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Precursor Alginate Fibres Containing Nano-particles of SiO_2

Abstract
Conditions for the manufacture of fibres from calcium alginate have been developed. These fibres contain nano-particles of SiO_2, and are characterised by a high total volume and internal surface. Their tenacity at a level of 20 cN/tex makes it possible to use them as precursors to the preparation of carbon fibres, which, in turn, can facilitate the process of bone reconstruction owing to the presence of calcium and silicon. The effects of fibre spinning conditions and the quantity of incorporated SiO_2 nano-particles on fibre sorption and strength characteristics have been assessed.

Key words: *precursor, alginate fibres, calcium alginate, nano-particles, bone reconstruction, spinning conditions, fibre sorption, fibre strength.*

Introduction

The growing importance of alginates in the manufacture of modern active wound dressings is associated first of all with their very good absorption properties (especially their capability to absorb wound secretions) and their unique ion-exchange capabilities (the exchange of calcium ions from a dressing for sodium ions) [1,2]. Thus, they can form a moist gel *in situ* when in contact with a wound secretion. This would allow the dressing to be gently removed without pain, and without disturbing the newly formed delicate tissues [3,4].

These properties are connected with the chemical composition of alginates and the presence of blocks derived from α-L-guluronic and β-D-mannuronic acids, owing to which alginate fibres can be gelatinised [5]. The commercial dressings adapted to wound healing [6] which is mostly available in the market, under trade names such as Sorbsan™, Kaltostat™ and Algosteril™, are manufactured from calcium alginate or calcium-sodium alginate with a high content of guluronic or mannuronic acid.

Another field of application for calcium alginate fibres may be their use as precursors to the preparation of carbon fibres. Implants obtained from such fibres will support the process of bone reconstruction. This process can also be advantageously affected by the presence of silicon, one of the main components necessary to rebuild bones. This can be achieved by incorporating nano-particles of SiO_2 into alginate fibres during the preparation of the spinning solution.

In that connection, the present study was aimed at the assessment of the effects of as-spun draw ratio and the related extent of deformation during fibre drawing on the structure and properties of calcium alginate fibres containing nano-particles of SiO_2. The results should help (with the use of computer-aided experiment design [7]) to select the best conditions for spinning precursor alginate fibres.

The selection of fibre spinning conditions aimed at the maximisation of strength properties should result in precursor fibres with a tenacity at a suitable level for carbonisation. At the same time, due to the medical use of carbon fibres, the fibres from calcium alginate should show increased porosity.

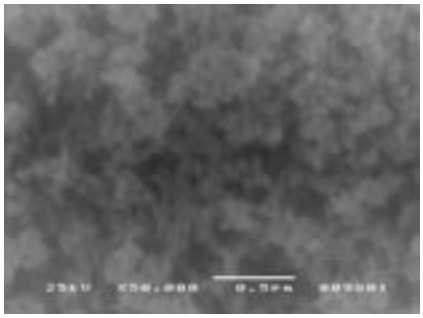

***Figure 1.** Scanning electron microscope image of SiO_2 nano-particles.*

Experimental

Characteristics of spinning solution

Spinning solutions were prepared from sodium alginate, Protanal LF 60/20, possessing in its structure more groups of guluronic acid than of mannuric acid. The spinning solutions were prepared with 3% and 5% additions of nano-particles of SiO_2 in relation to the polymer. The majority of the added SiO_2 nano-particles had a diameter of about 50 nm, as can be seen in the scanning microscope image (Figure 1). They showed a considerable tendency towards agglomeration. Alginate fibres were spun from 7% aqueous solutions of sodium alginate with a viscosity of 42.86 mPas.

The rheological properties of spinning solutions were determined by means of a rotary Rheotest RV. Measurements were performed with the use of an H cylinder within the range of shearing rate from 0.2 to $1.31\times10^3 s^{-1}$, while the shearing stress ranged from 12 to 3×10^3 N/m^2, at a temperature of 20°C.

Based on the obtained flow curves (Figure 2) of 7% sodium alginate solutions containing a 3% addition of SiO_2 nano-particles, one can state that these solutions are non-Newtonian fluids with no flow limit. The shearing stress increases less than proportionally with the increase in the shearing rate, while the flow curves cross the origin of the co-ordinates. The character of the flow curves of solutions containing higher SiO_2 additions is the same as that of the solution with a 3% SiO_2 addition. They show only different

Table 1. *Rheological properties of sodium alginate spinning solutions with SiO_2 nano-particles. The solution containing 10% and 15% of SiO_2 nano particles were only used to assess the effect of nano-particles content on their rheological properties.*

Spinning solution of sodium alginate	Rheological parameters			
	Initial solution		Solution after 168 h	
	n	K	n	K
without SiO_2 nano-particles	0.89	22.53	0.87	22.81
with 3% SiO_2 nano-particles	0.85	27.40	0.88	21.94
with 5% SiO_2 nano-particles	0.83	29.15	0.83	27.92
with 10% SiO_2 nano-particles	0.82	31.76	0.83	29.15
with 15% SiO_2 nano-particles	0.82	34.14	0.88	30.05

values of parameters *n* and *K* (Table 1) determined from the flow curves plotted in a double logarithmic system, where *n* and *K* are rheological parameters in Ostwald de Wael's power model [8].

The dynamic apparent viscosity decreases with the increase in the shearing rate (Figure 3) which is typical for polymeric fluids, and the character of this relationship is not changed with the SiO_2 nano-particle content. From the analysis of parameters *n* and *K*, it follows that the incorporation of SiO_2 nano-particles only slightly decreases parameter *n*, while it increases parameter *K*. This is a measure of the 'solution consistency'. One may assume that the nano-particles of SiO_2 which penetrate the polymer macromolecules bring about an increase in the internal friction of the system, and can change the intensity of solvation sheath tearing-off. Such phenomena are characteristic of fluids rarefied by shearing, and appear during the action of shearing stresses. The presence of SiO_2 nano-particles can also facilitate the secondary bond breakdown and alginate macromolecule straightening, which causes the system to assume a more non-Newtonian character. The addition of SiO_2 nano-particles dispersed in the polymeric solution increases the rheological parameter *K*. This increase rises as does the SiO_2 content in the system. The examination of spinning solutions containing the nano-particles of SiO_2 shows good stability of parameters *n* and *K* for a long period of time (168 h), and the flow curves obtained are practically superimposed on the curves obtained for the solution just after its preparation.

Fibre spinning

Fibres were spun from sodium alginate solution by the wet process, using a spinneret with 500 orifices of 0.08 mm in diameter. A laboratory spinning machine was used, which made it possible to stabilise the technological parameters at a predetermined level and keep them under continuous control. The solidification of fibres was performed in a bath containing 3-5% aqueous $CaCl_2$ solution and 0.3% HCl at a temperature below 50°C. The fibre drawing process was performed in two stages: in a plasticising bath with the same concentration as that of the solidification bath, and then in an atmosphere of overheated steam at 140°C. After the solidification the bath residues were washed off, and the fibres were dried at 40-60°C under isometric conditions.

Analytical methods

Fibre porosity was measured by means of a mercury porosimeter from Carlo-Erba, linked to a computer system to register the numerical values of the parameters measured. The determinations included the following: the total pore volume, the total internal surface, the volume of capillary group with a defined radius and the percentage content of pores. This method allows the percentage pore content to be determined with given ranges in the capillary set of a size of 5-7500 nm.

Moisture absorption at 65% and 100% relative air humidity was determined by the desiccator method according to the Polish standard PN-71/P-04635.

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

Fibre tenacity and elongation at break were measured according to the Polish standard PN-85/P-04761/04, referring to the breaking force to the linear density in tex.

The degree of sodium ion replacement with calcium ions [9] was also determined.

Results and Discussion

In the method of fibre spinning from solution by the wet process, fibre properties depend on the structure that has been formed during solidification and its deformability during the plastifying

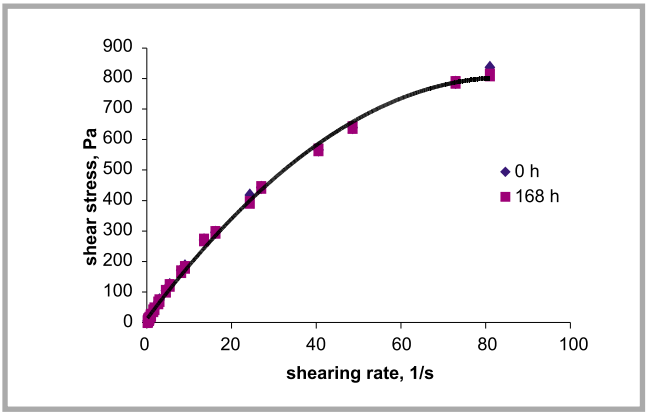

Figure 2. *Dependence of the shearing stress on the shearing rate for 7% sodium alginate solution containing 3% of SiO_2 nano-particles initially and after storing at 20°C for 168 h.*

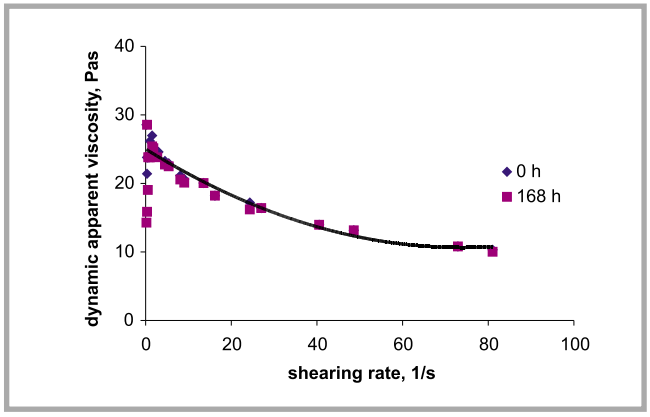

Figure 3. *Dependence of the dynamic apparent viscosity on the shearing rate for the solution as in Figure 1, initially and after storing at 20°C for 168 h.*

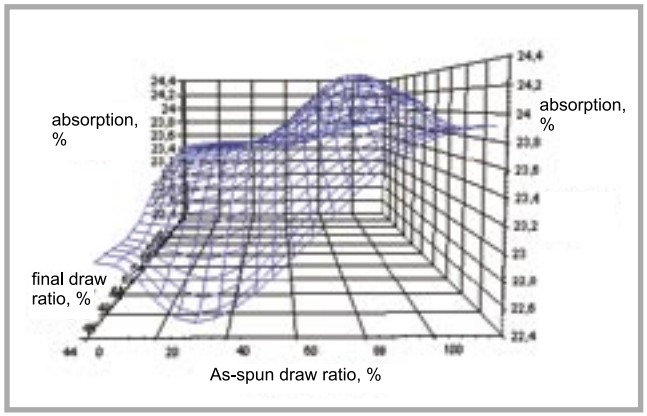

Figure 4. *Dependence of the moisture sorption at 65% RH on the as-spun draw out ratio and the total draw ratio for calcium alginate fibres containing 3% SiO_2 nano-particles.*

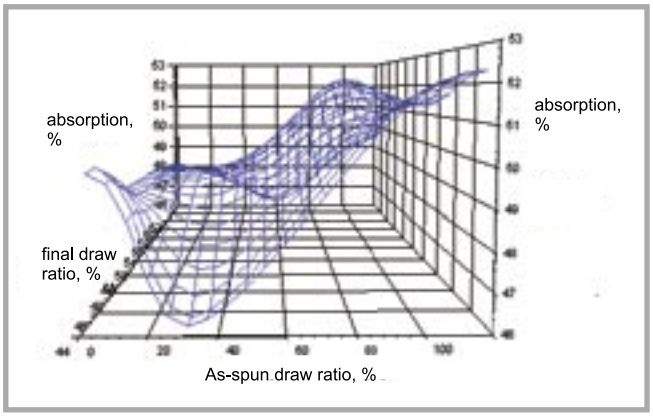

Figure 5. *Dependence of the moisture sorption at 100% RH on the as-spun draw out ratio and the total draw ratio for calcium alginate fibres containing 3% SiO_2 nano-particles.*

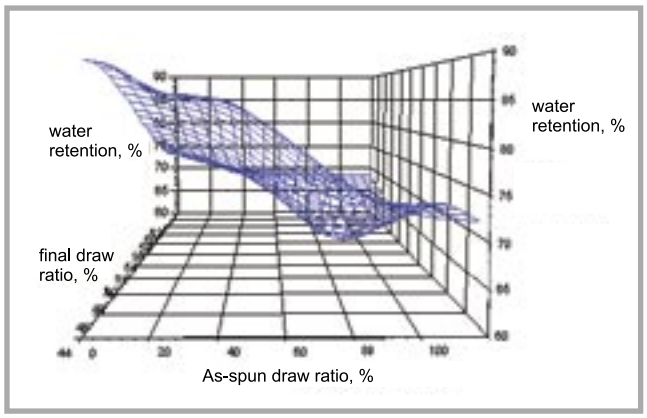

Figure 6. *Dependence of the water retention on the as-spun draw out ratio and the total draw ratio for calcium alginate fibres containing 3% SiO_2 nano-particles.*

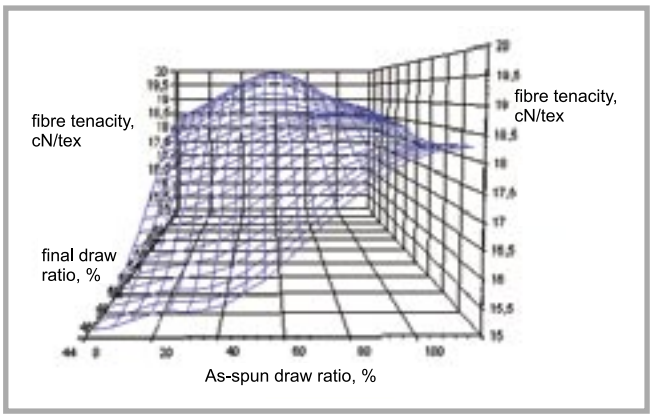

Figure 7. *Dependence of the tenacity on the as-spun draw out ratio and the total draw ratio for calcium alginate fibres containing 3% SiO_2 nano-particles.*

drawing. One of the basic parameters is the extent of the as-spun draw out ratio, and consequently the value of the related deformation during fibre drawing. The as-spun draw out ratio varied from 1% to 118.35% for fibres with 3% SiO_2 addition. The fibres spun from solutions containing 5% of SiO_2 nano-particles were formed with the as-spun draw out ratio amounting to 90.23% and 119.10%. When the addition of SiO_2 nano-particles was increased by more than 5%, the fibre forming process was disturbed.

The degree of replacement of sodium ions with calcium ions ranged from 8.5 to 9% (theoretical value: 10.27%), irrespective of the change in spinning conditions.

The change in the as-spun draw out ratio towards higher values (Figures 4 and 5) is accompanied by an increase in moisture absorption at 65% and 100% RH, with the maximum values of both indices being obtained by the fibres spun with the as-spun draw out ration amounting to 90%.

The value of water retention (Figure 6) is high, and ranges from 61% to 89%, assuming a different character of changes versus the parameters under investigation. The highest values of retention, from 65 to 85%, are obtained for fibres formed with the as-spun draw out ration below 30%.

The different characters of changes in water retention and sorption properties can be connected with different porous structures formed at various values of the as-spun draw out ratio and deformation during the fibre drawing stage. In the studies on other fibre-forming polymers [10], it has been found that these parameters considerably affect the percentage content of pores of particular types. The high values of water retention of alginate fibres are connected not only with the total volume of pores and the character of the porous structure formed under variable spinning conditions, but also with fibre swelling and water penetration into the supermolecular structure.

The tenacity of fibres (Figure 7) shows a growing trend with the change in the as-spun draw out ratio and the total draw

Table 2. *Percentage contents of capillary sets, internal surface and the total pore volume of calcium alginate fibres. Porosimetric measurements were performed in the Institute of Chemistry and Technology of Kerosene and Carbon at the Wrocław Technical University.*

Fibres from calcium alginate obtained from solutions with SiO_2 nano-particles	Total pore volume, mm^3/g	Internal surface of pores, m^2/g	Percentage pore content, %			
			small 4-12.3, mm	medium 12.3-75, mm	large 75-750, mm	very large 750-7500, mm
without SiO_2	54.32	1.82	6.82	0.0	11.36	81.72
3% SiO_2	91.25	4.53	18.07	8.22	10.96	65.75
5% SiO_2	90.69	5.53	16.67	11.54	10.26	61.53

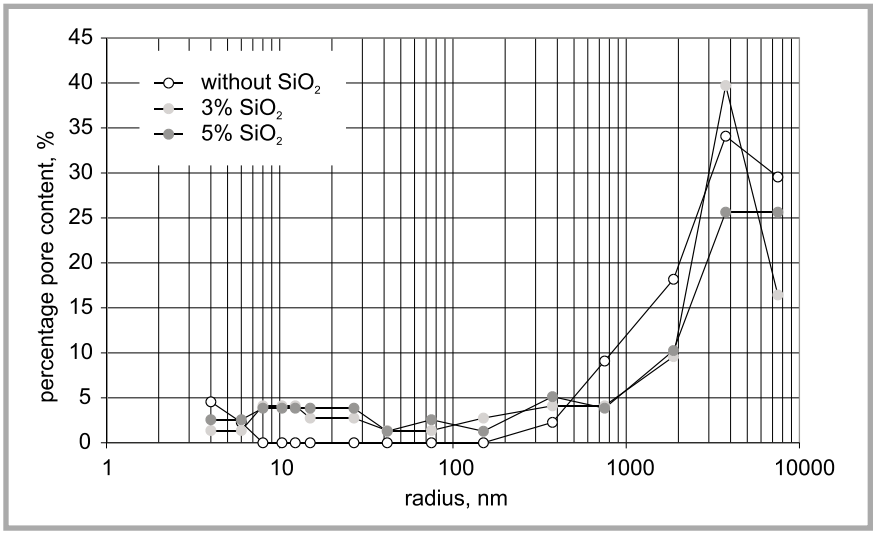

***Figure 8**. Curves of pore distribution versus pore radius; a - fibres without SiO_2 nano-particles, b - fibres spun from alginate solution containing 3% SiO_2 nano-particles, c - fibres spun from alginate solution containing 5% SiO_2 nano-particles.*

***Table 3.** Properties of alginate fibres obtained from solutions without and with 3% and 5% of SiO_2 nano-particles depending on the spinning conditions.*

SiO_2 content in the spinning solution	As-spun draw out ratio, %	Total draw ratio, %	Moisture sorption at 65% RH, %	Moisture sorption at 100% RH, %	Retention, %	Tenacity, cN/tex
without SiO_2	70.37	54.65	23.21	45.68	69.68	23.53
3%	60.00	63.66	23.48	46.43	69.44	19.93
5%	90.23	59.03	22.36	45.58	66.35	19.29

ratio towards higher values. The highest tenacity, amounting to about 20 cN/tex, is shown by the fibres formed at an as-spun draw out ratio of 60%. This is associated with the fact that with this as-spun draw out ratio, it was possible to obtain the highest total draw ratio (over 63%) in the fibre drawing stage.

From the analysis of the effect of SiO_2 nano-particles on the porous structure and sorption properties of fibres spun under the selected conditions, it follows that the fibres with the nano-particles of SiO_2 are characterised by an almost twice as high total pore volume as well as an internal surface that is 2.5 times greater in comparison with alginate fibres without SiO_2 nano-particles (Table 2). Generally, the porous structures are of similar character (Figure 8).

The pore distribution curves are characterised by a flat shape within the range of small and medium pores, and a high maximum within the range of very large pores. Depending on the quantity of the SiO_2 nano-particles incorporated, the quantitative contents of particular types of pores are different (Table 2). Fibres with SiO_2 nano-particles show an advantageous increase in the percentage contents of small and medium pores. With similar contents of large pores, about 10-11%, the incorporation of SiO_2 nano-particles into fibres is accompanied by a considerable decrease in the content of very large pores, amounting to about 20%. This is a very advantageous phenomenon, as these pores can cause structural defects which also appear in carbon fibres after carbonisation [11].

The domination of the porous structure by the high total content of large and very large pores may be explained by the fact that, despite some differences in the spinning conditions (the as-spun draw out ratio from 60 to 90% and the total draw ratio from 44.5 % to 63%) (Table 3) and significant differences in the values of total pore volume and internal surface, both the fibres with and without SiO_2 nano-particles show similar sorption properties and water retention.

Despite the increased total content of pores capable of absorbing moisture by capillary condensation (small and medium pores) from the level of 6.8% for fibres with no SiO_2 to 23.3-28.2% for fibres with 3% and 5% SiO_2, respectively, and a considerable increase in the total pore volume, the increase in moisture absorption at 100% RH is rather small, amounting to only 1%. Thus, one may assume that the sorption properties of fibres are subject to the dominating effect of the hydrophilic character of the fibre-forming polymer. The values of water retention of these three types of fibres are also similar. This is quite understandable due to the similar contents of large pores, about 10-11%.

The fibres without the addition of SiO_2 nano-particles were spun under conditions which are favourable due to their sorption properties. The total deformation of the fibres without SiO_2 and with 3% of SiO_2 was the same, whereas those of the fibres with 5% of SiO_2 was slightly higher.

The value of retention is connected with the percentage content of pores that are large enough to be able to absorb water and small enough to retain water after the operation of its mechanical removal.

The incorporation of SiO_2 nano-particles into alginate fibres brings about a decrease in fibre tenacity of about 15%.

One may assume that the sometimes larger agglomerates of SiO_2 nano-particles between macromolecules can hinder their mutual approach and linkage with secondary bonds. Some effect on the fibre tenacity can be exerted by the presence of the non-fibre-forming SiO_2 nano-particles, which have no laminar structure as in the case of the intercalated montmorilonite. However, when the SiO_2 content is increased up to 5%, there is no further decrease in the fibre tenacity.

Generally, the value of fibre tenacity at a level of 20 cN/tex is suitable for their processing into carbon fibres. Due to the fact that carbon fibres would be designed for implants used for bone reconstruction, in addition to the presence of calcium and silicon, the high porosity and internal surface of the precursor fibres are also of paramount importance.

Conclusions

- The spinning solutions of sodium alginate containing SiO_2 nano-particles are non-Newtonian fluids, rarefied by shearing without a flow limit, and show good stability of rheological parameters for a long period of time. The

incorporation of SiO_2 nano-particles into alginate fibres is accompanied by a decrease in rheological parameter *n* and a increase in parameter *K*.

- The incorporation of SiO_2 nano-particles into alginate fibres made it possible to obtain precursor fibres, which after carbonisation could be used to produce implants which should activate and support the process of bone reconstruction due to the presence of calcium and silicon. The further processing of the alginate fibres obtained into carbon fibres will be the aim of our future investigations.
- The alginate fibres obtained under the selected conditions are characterised by an high total pore volume which is advantageous, due to the fibre's future use, and an internal surface with a tenacity of 20 cN/tex that is suitable for the carbonisation process.
- The incorporation of SiO_2 nano-particles in an amount of 5% does not significantly influence the fibre sorption properties despite increased fibre porosity, but it causes the fibre tenacity to decrease by 15%.

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