.

Materials and Methods

The following were used as raw materials for fibrid manufacture:

- Sodium alginate of the LF 10/60 type manufactured by the Norwegian Biopolymer FMC Company, used in general for manufacturing alginate fibres destined for sanitary use.
- Native potato starch manufactured in Poland, thermally modified at a temperature of 160°C over 2 hours.
- Keratin in a solid state obtained from hen feathers in the Institute of Chemical Fibres with a nitrogen content of 10.7% and a sulphur content of 1.25%.

Preparation of aqueous solutions of sodium alginate and starch

The aqueous solution of sodium alginate was prepared in a mixer equipped with a 1500 r.p.m. high-velocity stirrer. The LF 10/60-type sodium alginate was introduced into continually mixed water . The dissolving process was conducted at a temperature of 45°C over 120 minutes.

The aqueous spinning solution of potato starch was prepared in a Treiber mixer. Boiling water was poured into the potato starch which had been wetted by a small amount of cold water. A clear aqueous spinning starch solution was achieved.

Polymer solutions were filtered with the use of a frame filtration press using filtration woven fabrics retaining contamination of above 3 μm. The polymer solutions obtained were used for preparing polymer spinning solutions by dilution with water to a defined polymer concentration.

Microfibrid manufacturing by the spinneret method

A special prototype stand, intended to manufacture microfibrids by the spinneret method, was designed and constructed. The microfibrid formation was conducted in dynamic conditions. The polymer solution flowing out from the multi-orifice spinneret was carried further by the coagulation bath, which was forced to flow parallel to the polymer solution stream. The spinning conditions were especially selected to allow us to draw the polymer stream in the coagulation bath, and at the same time to force the breakage of the microfibrids formed. Various outflow velocities of the polymer solution stream and the coagulation bath were chosen in the tests carried out. The bath containing fibrids were continuously transported to a receiver, and then separated and washed out by water. The microfibrid content was assessed in the concentrated aqueous dispersion obtained after washing. It is possible to use microfibrids in this form also in nonwoven manufacture for medical and sanitary use.

Analytical methods

Determination of polymer content in the spinning solution

Approximately 3±0.0002 g of alginate spinning solution was poured onto a glass plate. Next, the alginate film obtained on the glass plate was soaked with a coagulation bath of pH 4.5 containing aqueous hydrochloric acid solution and 25 g/l of calcium chloride. The alginate film was removed, washed in distilled water and dried to a constant weight at a temperature of 105°C. The polymer content was determined from the following equation:

$$X = \frac{m_2 \cdot 100}{m_1} \quad [\%]$$

where:

m_1 - weight of the alginate spinning solution sample, in grams, and

m_2 - weight of the dry alginate film, in grams.

Determination of dynamic viscosity of the spinning solutions

The dynamic viscosity of the aqueous solutions of alginate, starch and alginate-starch mixtures was determined with the use of a DS/3/4 Brookfield viscometer at a temperature of 20°C.

Determination of corrected clogging value K_w of the spinning solutions*

The corrected clogging value K_w* was determined according to the standard used in the viscose fibre industry from the following equation:

$$K_w^* = \frac{1}{6} K_w \cdot y^{-a}$$

where:

y - ball viscosity at 20°C,

a - constant (a=0.321(1 - lg P)),

P - permeability of filtering material, and

K_w - clogging value.

The permeability was calculated from:

$$P = \frac{Q}{S \cdot H}$$

where:

Q - air flow in l/h indicated by a rotameter,

S - blowing through filter surface in cm^2, and

H - pressure difference between both filter sides in mm H_2O.

The clogging value was calculated from:

$$K_w = \frac{100000\left(2 - \frac{m_2}{m_1}\right)}{m_2 + m_1}$$

where:

m_1 - weight of the filtered solution after 20 min, in grams, and

m_2 - weight of the filtered solution after 40 min, in grams.

Microscope analysis of the microfibrids

The form and dimensions of the alginate, alginate-starch and alginate-with-keratin microfibrids obtained in tests were estimated with the use of a Biolar polarisation microscope (ZPO, Warsaw) working with the computer image analyser manufactured by IMAL.

Determination of the microfibrids' water retention value (WRV)

A sample of swelled microfibrids was centrifuged at a velocity of 4000 r.p.m. for 10 minutes. The sample was

Table 1. Properties of aqueous solutions of the polymers used.

Solution denotation	Polymer kind	Polymer content, % wt.	Dynamic viscosity, cP	Dynamic viscosity after 24 h, cP	Kw* (solution unfiltered)
R-alg	sodium alginate	6.0	9300	9295	112
R-sta	starch	2.0	270	267	123

Table 2. Properties of the aqueous solution of sodium alginate.

Solution denotation	Polymer content, % wt.	Dynamic viscosity, cP	Dynamic viscosity after 24 h, cP	Kw*
R-alg-1	0.50	10	9.5	0

Table 3. Selected properties of alginate microfibrids (concentration of calcium chloride in the coagulation bath - 3 g/l; V_r:V_k - ratio of the spinning solution outflow velocity to the outflow velocity of the coagulation bath).

Test denotation	V_r:V_k	pH of coagulation bath	Microfibrid content in the aqueous dispersion, % wt.	WRV, %	Ranges of the average microfibrid dimensions	
					diameter, µm	length, µm
F - 1	1:11	4.6	0.5	838	1 - 20	300 - 500
F - 2	1:57	5.6	1.2	895	1 - 20	300 - 500
F - 3	1:72	5.6	1.0	950	1 - 10	100 - 150

Table 4. *Selected properties of the M-A/S alginate-starch solution mixtures.*

Solution denotation	Solution content			Dynamic viscosity at 20°C, cP	Dynamic viscosity after 24 h at 20°C, cP	Kw*
	Alginate content, % wt.	Starch content, % wt.	Share of starch in the polymer mixture, %wt.			
M-A/S 1	0.43	0.21	33	9.0	9.0	0
M-A/S 2	0.38	0.38	50	10.0	9.5	0
M-A/S 3	0.21	0.43	68	13.5	13.0	0

weighed and then dried to constant weight at a temperature of 105°C. The water retention value was calculated from the equation:

$$WRV = \frac{S_d - S_s}{S_s} \cdot 100\%$$

where:
S_d - weight of the microfibrids after centrifugation, in grams, and
S_s - weight of the dry sample, in grams.

Research Results and Discussion

Aqueous solutions of sodium alginate and starch of the properties presented in Table 1 were used in tests. The tests carried out allow us to state that the sodium alginate and the thermally modified potato starch have good solubility in water. The thermal modification of starch ensures the obtention of a spinnable solution. The aqueous solutions of sodium alginate and potato starch were characterised by good filtration properties (clogging value K_w*) and good stability over 24 hours. Spinning solutions were prepared from solutions with the properties shown in Table 1.

Table 5. Selected properties of alginate-starch microfibrids; polymer concentration in the spinning solution - 0.74% wt. (V_r:V_k - ratio of the spinning solution outflow velocity to the outflow velocity of the coagulation bath).

Test denotation	V_r:V_k	Starch content in the polymer mixture, % wt.	Microfibrid content in the aqueous dispersion, % wt.	WRV, %	Ranges of the average microfibrid dimensions	
					diameter, µm	length, µm
F - 4	1: 21	33	0.4	788	2 - 20	300 - 500
F - 5	1: 56	33	0.2	827	2 - 20	300 - 500
F - 6	1: 106	33	0.2	812	1 - 5	350 - 800
F - 7	1: 115	33	0.4	797	1 - 5	150 - 300
F - 8	1: 115	50	0.3	800	1 - 3	150 - 200
F - 9	1: 115	68	0.6	1188	5 - 15	150 - 200

Table 6. Selected properties of alginate microfibrids with keratin addition; alginate concentration in the spinning solution - 0.74% weight, calcium chloride content in the coagulation bath - 3 g/l (V_r:V_k - ratio of the spinning solution outflow velocity to the outflow velocity of the coagulation bath).

Test denotation	V_r:V_k	Ratio of alginate to keratin content	Microfibrid content in the aqueous dispersion, % wt.	WRV, %	Ranges of the average microfibrid dimensions	
					diameter, µm	length, µm
F - 10	1: 85	1: 0.5	0.5	786	2 - 20	300 - 500
F - 11	1: 85	1: 1.0	0.5	827	1 - 10	300 - 500
F - 12	1: 85	1: 2.0	0.7	913	1 - 5	350 - 800

Investigation of the manufacturing process of alginate microfibrids
The alginate microfibrids were formed from the spinning solution of sodium alginate presented in Table 2. Selected properties of the microfibrids obtained are listed in Table 3. From the property analysis, the results show that in certain ranges of the velocity ratio (the polymer stream outflow velocity to the coagulation bath outflow velocity) this ratio influences the microfibrids' dimensions. The data presented in Table 3 allow us to state that at the velocity ratio (V_r:V_k) of 1:11, microfibrids of average diameters ranging from 1 µm to 20 µm and lengths ranging from 300 µm to 500 µm were obtained. Increasing the V_r:V_k ratio up to 1:57 did not influence the microfibrids' dimensions.

However, changing the V_r:V_k ratio to 1:72 caused the microfibrids obtained to be characterised by a fundamentally smaller length ranging from 100 µm to 150 µm, and by diameters within the range of 1-10 µm. What is more, on the basis of several tests carried out, we stated that the alginate microfibrids obtained at higher V_r:V_k ratios were characterised by higher uniformity. From the data presented in Table 3, the WRV proved to be within the range from 838% to 950%. A microscope photo of the alginate microfibrids obtained in the F-1 test is presented in Figure 1.

Selected natural polymers such as starch and keratin were introduced into the sodium alginate spinning solution in order to achieve modified properties of the alginate microfibrids.

Investigation of the manufacturing process of alginate-starch microfibrids
The aqueous starch and sodium alginate solutions were mixed in determined weight ratios with the aim of obtaining a spinning solution for manufacture alginate-starch microfibrids. The weight content of starch in the polymer solution was kept within the

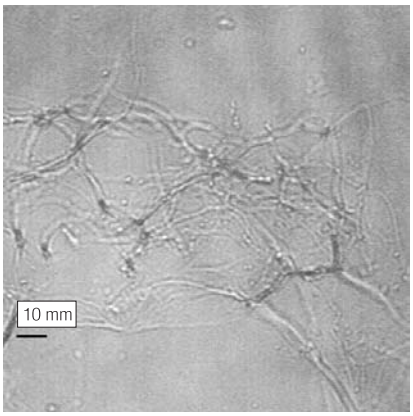

Figure 1. Microscope photo of the alginate microfibrids from the F-1 test.

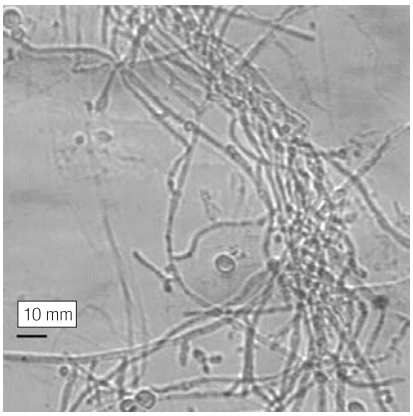

Figure 2. Microscope photo of the alginate-starch microfibrids from the F-7 test.

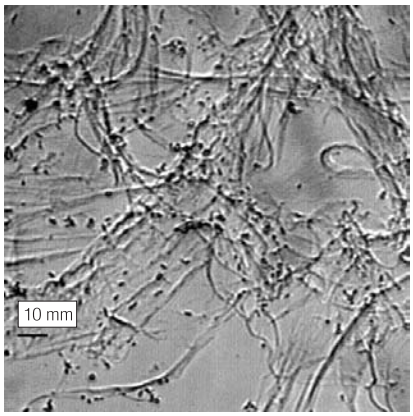

Figure 3. Microscope photo of the alginate microfibrids with keratin addition from the F-11 test.

range from 33% to 68%. Some properties of the M-A/S alginate-starch solution mixtures are presented in Table 4.

Evaluating the data of the alginate-starch solution mixtures shown in Table 4 allows us to state that an increased starch content in the mixture causes an increase in its viscosity from 9 cP to 13.5 cP. All these solutions are characterised by relatively low viscosity and sufficient stability over time, which secures the possibility of manufacturing microfibrids. The microfibrids were formed from the prepared mixed solutions using an aqueous solution of calcium chloride (3 g/l) and hydrochloric acid as the coagulation bath. The influence of the V_r:V_k velocity ratio and of the starch content in the polymer mixture on the properties of the microfibrids obtained were tested. Selected properties of alginate-starch microfibrids are presented in Table 5.

With the increase in the coagulation bath velocity, a decrease in diameter and increase in the length of the microfibrids obtained was observed. The starch contents in the spinning solutions caused an increase in WRV of all microfibrids while maintaining a constant velocity ratio of both the streams over the spinning process.

It was stated that microfibrids of higher dimension uniformity could be obtained at a velocity ratio of the M-A/S1 spinning solution to the coagulation bath of 1:106. Solutions of starch content in the polymer mixture of 33% to 68% were also prepared within the range of this investigation. It was stated that the starch content in the spinning solution mixture influenced the properties of the alginate-starch microfibrids. The microfibrids obtained were also characterised by high dimension uniformity and high water retention values. The starch content in the solution mixture at the level of 68% caused an increase in the diameters of the microfibrids manufactured.

On the basis of the research results, it can be stated that a possibility exists to manufacture microfibrids of a diameter ranging from 1 µm to 5 µm at the tested velocity ratio above 1:106 and starch content in the polymer mixture ranging from 33% to 50%. A microscope photo of the alginate-starch microfibrids from the F-7 test is presented in Figure 2.

Investigation of the manufacturing process of alginate microfibrids with the addition of keratin

The possibility of modifying alginate microfibrids by introducing solid keratin particles of a diameter of about 1 µm into the alginate spinning solution was proved. Selected properties of the alginate microfibrids with keratin addition are presented in Table 6.

The data presented in Table 6 allows us to state that the microfibrids obtained were thinner and longer when more keratin was introduced. Interpretation of this phenomenon demands further investigation. The water retention value of the alginate microfibrids with keratin addition ranged from 786% to 913%. Figure 3 presents a microscope photo of alginate microfibrids with keratin addition from the F-11 test. In the photo, keratin particles can be seen in the form of dark points inside the microfibrids as well as in their immediate surroundings. Only partial allocation of the keratin particles in the microfibrids was observed.

Conclusions

- The novel method of microfibrid manufacture developed at the Institute of Chemical Fibres allows us to obtain alginate microfibrids of diameters ranging from 1 µm to 5 µm by the spinneret wet method.
- The results achieved indicate the possibility of controlling the process conditions aimed at obtaining microfibrids of assumed dimensions.
- A possibility exists to modify alginate microfibrids by means of starch and keratin with the aim of achieving alginate-starch microfibrids and alginate microfibrids with the addition of keratin

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