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Sorption and Tensile Strength Properties of Selected Fibres of Cupric Alginate

Abstract

A comparative analysis of the sorption properties, water retention and tensile strength properties of cupric alginate fibres obtained from polymers with different molecular weights was carried out. The fibres obtained were characterised by high sorption properties and a tenacity suitable for processing them into a flat textile product dedicated to medical applications.

Key words: alginate fibres, sorption properties, tenacity, medical application.

the most often used among all alginate fibres. The main advantage of these fibres are their high sorption properties and the ability of transmission in a gel form; this is influenced by wound secretion, which assures painless changing of dressing [5]. Sodium alginate fibres have the ability to totally change into a gel [6]. However, for calcium alginate fibres to undergo this process depends on the majority of blocks, which have their origins in the mannuronic acid (M) of the fibre-grade matrix, as their stereo-chemical structure prevents the blocking of Ca^{++} ions and, at the same time, their transformation into sodium ions [2]. Inserting appropriate divalent metal ions, such as copper or zinc ions, into the fibre matrix during the reaction which takes place in the solidification bath is a method devoted to introducing new properties of alginate fibres, and at the same time increases their functionality.

The result of works carried out at the Department of Man-Made Fibres and described in [7] indicates that fibres obtained from cupric alginate by the above-mentioned method are characterised by antibacterial activity. In these fibres we also observed a change in their electroinsulation properties, which was an increase in the electrocoactivity to a degree depending on the relative air humidity [8]. These fibres generate a negative electrostatic charge when in contact with skin, which causes a decrease in pain felt by patients with alginate dressings, which was confirmed by clinical research conducted using fibres made of other fibre-grade polymers, for example PCV [9]. This behaviour creates possibilities of applying cupric alginate fibres to medical products dedicated to antirheumatic bans which decrease the feeling of pain, and to hospital linen.

The aim of this work was to determine the influence of the molecular weight of

sodium alginate on the sorption properties and tenacity of cupric alginate fibres obtained from sodium alginate by substituting ions Cu^{++} in the place of Na^+ ions.

Materials and research method

Materials

The following two types of sodium alginate polymers of the FMC Biopolymer Company, differentiated by the molecular weight, were used for preparing the spinning solution:

- Protanal LF 20/60 with a higher molecular weight, and
- Protanal FE 10/60 with a lower molecular weight.

Both biopolymers were characterised by a greater amount of blocs, which were formed from guluronic acid, in relation to the residue of mannuronic acid.

Fibre formation

The alginate fibres were spun by the wet method from a sodium alginate solution with distillate water as a solvent. An extended laboratory spinning machine was used, whose construction enabled the stabilisation of the technological parameters at accepted levels, a continuous monitoring, and gave the possibility of changing the process parameters within great ranges. The solidification process of the cupric alginate fibres was conducted in a bath containing 3% CuCl_2 and 0.03% HCL at a temperature of 22 °C. The drawing process was realised in two-stages in a plastification bath of the same concentration as the solidification bath, at a temperature of 70 °C, and in preheated steam at a temperature of 140 °C. The fibres were continuously taken-up on a bobbin. After the drawing process and rinsing, the fibres were dried at a temperature of 25 °C at isometric conditions.

Introduction

Alginate fibres form a group of biomaterials which finds broad application in medicine as it is used to manufacture modern dressing materials that are adapted to the kind of wound and its healing stage. Due to their biocompatibility, bioactivity and lack of toxic activity, they are presently an alternative for the cotton and viscose dressings commonly used, and they can also compete with chitossan dressings.

Alginates are natural polymers with a linear structure of macromolecules built from residue of β -D mannuronic.(M) and α -L guluronic.(G) acids [1, 2]. The acid groups in the guluronic acids are placed at the vortex of the carbon/carbon/oxygen triangle, which causes an increase in their activity in comparison to the mannuronic acid [3,4]. Presently, sodium alginate and calcium alginate fibres are

Test methods

The polymer characteristics were estimated on the basis of gel chromatography analysis with the following parameters:

- solvent (mobile phase): 0.1 mol/dcm³ of NaCl, which before being used was filtered and degassed (Sartorius filters of PTFE, 0.45 µm);
- Set of columns: 2 × TSK gel™ Column GMPWXL, 30 cm × 7.8 mm (TOSO HAAS);
- Temperature of the columns: 30 °C;
- Flow rate of the mobile phase: 0.5 ml/min;
- Volume of the sample doses: 100 µl;
- Calibration standard: pullulanes with a molecule weight from 22,900 to 152,000 and polydispersity from 1.07 to 1.13 (Pollygen).

The analyses were carried out at the Institute of Biopolymers and Chemical Fibres in Łódź.

The rheological properties of the spinning solutions were assessed by a Rheotest RV rotary rheometer. The measurements were conducted with a shearing rate of 0.2 - 1.31 × 10³ sek⁻¹ and shearing stress of 12 - 3 × 10³ N/m², at a temperature of 20°C with the use of an "H" cylinder. Rheological parameters *n* and *k* were determined on the basis of flow curves presented in a logarithmic coordinate system, but without consideration of the shearing stress range below 10 read-out divisions.

The tenacity of the fibres was assessed in accordance with Standard PN-EN ISO 5079:1999.

The sorption of water moisture was determined at the conditions of 65% and 100% relative air humidity in accordance with Polish Standard PN-71/P-04653.

Water retention was determined using a laboratory centrifuge which enabled the mechanical rejection of water from the fibres in the centrifugation process with an acceleration of 10,000 m/sek². The retention value was determined by relating the weight of water retained in the fibres after centrifugation to the weight of the dried fibres.

The degree of crystallisation and the dimensions of crystalline domains were determined by the method of wide angle X-ray diffraction (WAXS). The tests were performed with the use of an URD6 diffractometer from Seifert Co., Germany, equipped with a copper lamp emitting radiation with a wavelength of λ = 1.54 Å operating at a voltage of U = 40 kV and current of I = 30 mA. Monochromatic radiation was used due to the nickel filter. Diffraction curves were recorded by the reflection method and jump measuring mode.

The fibre porosity was determined by the mercury porosimetry method using a Carlo-Erba porosimeter linked to a computer system which allows to determine the total volume of pores, the percentage content of pores with dimensions within the range of 5 - 7,500 nm, as well as the total internal surface of pores.

Discussion of the results

On the basis of the analysis of the GPC results for the two types of sodium alginate and molecular weight distribution curves obtained (**Table 1**, **Figure 1**), one can indicate that the Protanal LF 20/60 sodium alginate is characterised by a significantly higher value of the average molecular weight and the average molecular weight by weight in comparison to those of Protanal LF 10/60 sodium alginate. The polymolecular index for Protanal LF 20/60 is equal to 4.7, whereas for Protanal LF 10/60 it is equal to 4.6. At the same time, in both cases the molecular weight distribution curves are characterised by a limited content of low and high fractions, and only the molecular weight distribution curve of Protanal LF 20/60 is slightly displaced in the direction of higher molecular weight. Such a distribution is advantageous as from the point of view of the fibre forming conditions of the polymer, considering the limited content of fractions with a too low molecular weight ($M < 10^4.5$), as well as a too high molecular weight ($M > 10^6.5$).

The processability as well as the final properties of the fibres obtained depend, to a significant degree, on the rheological properties of the spinning solution. The dynamic viscosity of the liquids is one of the parameters on which the following depend: the character of the speed distribution during the flow of the spinning solutions in the spinneret channel, the curves of relaxation processes in the zone behind the spinneret, as well as the value of the transverse gradient of the speed which changes along the way of the fibre during fibre formation. In cases of a too high viscosity, the application of an inappropriately selected take-up force can be the cause of fragile fibre breakage. On the other hand, a too low viscosity of the liquid led to capillary destruction. The danger that both of the phenomena mention-above pose may exist while using the method of wet spinning from a solution. The characteristic of the polymer and the spinning solutions (intrinsic viscosity, the type of polymer and its concentration in the spinning solution, as well as the apparent dynamic viscosity) also influence the formation process as well as the appropriate selection of parameters on which the structure and properties of fibres depend [10]. In order to properly select the spinning conditions, rheological investigations of the spinning solutions with different poly-

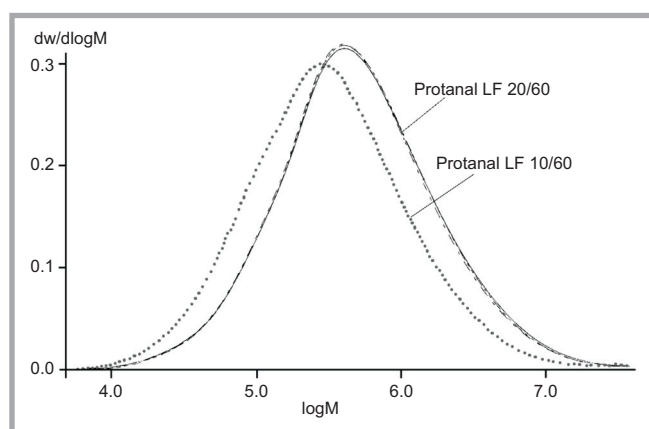


Figure 1. Molecular weight distribution curves for two types of sodium alginate.

Table 1. Results of GPC analysis of polymers used.

Polymer description	Mn, g/mol	Mw, g/mol	Mw/Mn
Protanal LF 20/60	227,900	1,069,300	4.7
Protanal LF 10/60	150,700	695,600	4.6

mer concentrations were carried out; the values of concentrations were selected on the basis of preliminary tests carried out by us. In the case of the polymer with a lower molecular weight (Protanal LF 10/60), the sodium alginate was equal to 9.2%, whereas for the alginate with a higher molecular weight, the concentration was equal to 7%. The good stability of the rheological parameters during the storage of the spinning solutions at a temperature of 20 °C for long time periods was also stated. On the basis of the flow curves obtained (**Figure 2**) and the rheological parameters n and k determined (**Table 2**) for both spinning solutions, we can state that the solution are non-Newtonian fluids thinned by shearing and without a flow limit, as the tangential stresses increase less proportionally with an increase in the shearing rate, alginate spinning solutions during which the flow curves cross the origin on the coordinate system.

For the particular types of cupric alginate fibres used by us, the solidification process was conducted in a way to achieve maximum tensile strength properties and at the same time to increase the sorption properties. This was realised by conducting the solidification process at moderately high, positive values of the as-spun-draw ratio. In the case of cupric alginate fibres obtained from the polymer with a higher molecular weight, a slight increase in moisture sorption was observed at 100% RH after a change of the as-spun-draw ratio in the direction of lower values. This was accompanied by a small change of 1 - 2% in the moisture sorption at 65% RH (**Table 3**). As was indicated in [7], these properties are mainly connected with the hydrophilic character of the fibre matrix. Similar changes in the sorption properties also occur in the case of cupric alginate fibres obtained from the polymer with a lower molecular weight (Protanal LF 10/60). However, the moisture sorption values at 65% RH and 100% RH were at a lower level, within the range of 18.17 - 19.67 % at 65% RH, and 32.78 - 35.27% at 100% RH (**Table 3**). A significantly greater difference occurred for the water retention value, which was substantially higher for fibres obtained from the polymer with a higher molecular weight (Protanal LF 20/60). At the same time the character of changes in this factor as a function of the as-spun-draw ratio was similar for fibres obtained from both polymer types and indicated a tendency

Figure 2. Flow curves of sodium alginate spinning solutions with different molecular weight.

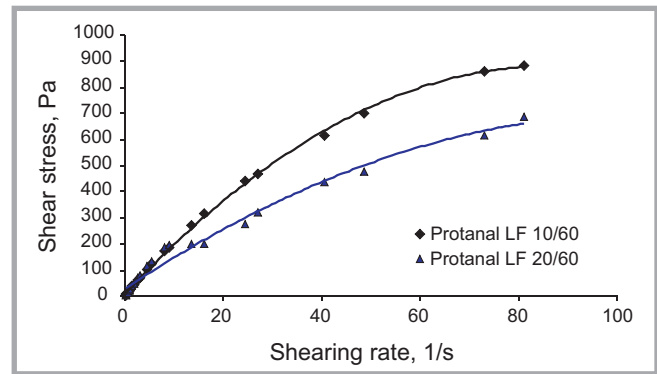


Table 2. Rheological properties of the spinning solutions.

Polymer descriptions	Polymer concentration in the solution, %	Rheological parameter n	Rheological parameter k
Protanal LF 20/60	7,0	0.89	22.53
Protanal LF 10/60	9.2	0.84	27.05

Table 3. Sorption properties and tenacity of cupric alginate fibres obtained from the two types polymers; A_{120/60} - A_{320/60} - fibres formed from sodium alginate of trade mark Protanal LF 20/60, A_{110/60} - A_{310/60} - fibres formed from sodium alginate of trade mark Protanal LF 10/60.

Sample symbol	As-spun draw ratio, %	Total drawing, %	Moisture sorption at 65% RH, %	Moisture sorption at 100% RH, %	Water retention, %	Tenacity, cN/tex	Elongation at break, %
A _{120/60}	120	73,3	21,35	37,58	61,54	21,41	2,58
A _{220/60}	90	72,5	22,82	39,15	61,09	20,18	3,26
A _{320/60}	60	70,6	21,28	41,37	55,19	18,47	2,73
A _{110/60}	120	56,3	18,41	35,27	52,12	12,84	2,24
A _{210/60}	100	53,8	16,17	32,78	51,68	14,34	2,28
A _{310/60}	80	59,64	19,62	34,71	51,49	12,09	2,02

Table 4. Porous and macromolecular structure of cupric alginate fibres obtained from the polymers of different molecular weight.

Sample symbol	As-spun draw ratio, %	Total drawing, %	Total volume of pores, cm ³ /g	Total internal surface of pores, m ² /g	Degree of crystallinity, %	Dimension of crystallites, Å
A _{120/60}	120	73,3	0,16	4,98	9,5	16
A _{210/60}	100	53,8	0,15	5,02	6,9	14

to decrease with changes in the as-spun-draw ratio in the direction of lower values.

Notwithstanding notable differences in the values of moisture sorption and water retention, the fibres obtained from polymers with different polymer weights are characterised by a similar porous structure. The total volume of pores and their total internal surface are at a similar low level of 0.15 cm³/g and 5.02 m²/g, respectively, for cupric alginate fibres obtained from Protanal LF 10/60, and 0.16 cm³/g and 4.98 m²/g for fibres obtained from Protanal 20/60 - the polymer with a higher molecular weight (**Table 4**). The curves of pore distribution as a function of their radii are also characterised by almost identical curves - in both cases distinct maxima occurred within the

range of very great pores (**Figure 3** see page 42). This means that at a relatively low total volume of pores, as well as with an insignificant content of small pores for both types of cupric alginate fibres, the absorption of moisture on the basis of the phenomenon of capillary condensation plays a smaller part. Furthermore, the hydrophilic chemical structure of the fibre matrix mainly influences moisture absorption. On the other hand, the high water retention values are, without doubt, influenced by the specific 'egg-box' structure of the fibre matrix of this kind of fibre [11, 12], which enables the retention of greater amounts of water, also in the form of greater polymorphic clusters placed in the fibre matrix, as well as bond in the internal parts of capillaries with great and very great dimensions. Although a sig-

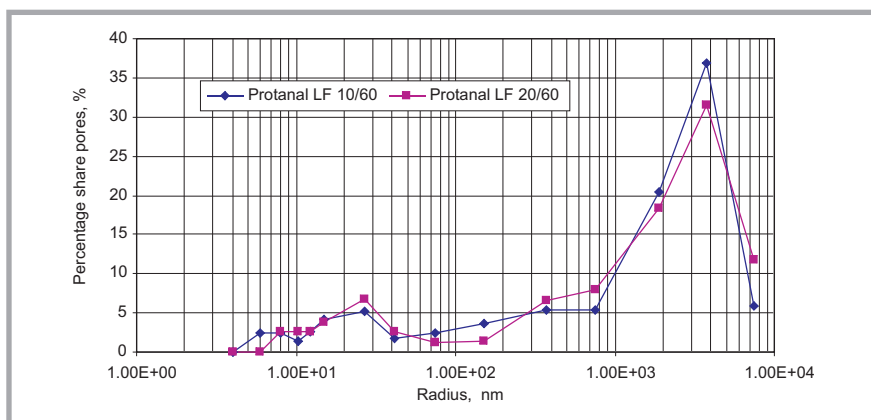


Figure 3. Curves of the percentage of pores in dependence on their radii for fibres from cupric alginate obtained from to polymer types.

nificant content of very great pores with dimensions up to 7,500 nm was indicated by the mercury porosimetry method for the fibres obtained from the polymer of higher as well as lower molecular weight, the pores were not visible on photographs taken by a scanning electron microscope; in **Figure 4** a cross section of the fibres obtained from the polymer with a higher molecular weight is presented as an example. This is probably connected with the low total value of pores of this type of alginate fibres. The shape of the cross section of both fibre types is similar to the shape of a bean. This proves that during the solidification process, gel formation probably takes place under the syneresis process.

Similarly as in the case of the sorption properties, the fibres of cupric alginate obtained from the polymer with a higher molecular weight are characterised by considerably higher tensile strength properties. The alginate fibres spun at an as-spun-draw ratio of 120% had the highest value of tenacity - 21.41 cN/tex. On the other hand, of the fibres obtained from alginate of lower molecular weight, those spun at an as-spun-draw ratio of 100%

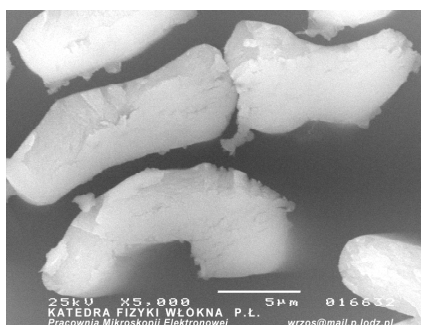


Figure 4. Photos of cross-sections of cupric alginate fibres obtained from the polymer with higher molecular weight.

had the highest level of tenacity but only 14.34 cN/tex. For fibres characterised by the highest values of tenacity in a particular series, structural investigations of the macromolecular structure were carried out by the method of wide angle X-ray diffraction. The fibres obtained from the polymer with lower as well as higher molecular weight were characterised by a low value of crystallisation degree, within the range of 6.9 - 9.5%, and by the dimensions of the crystallites, which were at the level of 14 - 16 Å (**Table 4**). The cause of the low value of the degree of crystallisation of these fibres is primarily their 'egg-box' structure, which is connected with the greater distances between the macromolecules. On the basis of the above-mentioned indication, we can state that the significantly higher values of tenacity for fibres obtained from the polymer with a higher molecular weight (LF 20/60) are caused not only by the difference in molecular weight and the slightly higher value of the degree of crystallisation, but also by higher susceptibility to fibre matrix deformation at the drawing stage. The latter is the effect of the phenomenon that the orientation of macromolecules in the direction of the fibre axis depends on the value of the total drawing. In the case of both of the types of fibres discussed, the value of the elongation at break is within the range of 2.02 - 3.26% (**Table 3**).

Generally, we can state that the levels of sorption and tensile strength properties of both types of cupric alginate fibres are suitable for them to be processed into flat textile products devoted to medical applications, primarily to those products should which decrease the pain of patients and hospital linen.

Conclusions

1. Solutions of sodium alginate with water are non-Newtonian liquids thinned by shearing, without a flow limit irrespective of the molecular weight of the polymer.
2. With the application of sodium alginate with a lower molecular weight, there is a necessity to increase the polymer concentration in the spinning solutions.
3. The use of sodium alginate with a lower molecular weight does not significantly influence the changes in sorption properties of the cupric alginate fibres in comparison to those obtained from the polymer with a higher molecular weight.
4. The tensile strength properties of cupric alginate fibres absolutely depend on the molecular weight of the polymer. Its decrease causes a reduction in the susceptibility of the fibre matrix to deformation processes at the drawing stage, as well as resulting in a tenacity lower by 7 cN/tex in comparison to fibres obtained from the polymer with a higher molecular weight.

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