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Zinc Alginate Fibres with a Silica (SiO₂) Nanoadditive

Abstract

Conditions were found for the manufacture of zinc alginate fibres with a silica (SiO_2) nanoadditive based on earlier studies involving nanocomposite zinc alginate fibres with a TCP nanoadditive. In this study, we determined the effect of the basic parameters of the forming process, such as the as-spun draw ratio and associated deformation at the drawing stage, on the porous and supramolecular structure as well as sorption and strength properties of zinc alginate fibres with nanoadditive SiO_2. A comparative analysis was made of the structure and properties of fibres containing nanoadditives tricalcium phosphate (TCP) and SiO_2. The effect of the type of nanoadditive on the structure and properties of the fibres studied was determined.

Key words: *alginate fibres, nanoadditive, fibre forming, properties nanocomposite fibres.*

Introduction

The use of alginate fibres in medicine, particularly in the form of dressing materials, is based on specific properties which support the wound healing process. Dressing materials available on the market which are produced using alginate fibres include Kaltocarb®, Kaltostat®, Kaltogel® (Conva Tec), Sorbsan® (Pharma-Plast), Sorbalgon® (Hartmann) and Algisite M® (Smith&Nephew). [1] However, there are no products on the market made from zinc alginate fibres. Modification of fibre material through the addition of antibiotics or a silver nanoadditive during the fibre forming process gives it an antibacterial function [2, 3] or provides the resulting dressing with specific properties. An important role is also played by the high sorption properties of alginate fibres, which enable the removal of moisture from the wound, thus creating a suitable microclimate for regenerative processes.

The obtaining of biocomposites containing calcium alginate fibres with various types of ceramic nanoadditives, such as hydroxyapatite (Hap), tricalcium phosphate (TCP), silica (SiO_2) and montmorillonite (MMT) [4, 5, 6], increases their scope of application and may lead to the development of modern implant materials supporting the regeneration of bone tissue. Polymer-fibrous composites may become a breakthrough material, taking the place of traditional metallic implants. This is due not only to the similarity of the three-dimensional structure of such a composite to natural bone but also to the presence of a nanoadditive in the fibre material with a osteoconductive or osteoinductive effect.

The presence of alginate fibres in such a biocomposite will improve the biocompatibility of an implant with bone cells. [7] The introduction of alginate fibres from zinc alginate means that the surface of the implant will undergo modification under the influence of body fluids. As a result of the resorption of nanocomposite alginate fibres, a porous structure will also be formed, which will favour the adhesion of the newly formed cells and better integration of the implant with the patient's own tissue. Moreover the nanoadditive released will act osteoconductively.

The original concept of using nanocomposite alginate fibres is based on their use to produce a biocomposite in the form of a double-layer fibrous material, also containing nanofibres made from another less easily resorbable polymer.

The present work is a continuation of research aimed at identifying conditions for the manufacture of zinc alginate fibres containing various ceramic nanoadditives. The structure and properties of fibres containing nanoadditive SiO_2 will be compared with fibres containing nanoadditive TCP. [8] A comparative analysis will also be made of the supramolecular structure of the two types of nanocomposite zinc alginate fibres.

The aim of this work is to determine the effect of a basic process parameter, namely the as-spun draw ratio, and associated (attainable) deformation at the drawing stage on the porous and supramolecular structure as well as sorption and strength properties of zinc alginate fibres containing nanoadditive SiO_2.

Experimental section materials and methods

Description of the polymer, nanoadditive and spinning solution

A description of the polymer used to form zinc alginate fibres is contained in [5].

The nanoadditive used in the case of the fibres studied was SiO_2 (a commercial product from Sigma Aldrich). The methodology of introducing the nanoadditive in a quantity of 3% relative to the mass of the polymer, and the concentration of the spinning solution were analogous to those in [5].

The spinning solution containing nanoadditive SiO_2 obtained had the following rheological parameters: $n = 0.709$, $k = 34.183$.

Experimental methods

The nanoadditive used had a medium particle size, as determined by the dynamic light scattering technique. A detailed description of the nanoadditive, including the distribution of particles by quantity and volume, can be found in [9]. The methods used to determine the properties of the fibres and their porous structure are described in [8].

For investigation of the macroscopic structure, a JEOL JSM 5400 scanning electron microscope was used.

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The distribution of nanoadditives in the fibres was analysed based on images produced using a JSM 5400 scanning electron microscope with an OXFORD INSTRU-MENTS EDX LINK ISIS analyser of the dispersion of characteristic radiation energy. The results of the EDX analyses are presented in the form of an EDX spectrum and maps of the distribution of selected elements within the region analysed.

The topography of the surface of the fibres was investigated using an atomic force microscope (AFM).

The index of the change in the shape of the cross-section of fibres was determined based on images produced using the JSM 5400 scanning electron microscope, by measuring the radii of the smallest circumscribed circle and the largest inscribed circle of the cross-section. Measurements were made using a CSS Scan Multi Scan computer program. The value of the index of the change in the shape of the cross-section was determined as a ratio of the smallest circumscribed circle to the largest inscribed circle of the cross-section. This value lies within the range of 1 to infinity; the larger it is, the greater the deviation of the shape of the fibre cross-section from being circular. [10]

The average degree of the swelling of the fibres was investigated using a biological microscope integrated with a computer system, enabling measurement of the diameter of swollen fibres (CSS Scan Multi Scan). Tests were performed until the stabilisation of measurements of the fibre diameter in constant conditions was achieved. The average degree of swelling was determined as a ratio of the difference between wet and dry fibre diameters to the diameter of dry fibre, expressed as a percentage.

The degree of crystallinity was determined by the wide-angle X-ray diffraction (WAXS) method, using a Seifert URD 6 diffraction meter with a copper lamp emitting radiation of wavelength $\lambda = 0.154$ nm under supply parameters $U = 40$ kV, $I = 30$ mA. Diffraction curves were recorded using the reflective method and stepwise measurement. WAXS diffraction curves for alginate fibres were analysed using a WAXSFIT computer program [11, 12] The degree of crystallinity was calculated as a ratio of the integral intensity contained within the crystalline peaks to the integral intensity of radiation dispersed by the sample over the entire measurement range (after the subtraction of background radiation).

Zinc alginate fibres were formed by a wet process from solution using distilled water as a solvent. The coagulation process took place in a bath containing $ZnCl_2$ and HCl at a temperature of 40°C. The concentration of the spinning solution of sodium alginate was 7.4%. The drawing process was conducted in two stages: the first used a plasticisation bath containing $ZnCl_2$ and 0.03% HCl at a temperature of 67°C, and the second took place in a superheated steam atmosphere at 135°C.

Following the drawing process, the fibres were washed and dried.

A large-scale laboratory spinning machine was used for fibre formation. It was constructed so as to enable the stabilisation and monitoring of technological parameters and the regulation of the speed of the stretching systems.

The coagulation and plasticisation baths were subjected to constant circulation in order to keep their concentration constant, and a thermostat was used to maintain a constant temperature.

The spinning nozzles used had 240 holes, with a hole diameter of 0.08 mm.

Fibres were formed in conditions which had been previously established based on results obtained for zinc alginate fibres with nanoadditive TCP. [8]

The variable parameter was the value of the as-spun draw ratio, which varied over a range of positive values from +30% to +110%. The attainable deformation at the stretching stage associated with this parameter also varied.

Discussion of results

Effect of pull-out at the spinning nozzle and associated deformation at the stretching stage on the properties of zinc alginate fibres

Analysis of the sorption properties of zinc alginate fibres containing nanoadditive SiO_2 shows that, similar to the case of fibres containing nanoadditive TCP, their sorption properties are associated mainly with the hydrophilic nature of the material. Moisture sorption at 65% RH is within the range of 20.67-22.19%,
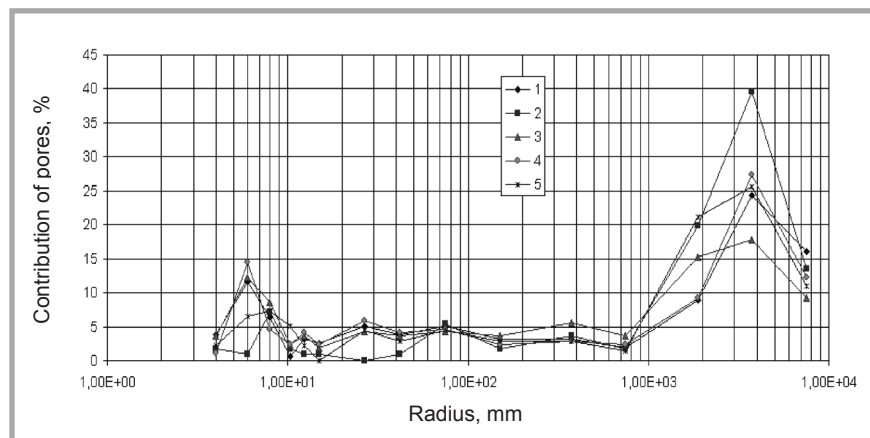

Figure 1. *Percentage contribution of pores as a function of their radius for zinc alginate fibres containing nanoadditive SiO_2. 1 – AZS1 as-spun draw ratio +30%; 2 – AZS2 as-spun draw ratio +50%; 3 – AZS3 as-spun draw ratio +70%; 4 – AZS4 as-spun draw ratio +90%; 5 – AZS5 as-spun draw ratio +110%.*

Table 1. *Porous structure and sorption properties of nanocomposite zinc alginate fibres containing nanoadditive SiO_2.*

Sample symbol	As-spun draw ratio, %	Total volume of pores, cm³/g	P_1, cm³/g	Total internal surface of pores, m²/g	Moisture sorption at 65% RH, %	Moisture sorption at 100% RH, %	Water retention, %	Zinc concentration, %
AZS 1	+30	0.332	0.1680	35.942	20.67	36.48	73.43	10.40
AZS 2	+50	0.231	0.0625	10.371	22.08	36.88	66.26	10.81
AZS 3	+70	0.354	0.2040	43.144	20.81	35.86	59.67	11.41
AZS 4	+90	0.351	0.1796	37.361	21.64	36.40	56.35	11.00
AZS 5	+110	0.291	0.1234	24.933	22.19	36.57	62.05	10.70

Table 2. *Conditions of forming and strength properties of nanocomposite zinc alginate fibres containing nanoadditive SiO₂.*

Sample symbol	As-spun draw ratio, %	Draw ratio, %			Stress at drawing, cN/tex			Total deformation	Linear mass, tex	Tensile strength, cN/tex	Standard deviation, cN/tex	Elongation at break, %
		R_1	R_2	R_c	σ_{coag}	σ_{plast}	σ_{steam}					
AZS 1	+30	179.83	4.77	193.18	0.038	1.598	0.848	3.81	54.07	22.74	0.61	5.73
AZS 2	+50	146..77	15.79	185..73	0.044	1.820	1.104	4.29	48.67	22.99	0.57	5.64
AZS 3	+70	150.21	22.73	207.08	0.051	2.285	1.463	5.22	39.63	24.38	0.72	5.69
AZS 4	+90	137..33	28.31	204.52	0.053	2.175	1.623	5.79	37.47	21.90	1.21	4.82
AZS 5	+110	134.77	9.27	156.54	0.063	2.704	0.964	5.39	38.03	21.36	1.06	4.65

which is slightly lower than for fibres containing nanoadditive TCP, for which these changes lie within the range 23.70-25.04%. However, a significantly lower level, by around 10%, was recorded for the range of changes in moisture sorption at 100% RH, the values of which are in the range 35.86-36.88%, compared with the higher values of 41.87-43.72% obtained for zinc alginate fibres containing the TCP nanoadditive. [8]

These differences may result from the nature of the porous structure and the value of the total pore volume. Considering the porous structure as similar to that in the work on alginate fibres containing TCP, the value P_1 was taken to be the total volume of pores corresponding in the fibres to pores in the radius range of 4-1000 nm, ascribed to the porosity of elementary fibres. P_2 was taken to be the value of the total volume of pores in the sample with radii in the range of 4-5000 nm, which includes the porosity of the fibrous material in addition to P_1. [8]

Comparison of the value for the total volume of pores in the two types of nanocomposite zinc alginate fibres shows that the slightly lower value of P_1, reaching 0.204 cm³/g (compared with 0.343 cm³/g for fibres containing TCP), is also associated with the lower values of moisture sorption at 100% RH for fibres containing nanoadditive SiO₂. This corresponds to the height of the first maximum on the graph showing the percentage contributions of pores as a function of their radius (*Figure 1*). At the same time the bimodal nature of the pore distribution curve was maintained for both types of nanocomposite fibres.

The value of water retention, being at a high level – around 56.35-73.43% (*Table 1*), is also associated with the proportions of pores in the fibrous material with dimensions in the range of 1000–7500 nm, which corresponds to the occurrence of the last maximum on the

graph showing the percentage contributions of pores as a function of their radius (*Figure 1*).

This type of porosity is probably due to the presence of empty spaces between monofilaments and to the non-uniformity of the fibre surface. In spaces of this type, it is possible for water to be retained as a result of the linking of polymorphic clusters via hydrogen bridges with unsubstituted OH groups in the material. A porosity higher than 50% is advantageous in the range 1000-7500 nm because it will favour the penetration of body fluids and the adhesion of newly formed cells in an implant material made using such fibres. [16]

When considering the high level of water retention of fibres containing nano-SiO₂, account must be taken of the fact that it also includes the swelling of fibres, as determined based on the change in their diameter. The value of the average degree of swelling (*Figure 2*) is at a significantly lower level (compared with the water retention value), lying within the range of 23.51-39.37%. It is notable that this index tends to increase along with thespun draw ratio. In the case of retention, no such relationship was observed.

In determining the swelling value, account was taken of changes occurring within a time of up to 30 minutes, and the
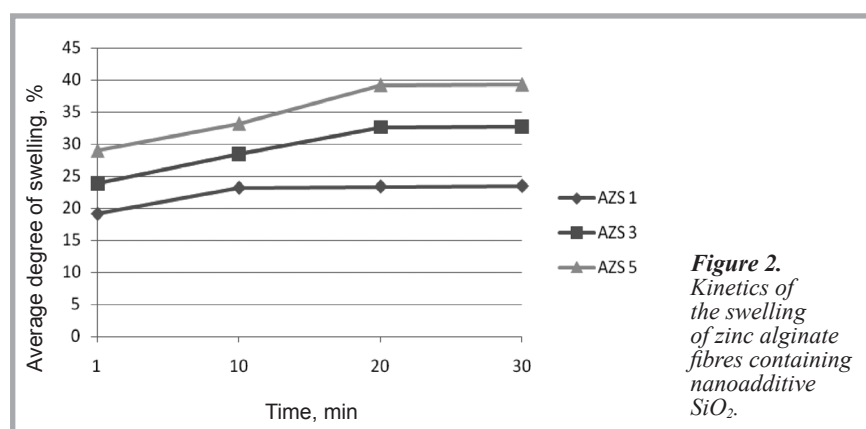

Figure 2. Kinetics of the swelling of zinc alginate fibres containing nanoadditive SiO₂.

Table 3. *Degree of crystallinity and dimensions of crystallites in zinc alginate fibres containing nanoadditives SiO₂ (AZS 1, 3, 5) and TCP (AZT 1, 3) and without a nanoadditive (AZ 2).*

Sample symbol	As-spun draw ratio, %	Total draw ratio, %	Degree of crystallinity, %	Dimensions of crystallites		
				D_{100} (M), nm	$D_{110/011}$ (G), nm	D_{101} (M/G), nm
AZS 1	+30	193.18	18	5.6	4.7	5.7
AZS 3	+70	207.08	16	4.8	4.2	5.2
AZS 5	+110	156.54	20	5.4	4.2	4.9
AZT 1	+30	231.75	17	4.2	3.9	3.4
AZT 3	+70	169.97	15	4.7	4.1	3.7
AZ 2	+50	246.46	16	3.9	3.1	3.5

D_{100} (M) = dimension of crystallites in a direction perpendicular to the planes (100) in mannuronic crystallites, $D_{110/011}$ (G) = average dimension of crystallites in directions perpendicular to the planes (110) and (011) in guluronic crystallites, D_{101} (M/G) = average dimension of crystallites in directions perpendicular to the planes (110) and (011) in guluronic and mannuronic crystallites.
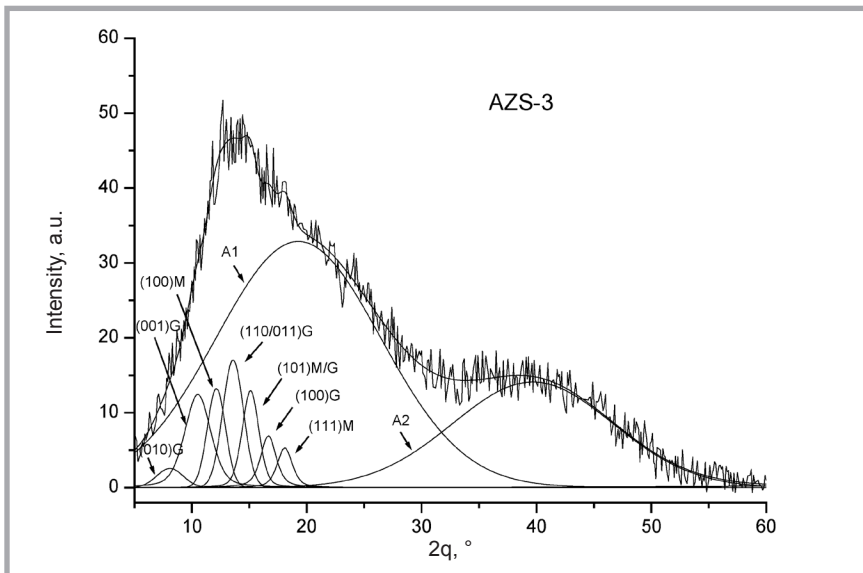
Figure 3. *Distribution of the diffraction curve for zinc alginate fibres containing nanoadditive SiO₂; a.u. – arbitrary unit.*

nature of the curves showing the kinetics of swelling indicate that the process stabilises after the expected time (**Figure 2**).

Analysis of the strength properties of nanocomposite zinc alginate fibres containing nanoadditive SiO₂ (**Table 2**) shows that the tensile of the fibres is significantly affected by the value of the as-spun draw ratio and associated deformation at the drawing stage. The highest value of this indicator was found for fibres formed at an as-spun draw ratio of +70%, similar to the case of calcium alginate fibres containing SiO₂. [6] However, the highest values of tensile strength for zinc alginate fibres containing nanoadditive TCP were obtained when fibres were formed at an extreme low value of the as-spun draw ratio (+30%). Moreover the level of strength properties for both types of na-

nocomposite zinc alginate fibres is similar: 24.38 cN/tex and 24.72 cN/tex (for zinc alginate fibres containing TCP). [8] Here the decisive factor behind the highest strength properties of fibres containing nanoadditive TCP was the highest achievable value of the total draw ratio (at a level of 244.30%). In the case of fibres containing SiO₂, the decisive factor was the deformation of the still liquid stream of polymer as the value of the total draw ratio was 40% lower than that for fibres containing TCP .

In the coagulation process, the structure of fibres containing SiO₂ was shaped by the influence of the higher stresses (**Table 2**), compared with fibres containing nano-TCP. [8] In particular this applies to the fibres with the highest strength properties in the series. For fibres containing

SiO₂ the stresses in coagulation are twice as high as in the case of fibres containing nano-TCP [8], which explains the similarity of strength properties for both types of nanocomposite fibres in spite of the lower attainable value of the total draw ratio for fibres containing nano-SiO₂. It is known that higher stresses are favourable for the effectiveness of deformation processes and associated strength properties. [6]

It is known that the strength properties of alginate fibres are dependent on the number of bonds between macromolecules, zinc and on the number of secondary bonds. [8] These properties are also connected with the occurrence of an egg-box structure [2] and supramolecular structure. A detailed analysis of the effect of these two factors on the properties of calcium alginate fibres, including those containing nanoadditives, can be found in our earlier work. [5, 13]

Analysis of the crystalline structure of zinc alginate fibres

The crystalline structure of zinc alginate fibres was analysed for both fibres without a nanoadditive (AZ 2) and for fibres with nanoadditives SiO₂ and TCP, having the highest strength properties (AZS 3, AZT 1). The tests also included fibres containing nano-TCP formed at an as-spun draw ratio of +70% (AZT 3), as well as fibres containing nano-SiO₂ formed at an as-spun draw ratio of +30% (AZS 1) and at an extreme positive value of pull-out: +110% (AZS 5). [8]

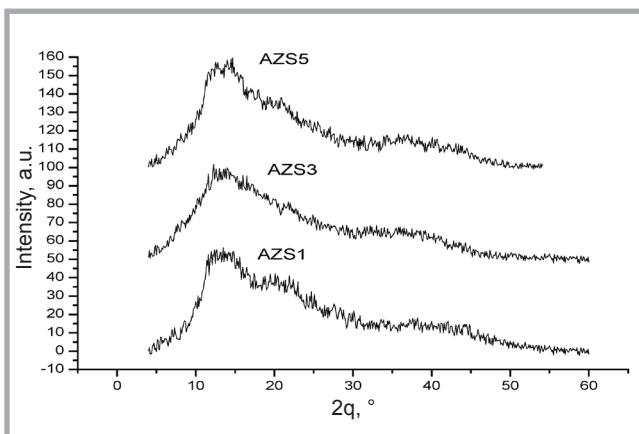An example of the distribution of a diffraction curve into crystalline peaks

Figure 4. *Comparison of diffractograms for zinc alginate fibres containing nanoadditive SiO₂; a.u. – arbitrary unit.*
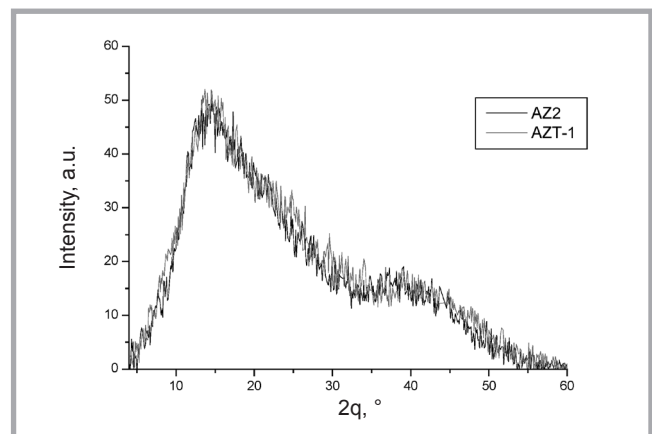

Figure 5. *Comparison of diffractograms for zinc alginate fibres containing nanoadditive TCP (AZT 1) and those for zinc alginate fibres without a nanoadditive (AZ 2); a.u. – arbitrary unit.*
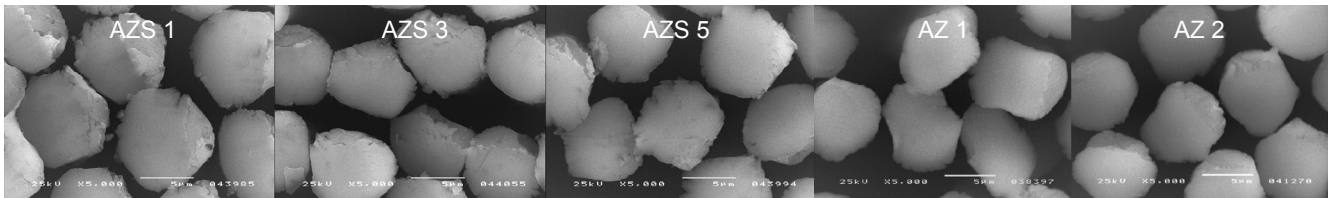
Figure 6. Cross-sections of zinc alginate fibres containing nanoadditive SiO_2 (AZS 1, 3, 5) and of fibres without a nanoadditive (AZ 1, 2).

originating from crystallites built of mannuronic (M) and guluronic (G) blocks is given in *Figure 3* for fibres containing SiO_2 formed at an as-spun draw ratio of +70%. A comparison of diffractograms for fibres containing nano-SiO_2 formed at different values of the as-spun draw ratio is shown in *Figure 4*. A comparison of diffractograms for zinc alginate fibres containing nano-TCP and zinc alginate fibres without a nanoadditive is shown in *Figure 5*.

Values for the degree of crystallinity and dimensions of crystallites for the fibres analysed are given in *Table 3*.

Based on the analysis of the results (*Table 3*), it can be concluded that the introduction of nanoadditives SiO_2 or TCP into the fibre material and the value of the as-spun draw ratio have only a small effect on the degree of crystallinity and do not cause significant differences in the dimensions of crystallites. The crystallinity of all the zinc alginate fibres analysed is practically within the range of measurement error and can be regarded as similar. The same also applies to the dimensions of crystallites, as the high overlapping of peaks for particular planes means that the measurement error for crystallite dimensions is of an order of between 0.5 and 1 nm.

Analysis of the shape of the fibre cross-section, fibre surface and distribution of the nanoadditive in zinc alginate fibres

The shape of the cross-section of both fibres without a nanoadditive and those containing nano-SiO_2 is close to being circular (*Figure 6*), with values of the index of the change in shape of the cross-section lying within the range of 1.21–1.26 (*Table 4*).

A slightly lower value for this index, equal to 1.18, was obtained for fibres containing SiO_2 formed at an extreme positive value of the as-spun draw ratio. This may be connected with the fact that

when the as-spun draw ratio is higher (fibres from gel with a smaller diameter), the gel syneresis process is more uniform. During the coagulation of alginate fibres, the processes of ion exchange and gel formation are accompanied by phase division and syneresis of the gel i.e. the solvent is pressed out of the system, and the net contracts. [14, 15]

The surface of fibres containing nanoadditive SiO_2 displayed cracks and scratches of various widths and lengths, this being typical of fibres formed by a wet process from solution. Analysis of the topography of the surface using an atomic force microscope also showed the presence of scratches on the surface, shown in *Figure 7* for fibres without a nanoad-
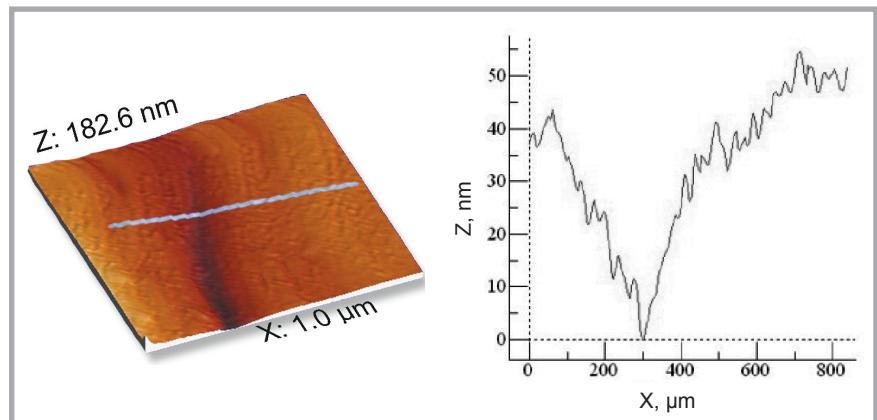

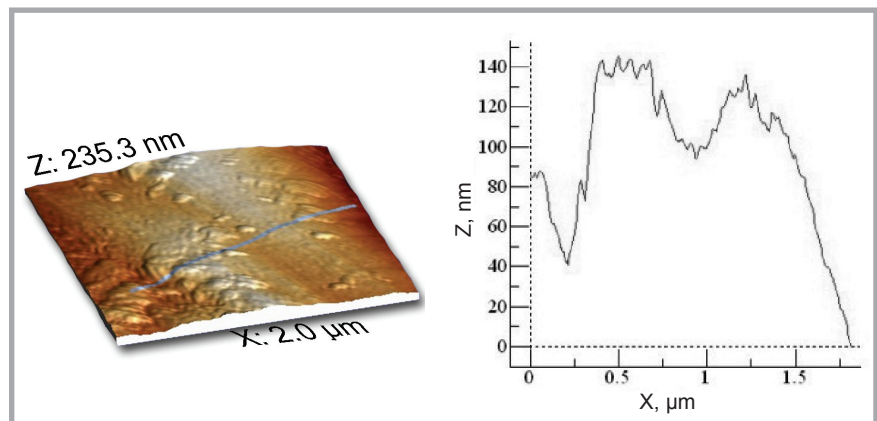*Figure 7. Analysis of the surface topography of zinc alginate fibres without a nanoadditive.*

Figure 8. Analysis of the surface topography of zinc alginate fibres containing nanoadditive SiO_2.

Table 4. Values of the index of the change in shape of a cross-section of zinc alginate fibres containing nanoadditive SiO_2 (AZS 1, 3, 5) and of fibres without a nanoadditive (AZ 1, 2).

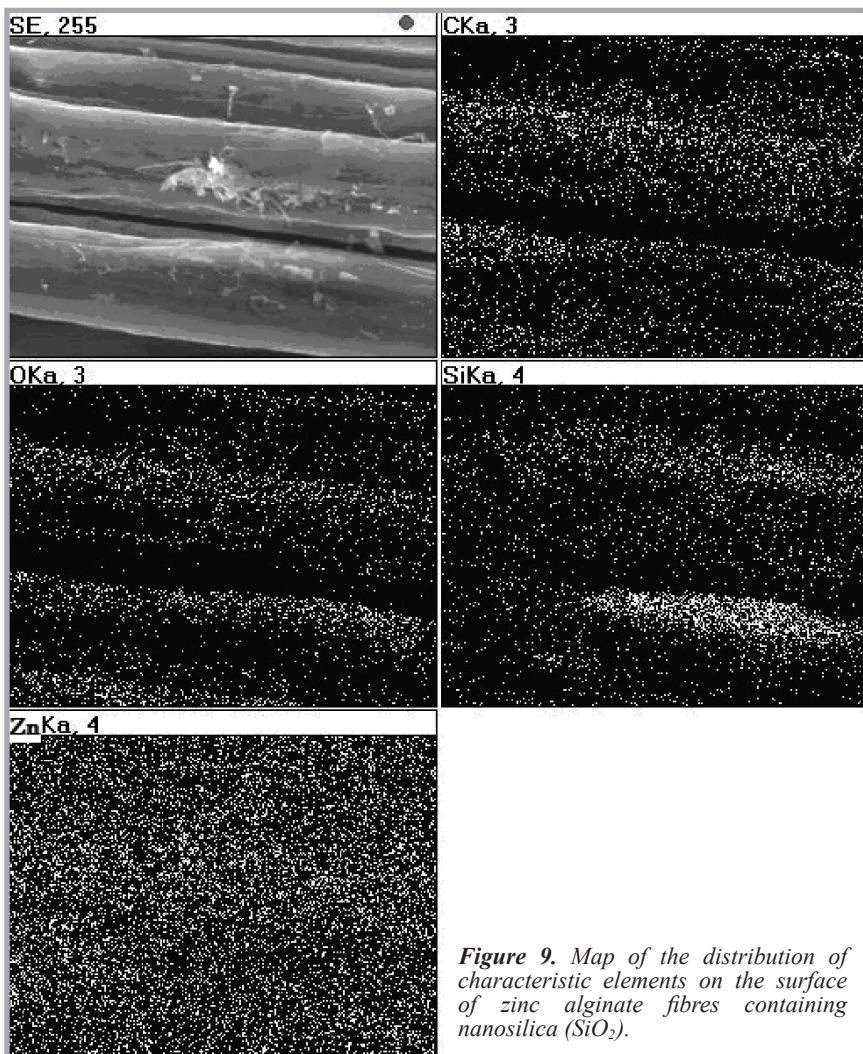| Sample symbol	As-spun draw ratio, %	Index of change in shape	Standard deviation	Tensile strength, cN/tex
AZS 1	+30	1.26	0.25	22.74
AZS 3	+70	1.23	0.22	24.38
AZS 5	+110	1.18	0.19	21.36
AZ 1	+30	1.21	0.18	27.98
AZ 2	+50	1.22	0.23	28.69

Figure 9. *Map of the distribution of characteristic elements on the surface of zinc alginate fibres containing nanosilica (SiO₂).*

ditive, and the non-uniformity of the surface, connected with the presence on it of agglomerates of nanoadditive SiO_2 (**Figure 8** – see page 43). Both of these phenomena are favourable with regard to the adhesion of newly formed cells.

The presence of characteristic chemical elements originating from the material of the fibres and the nanoadditive was confirmed by SEM+EDS analysis. The distribution of the nanoadditive on the surface of the fibres can be considered as being fairly uniform (**Figure 9**). Larger concentrations of elements originating from the SiO_2 nanoadditive only occur sporadically on the surface of fibres.

■ Summary

The sorption properties of nanocomposite zinc alginate fibres are determined by the hydrophilic nature of the material. The approximately 10% lower values of moisture sorption at 100% RH obtained for fibres containing nano-SiO_2 compared with those containing nano-TCP are connected with differences in the nature of the porous structure up to 100 nm. Differences in the values of water retention for the two types of nanocomposite zinc alginate fibres are linked to the porosity of the fibrous material.

To obtain a tensile strength of 24.3 cN/tex for fibres containing nano-SiO_2, they must be formed with a higher value of the as-spun draw ratio (around +70%) than for fibres containing nano-TCP.

With comparable degrees of crystallinity and crystallite dimensions, the highest tensile strength obtained for fibres containing nanoadditive SiO_2 is due to the deformation of the still liquid stream, which is connected with the value of the as-spun draw ratio, while for fibres containing nanoadditive TCP, a greater role is played by the attainable value of the total draw ratio.

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