Zinc Alginate Fibres with a Tricalcium Phosphate (TCP) Nanoadditive

Abstract

Conditions were found for the manufacture of zinc alginate fibres with a tricalcium phosphate (TCP) nanoadditive. The effect of essential forming process parameters were determined, such as temperature, solidification and plasticisation bath concentration, as well as as-spun draw ratio values for a porous structure and strength properties of nanocomposite zinc alginate fibres. A comparative analysis of the fibre properties with and without the nanoadditive was conducted.

Key words: alginate fibres, nano-additive, fibre forming, nanocomposite fibre properties.

Introduction

Recently the use of alginate fibres in the manufacture of advanced active dressings has been increasing [1 - 4]. This is due to their specific properties, which include the capability to facilitate wound healing processes and favourable sorption properties. Furthermore, alginate fibres can be rendered bacteriostatic or their electric properties can be modified, extending the range of medical applications [5 - 7].

The presence of nanoadditives with osteoconductive (HAp and TCP) or osteoproducive (SiO₂ and bioglass) nanoadditives in fibres determines their use for the manufacture of a new generation of implantable materials [8]. Structural penetrability by physiological fluids and related sorption properties determines the biodegradation rate of the alginate fibres that make up the biocomposite as well as the release of the nanoadditives they contain. Their properties are also related to the structure of the original polymer, sodium alginate.

The prevalence of blocks originating from guluronic or mannuronic acid in the macromolecule chain determines the properties of divergent metal alginites and, in particular, the capability of gelting, as well as the properties of the resulting gel.

The stoichiometric structure of guluronic acid blocks and the spatial arrangement of acidic groups are the conditions for the formation of the egg-box structure, which hinders the process of ion exchange occurring in an aqueous environment. Gels that form from fibres originating from HG (high-guluronic) alginites are classified as hard gels, and those originating from HM (high-mannuronic) alginites are considered soft gels, because the water absorbing and ion exchange capacity is increased in the latter. Furthermore, the rigidity of individual blocks in chains was found to rise in the sequence MG < MM < GG [9 - 11].

Due to these properties, high-mannuronic acid sodium alginate was selected as the polymer for the preparation of the alginate fibres used throughout the present study. It was assumed that the increased content of mannuronic acid blocks would make macromolecule fragments approach one another and be linked with secondary bonds. Furthermore, higher chain flexibility should contribute to higher deformations at the drawing stage as compared to fibres manufactured from high-guluronic alginate, which should result in a better tensile strength with a simultaneously increased elongation at break; both being relevant to easy fibre processability into unwoven fabrics. As our previous results prove [12], this is especially important due to the fact that the presence of nanoadditives in the material reduces the sensitivity/susceptibility to deformation at the drawing stage. The resulting gel form (“soft gels”) may favourably contribute to cellular growth processes and the easier biodegradation of the composite material manufactured from such fibres. The selection of zinc alginate fibres as the material was due to its bactericidal properties, which were determined by us earlier [13]. The TCP nanoadditive was selected because of its osteoconductive activity. These properties are beneficial, given the application of the biocomposite manufactured from the fibres.

The objective of the study was to select conditions for the solidification and plasticisation drawing stages as well as to determine the effect of the as-spun draw ratio and related deformation at the drawing stage on the structure and properties of zinc alginate nanocomposite fibres.

After the comparison of their structures and properties with those of fibres not containing the nanoadditive, the effect of the TCP nanoadditive on the material were be evaluated.

On the basis of the results, conditions were selected for the manufacture of zinc alginate nanocomposite fibres with supreme strength properties and, simultaneously, advantageous sorption properties, as these fibres are utilised in the manufacture of nonwoven fabrics as a component of a bi-layer composite produced with another biodegradable polymer.

Materials and methods

The intrinsic viscosity of the polymer was determined using distilled water as a solvent with the addition of lithium chloride at 25 °C. A dilution viscometer was used for the determination.

For the determination of the rheological properties of the spinning solutions, an Anton Paar rotary rheometer was used. Measurements were conducted at a shear rate of 80 1/s at 20 °C. Rheological parameters n and K were determined based on flow curves.

The nanoaditive grain size distribution was analysed with a Nano-ZS Zetasizer of Malvern Inc., which uses dynamic laser light scattering technology. The dynamic light scattering method is based on the Brownian movement of particles in a liquid and measures particles with equivalent diameters of 0.1 nm to approx. 6 μm in aqueous and non-aqueous media.

Specific surface measurements were carried out using a Nova 1200e Quanterme Inst. by the BET adsorption isotherm method. The multi-point procedure was applied by selecting six points in the relative pressure (P/Pₒ) range described in the BET equation (P/Pₒ = 0.05 – 0.3). Nitrogen was used as the adsorbate, and the measurement was conducted at liquid nitrogen temperature (77 K).

Samples were degassed prior to measurement at 150 °C for 4 hours.

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Samples were degassed prior to measurement at 150 °C for 4 hours.
The specific strength of the fibres was determined according to PN-EN ISO 5079:1999.

The sorption of water vapour of the fibres was determined at 65% and 100% relative air humidity according to Polish Standard PN-71/P-04653.

The fibre water retention was determined using a laboratory centrifuge to mechanically remove water from the fibres during centrifugation at an acceleration of 10,000 m/s² for 10 min. The retention value was determined as the ratio of the water mass that remained in a fibre after centrifugation to the mass of a completely dry fibre.

Fibre porosity was determined using mercury porosimetry, using a Carlo-Erba porosimeter coupled with a computer system which can determine the total pore volume and the total internal area of the pores.

Determination of the degree of substitution of sodium ions with zinc ions in zinc alginate fibres. The assay of zinc ions in alginate fibres was conducted spectrophotometrically using a Spekol 11 spectrophotometer with 4-(2-pyridylazo) resorcinol (PAR) as an indicator that reacts with Zn(II) in weakly alkaline solutions, yielding a red-orange chelate, being the basis for the spectrophotometric assay of zinc.

Working solutions with a metal ion concentration of 10 μg/ml were used in each case to plot the calibration curve.

The absorbance was measured at λ=495 nm against a blank.

The distribution of the TCP nanoadditive in the fibre was determined based on JSM 5400 SEM microscope images, obtained using an OXFORD INSTRUMENTS EDX LINK ISIS characteristic radiation dispersive energy analyser.

Properties of the polymer, nanoadditive and spinning solutions
For the preparation of zinc alginate fibres, Protanal LF10/60 LS high-mannuronic sodium alginate was selected with a prevalence of mannuronic acid blocks in the macromolecule chain was selected. The polymer properties are listed in Table 1.

β-TCP (Chempur, Poland), nano-milled at AGH University of Science and Technology in Kraków, was used as the nanoadditive.

Based on the results of nanoadditive grain size studies, it was found that the quantitative distribution of grain sizes in the nanoadditive sample reveals two fractions at 58 - 164 nm and 190 - 530 nm (respective proportions: 93% and 6%). The average β-TCP grain size was approx. 110 nm.

The specific surface of the nanoadditive determined by gas adsorption method (BET) was 570.9 m²/g.

Based on initial studies, a spinning solution concentration of 7.4% was selected for the sodium alginate used. This concentration was chosen so that the value of the apparent dynamic viscosity was at a level that ensured suitable processing properties in the wet spinning process, from a solution and forming process stability.

Polymer solutions at a concentration of 7.4% with a nanocomposite content of 3% per polymer mass were used to prepare nanocomposite fibres. The nanoadditive was dispersed using a Bandelin Sonopuls 2200HD ultrasonic probe suspended in the nanoadditive in a solvent prior to its addition to the spinning solution (time: 15 minutes, frequency: 20 kHz, power: 100 W).

The analysis of solutions without the nanoadditive and with the TCP nanoadditive also involved the determination of their n and k rheological parameters in the Ostwald-de Wael equation.

Not only are the rheological properties of the spinning solution relevant with respect to forming process stability, but they also determine the flow rate distribution during the flow of the spinning liquid in the spinneret channel, stream broadening in the extra-spinneret zone, and changes in the longitudinal speed rate along the forming path. Its value, which is also related to the reception force, determines the orientation of structural elements of the fibre as well as the susceptibility of the resulting structure to deformation processes at the drawing stage, and, as a result, fibre strength properties.

The analysis of flow curves (Figure 1) shows that both solutions (with and without the TCP nanoadditive) are non-Newtonian liquids diluted by shear without a

**Table 1. Characteristics of sodium alginate: *Dynamic viscosity of 1% water solution at 20 °C – product specification. **Bacterial tests (Escherichia Coli and Salmonella). – product specification, GA - Galuronic acid, MA - Mannuronic acid.**

<table>
<thead>
<tr>
<th>Type of alginate</th>
<th>Particle size, nm</th>
<th>Viscosity*, mPas</th>
<th>Dynamic viscosity of 1% solution, mPas</th>
<th>pH 1% of water solution</th>
<th>Structure, %</th>
<th>Bacterial tests**</th>
</tr>
</thead>
<tbody>
<tr>
<td>LF 10/60 LS</td>
<td>0.250</td>
<td>3.16</td>
<td>20 - 70</td>
<td>6 - 8</td>
<td>GA 35 - 45%</td>
<td>negative</td>
</tr>
<tr>
<td>Pure alginate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure alginate +</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure alginate 25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure alginate 50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 1.** Relationship between the shear stress and shear rate for the sodium alginate solutions; LF 10/60/LS, concentration: 7.4% with and without the TCP nanoadditive.

**Figure 2.** Relationship between the apparent dynamic viscosity and shear rate for the sodium alginate solutions; LF 10/60/LS, concentration: 7.4% with and without the TCP nanoadditive.
flow limit. Due to the addition of the nanoadditive to the solution, its properties are even less Newtonian, which is proved by the lower value of rheological parameter $n$ (Table 2).

Furthermore, the rheological parameter $k$, a measure of solution consistency, has values similar to the solution without the nanoadditive. The curves for the relationship between apparent dynamic viscosity and shear (Figure 2) are also similar for both solutions.

To summarise, it may be noted that it is favourable to use 7.4% Protanal LF 10/60 LS sodium alginate solutions, due to their rheological properties and processability into fibres. Furthermore, the apparent dynamic viscosity of 36-37 Pas ensures the suitable processability of solutions with 3% TCP nanoadditive. The solutions reveal highly stable rheological parameters for extended times.

Fibre forming

Alginate fibres were formed by a wet process from solution using distilled water as a solvent. A large-scale laboratory spinning machine was used whose design ensures stable process parameters, continuous control, and a wide range of parameter adjustment. 240-hole spinning nozzles of 0.08 mm diameter were used.

The coagulation process proceeded in a bath with various concentrations of CaCl$_2$ and 0.03% HCl. The drawing process was conducted in two stages in a plasticisation bath with CaCl$_2$ and small amounts of 0.03% HCl in a superheated steam atmosphere at 135 °C. The extent of drawing at both process stages was close to the maximum value possible in the conditions applied.

The fibres were washed and dried in isometric conditions after drawing. Two analytical series were completed.

In the first series, the coagulation, the plasticisation bath temperature and composition were changed (Table 3). The value of the as-spun draw ratio was selected as +70% based on the results of studies of fibre preparation from calcium alginate [12].

The other analytical series was completed with constant coagulation process parameters selected on the basis of the results of the first series.

The values of the as-spun draw ratio and related maximum deformation at both drawing stages were changed.

The value of the as-spun draw ratio was changed within positive values (+30% to +120%). In the case of rigid structures of macromolecules, it is advantageous, due to fibre strength properties, to carry out the forming process at positive as-spun draw ratio values [12].

Discussion of results

Selection of coagulation and plasticisation bath concentration as well as the temperature for zinc alginate fibres

The content of zinc chloride in the solidification bath is an essential parameter which determines the resulting degree of substitution of sodium ions (originating from the sodium alginate dissolved in water, constituting the spinning solution), with zinc ions in the zinc alginate, forming the building material for fibres. The rate of ion exchange is also affected by the temperature of the solidification bath: an increase in temperature results in higher rates.

The criterion for the selection of ZnCl$_2$ content in the solidification bath was to obtain as high substitution degrees as possible owing to the fact that it largely determines the tensile strength of alginate fibres.

Two zinc chloride concentrations were used in the solidification bath (3% and 5%). For both ZnCl$_2$ concentrations in the coagulation bath, plasticisation was conducted at 20 and 40 °C.

Since the degree of substitution may still increase at the drawing stage, the concentration of the plasticisation bath for coagulation in the 3% ZnCl$_2$ bath was identical to that in the coagulation bath. However, for coagulation in a 5% ZnCl$_2$ bath, the ZnCl$_2$ concentration in the plasticisation bath was increased to 7%. In all cases, the temperature of the plasticisation bath was maintained at 67 °C.

It follows from the data specified in Table 3 that the use of 3% ZnCl$_2$ in the coagulation bath and the same composition of the plasticisation bath in the drawing process (samples Z1 and Z2) makes it possible to achieve fairly low total draw values of 83 - 124%. Higher total draw values can be obtained for fibres coagulated in baths at a temperature of 20 °C. The content of ZnCl$_2$ in the coagulation bath increased to 5%, and therefore it can be stated that carrying out the drawing process in a 7% ZnCl$_2$ plasticization bath (samples Z3 and Z4) makes it possible to achieve quite high (for the material, at least) total draw values of 231 - 318%.

It is noted that higher total draw values can be obtained for fibres coagulated in baths at a temperature of 40 °C. It may be expected that such process conditions will contribute to a structure more prone to deformation at the drawing stage. Furthermore, fibres coagulated in such conditions have the highest degree of sodium ion substitution with zinc ions (12.38%; theoretical value: 15.73%). An increased content of ZnCl$_2$ in the solidification bath coupled with its fairly high temperature better facilitates zinc ion diffusion and the linking of neighbouring macromolecules in a chemical bond. Due to this structure, higher drawing stress values can be applied, and higher deformation at the drawing stage can be obtained. When solidification is carried out in 3% ZnCl$_2$ baths, excessively low substitution degrees occur (10.74 - 10.98), whose values are similar despite different bath temperatures. It was also found that the increase in the substitution degree

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**Table 2. Rheological parameters of spinning solutions of 7.4% sodium alginate solutions with and without the nanoadditive.**

<table>
<thead>
<tr>
<th>Type of solution</th>
<th>Rheological parameters</th>
<th>$n$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without nanoadditive</td>
<td></td>
<td>0.7205</td>
<td>36.36</td>
</tr>
<tr>
<td>With nanoadditive (TCP)</td>
<td></td>
<td>0.6772</td>
<td>35.36</td>
</tr>
</tbody>
</table>

**Table 3. Fibre forming conditions and properties of zinc alginate fibres formed at an as-spun draw ratio of +70%.**

<table>
<thead>
<tr>
<th>Sample symbol</th>
<th>Coagulation bath Temp., °C</th>
<th>Concentration, %</th>
<th>Draw ratio, %</th>
<th>Stress at drawing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z 1</td>
<td>40</td>
<td>3</td>
<td>80.4</td>
<td>83.3</td>
</tr>
<tr>
<td>Z 2</td>
<td>20</td>
<td>3</td>
<td>112.0</td>
<td>124.8</td>
</tr>
<tr>
<td>Z 3</td>
<td>40</td>
<td>5</td>
<td>303.3</td>
<td>318.5</td>
</tr>
<tr>
<td>Z 4</td>
<td>20</td>
<td>5</td>
<td>214.7</td>
<td>231.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample symbol</th>
<th>Moisture sorption at 65% RH, %</th>
<th>Moisture sorption at 100% RH, %</th>
<th>Water retention, %</th>
<th>Zinc concentration, %</th>
<th>Linear mass, tex</th>
<th>Tensile strength, cN/tex</th>
<th>Elongation at break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z 1</td>
<td>24.50</td>
<td>45.50</td>
<td>120.20</td>
<td>10.98</td>
<td>65.66</td>
<td>21.39 ± 0.83</td>
<td>8.37 ± 0.92</td>
</tr>
<tr>
<td>Z 2</td>
<td>24.92</td>
<td>47.46</td>
<td>84.50</td>
<td>10.74</td>
<td>49.18</td>
<td>26.05 ± 1.32</td>
<td>7.79 ± 0.81</td>
</tr>
<tr>
<td>Z 3</td>
<td>23.40</td>
<td>45.30</td>
<td>12.38</td>
<td>28.12</td>
<td>29.68 ± 2.28</td>
<td>7.03 ± 1.02</td>
<td></td>
</tr>
<tr>
<td>Z 4</td>
<td>23.70</td>
<td>45.20</td>
<td>48.10</td>
<td>11.42</td>
<td>36.90</td>
<td>28.57 ± 0.99</td>
<td>6.76 ± 0.53</td>
</tr>
</tbody>
</table>
in the ZnCl$_2$ plasticisation bath after the drawing stage is quite low (0.3%). The fibre strength properties are consistent with the resulting substitution degrees and total draw values.

Z-3 fibres have the highest tensile strength: 29.68 cN/tex. The analysis of drawing stress (Table 3) for sample Z3 proves that the highest deformation values at the drawing stage are achieved when the process is conducted at a stress of 0.037 cN/tex at the solidification stage, 3.891 cN/tex in the plasticisation bath and at a maximum of 1.045 cN/tex during stream drawing, as compared to fibres coagulated and drawn in the other conditions.

Furthermore, the fibres have elongation at break values of 7%: a factor highly vital, considering their processability into non-woven fabrics.

Moisture sorption at 65% RH of 23.4 to 24.9% and 100% RH of 44.5 to 47.5%, with water retention values of 44 to 120%, which result from the chemical structure, ensure high absorption rates of physiological fluids in implantable materials based on the fibres.

When considering adequately high fibre strength properties and good sorption properties as the criteria, it is noted that the alginate fibre solidification process should be conducted in a 5% ZnCl$_2$ bath at 40°C. The drawing process should be conducted in a plasticisation bath with the ZnCl$_2$ content increased to 7% at approx. 67 °C. The second drawing stage should be carried out in superheated steam at 135 - 140 °C.

Deformation values at both drawing stages should be lower than the maximum, which ensures spinning process stability and fibre bundle homogeneity.

**Effect of the as-spun draw ratio and deformation on the properties of zinc alginate fibres at the drawing stage**

It follows from the analysis of changes in the sorption properties of both fibre types (with and without the TCP nanoadditive), depending on the as-spun draw ratio, that the properties are determined by the hydrophilic nature of the material.

Moisture sorption at 65% RH is between 23.7 and 25%.

Moisture sorption at 100% RH is slightly higher (between 43.8 and 47.4%) for fibres without the nanoadditive, compared to those with TCP for which the value is between 41.8 and 43.7% (Table 4).

In order to include the porous structure in the analysis of the sorption properties of alginate fibres, it was decided to divide the results of mercury porosimetry measurements into two values:

- $P_1$ – pore volume for pores with radii of 4 - 1000 nm. The range was attributed to the porosity of elementary fibres.
- $P_2$ – total pore volume for the test sample (range: 4 - 5000 nm). Together with $P_1$, the range also includes the porosity of the fibrous material.

The classification criterion was the analysis of cross sections of alginate fibres. The effects of the specificity of porosity measurement by mercury porosimetry described in [14] were also included.

In the case of the internal area values of pores, which concerns those of less than 100 nm, no other value was selected for pores in the 4 - 1000 nm range; the same was for values of the total pore volume. The difference between the internal area of pores in the 4 - 1000 nm and 4 - 5000 nm ranges is low (approx. 0.2 m$^2$/g).

Despite differences in the total volume of pores within the range up to 1,000 nm (0.042 – 0.343 cm$^3$/g) and differences in

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**Table 4. Porous structure and sorption properties of calcium alginate fibres with and without the nanoadditive (AZ: without the nanoadditive; AZT: with the TCP nanoadditive).**

<table>
<thead>
<tr>
<th>Sample symbol</th>
<th>As-spun draw ratio, %</th>
<th>Total draw ratio, %</th>
<th>Zinc concentration, %</th>
<th>Volume of pores, cm$^3$/g</th>
<th>Total internal surface of pores, m$^2$/g</th>
<th>Moisture sorption at 65% RH, %</th>
<th>Moisture sorption at 100% RH, %</th>
<th>Water retencion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ 1</td>
<td>+30</td>
<td>294.46</td>
<td>10.09</td>
<td>0.112</td>
<td>0.240</td>
<td>22.75</td>
<td>23.91</td>
<td>43.83</td>
</tr>
<tr>
<td>AZ 2</td>
<td>+50</td>
<td>246.46</td>
<td>12.24</td>
<td>0.192</td>
<td>0.376</td>
<td>28.85</td>
<td>24.20</td>
<td>45.37</td>
</tr>
<tr>
<td>AZ 3</td>
<td>+70</td>
<td>224.20</td>
<td>12.40</td>
<td>0.160</td>
<td>0.306</td>
<td>9.69</td>
<td>24.26</td>
<td>44.95</td>
</tr>
<tr>
<td>AZ 4</td>
<td>+90</td>
<td>194.26</td>
<td>10.41</td>
<td>0.228</td>
<td>0.364</td>
<td>53.64</td>
<td>24.24</td>
<td>46.15</td>
</tr>
<tr>
<td>AZ 5</td>
<td>+110</td>
<td>179.70</td>
<td>10.66</td>
<td>0.343</td>
<td>0.500</td>
<td>77.38</td>
<td>24.84</td>
<td>47.46</td>
</tr>
<tr>
<td>AZ 6</td>
<td>+120</td>
<td>146.71</td>
<td>10.39</td>
<td>0.078</td>
<td>0.200</td>
<td>12.23</td>
<td>24.72</td>
<td>46.17</td>
</tr>
<tr>
<td>AZT 1</td>
<td>+30</td>
<td>244.30</td>
<td>10.35</td>
<td>0.204</td>
<td>0.412</td>
<td>56.40</td>
<td>23.70</td>
<td>41.67</td>
</tr>
<tr>
<td>AZT 2</td>
<td>+50</td>
<td>207.89</td>
<td>10.79</td>
<td>0.214</td>
<td>0.366</td>
<td>46.02</td>
<td>24.39</td>
<td>42.72</td>
</tr>
<tr>
<td>AZT 3</td>
<td>+70</td>
<td>179.45</td>
<td>11.45</td>
<td>0.137</td>
<td>0.293</td>
<td>21.65</td>
<td>23.70</td>
<td>43.39</td>
</tr>
<tr>
<td>AZT 4</td>
<td>+90</td>
<td>160.97</td>
<td>11.01</td>
<td>0.116</td>
<td>0.316</td>
<td>15.98</td>
<td>24.44</td>
<td>43.28</td>
</tr>
<tr>
<td>AZT 5</td>
<td>+110</td>
<td>155.77</td>
<td>10.79</td>
<td>0.228</td>
<td>0.428</td>
<td>52.04</td>
<td>23.73</td>
<td>43.72</td>
</tr>
<tr>
<td>AZT 6</td>
<td>+120</td>
<td>149.63</td>
<td>10.22</td>
<td>0.042</td>
<td>0.397</td>
<td>12.05</td>
<td>25.04</td>
<td>41.48</td>
</tr>
</tbody>
</table>

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![Figure 3. Relationship between the volume of pores and radii for; a) fibres without the nanoadditive, b) fibres with TCP.](image-url)
Figure 4. Relationship of the tensile strength, as-spun draw ratio and total draw for alginate fibres without the nanoadditive.

Figure 5. Relationship of the tensile strength, as-spun draw ratio and total draw for alginate fibres with the TCP nanoadditive.

Figure 6. Relationship between the stress at coagulation, drawing in the plasticization bath, and as-spun draw ratio for zinc alginate fibres.

Figure 7. Relationship between the stress at coagulation, drawing in the plasticization bath, and as-spun draw ratio for zinc alginate fibres with 3% TCP.

The high water retention values in both fibre types (51.5 - 69%) are related mainly to the chemical structure of the materials. The porosity of the fibrous material in the 1000 - 5000 nm range has some influence on the values of this parameter (last maximum in the plot, Figure 3). This is likely to result from the presence of cavities between monofilaments and fibre surface heterogeneity. Water can be retained in such cavities when polymeric clusters are linked by hydrogen bridges with unsubstituted OH groups of the material. Porosity in the 1000-5000 nm range of over 50% is advantageous because it facilitates the penetration of physiological fluids and the adhesion of newly formed cells to the implanted material containing the fibres.

Based on the studies of the sorption properties of the resulting fibres, it is hard to determine the effect of as-spun draw ratio values on moisture sorption values at 100% RH and the water retention in the fibres. This results from the fact that in hydrophilic polymers, such as zinc alginate, the values of these parameters are largely determined by the chemical structure of the material, with the porous structure of the fibre being of lesser importance; however, it determines the sorption properties of hydrophobic fibres [15].

The strength properties of both fibre types depend on the fundamental process parameter, that is, the as-spun draw ratio and related deformation values at the drawing stage. The tensile strengths of fibres without the nanoadditive achieve maximum values for fibres formed at an as-spun draw ratio of +50% but experience a decrease with a further rise in the as-spun draw ratio values (Figure 4). As for fibres with the TCP nanoadditive, the specific strength in the range of as-spun

do not significantly affect moisture sorption values at 100% RH.

It follows from the analysis of the porous structures of both fibre types that the curves of pore distribution, depending on the radii (Figure 3, see page 15), have maxima at a pore range of 4-15 nm (first maximum in the plot). Slightly higher values are seen for fibres without the nanoadditive, which may explain their slightly higher moisture sorption at 100% RH. The considerable volume fractions of such pores in hydrophobic materials determine moisture sorption values at 100% RH. In hydrophilic materials, however, varied volume fractions

Table 5. Strength properties of calcium alginate fibres with and without the nanoadditive (AZ: without the nanoadditive; AZT: with the TCP nanoadditive)

<table>
<thead>
<tr>
<th>Sample symbol</th>
<th>As-spun draw ratio, %</th>
<th>Draw ratio, %</th>
<th>Total deformation</th>
<th>Stress at drawing</th>
<th>Linear mass, tex</th>
<th>Tensile strength, cN/tex</th>
<th>Elongation at break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ 1</td>
<td>+30</td>
<td>189.48</td>
<td>36.11</td>
<td>294.46</td>
<td>5.128</td>
<td>0.0215</td>
<td>3.796</td>
</tr>
<tr>
<td>AZ 2</td>
<td>+50</td>
<td>170.22</td>
<td>28.21</td>
<td>246.46</td>
<td>5.197</td>
<td>0.0346</td>
<td>4.172</td>
</tr>
<tr>
<td>AZ 3</td>
<td>+70</td>
<td>146.60</td>
<td>31.46</td>
<td>224.20</td>
<td>5.511</td>
<td>0.0345</td>
<td>3.579</td>
</tr>
<tr>
<td>AZ 4</td>
<td>+90</td>
<td>119.26</td>
<td>34.20</td>
<td>194.26</td>
<td>5.591</td>
<td>0.0509</td>
<td>3.070</td>
</tr>
<tr>
<td>AZ 5</td>
<td>+110</td>
<td>129.18</td>
<td>22.04</td>
<td>179.70</td>
<td>5.874</td>
<td>0.0687</td>
<td>3.799</td>
</tr>
<tr>
<td>AZ 6</td>
<td>+120</td>
<td>71.25</td>
<td>44.06</td>
<td>146.71</td>
<td>5.428</td>
<td>0.0320</td>
<td>1.215</td>
</tr>
<tr>
<td>AZT 1</td>
<td>+30</td>
<td>231.75</td>
<td>3.78</td>
<td>244.30</td>
<td>4.476</td>
<td>0.0203</td>
<td>3.103</td>
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<tr>
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<td>+50</td>
<td>136.78</td>
<td>30.03</td>
<td>207.89</td>
<td>4.618</td>
<td>0.0296</td>
<td>2.385</td>
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<tr>
<td>AZT 3</td>
<td>+70</td>
<td>169.97</td>
<td>3.51</td>
<td>179.45</td>
<td>4.751</td>
<td>0.0460</td>
<td>3.556</td>
</tr>
<tr>
<td>AZT 4</td>
<td>+90</td>
<td>120.64</td>
<td>15.28</td>
<td>160.97</td>
<td>4.958</td>
<td>0.0514</td>
<td>2.644</td>
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<tr>
<td>AZT 5</td>
<td>+110</td>
<td>126.14</td>
<td>13.10</td>
<td>155.77</td>
<td>5.371</td>
<td>0.0627</td>
<td>3.269</td>
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<tr>
<td>AZT 6</td>
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<td>81.40</td>
<td>37.62</td>
<td>149.63</td>
<td>5.492</td>
<td>0.0420</td>
<td>1.817</td>
</tr>
</tbody>
</table>
draw ratio values applied decreases for both process parameters (Figure 5). Fibres formed at an as-spun draw ratio of +30% have the highest tensile strength: 24.72 cN/tex, which is 3.26 cN/tex lower than for fibres without the nanoadditive (Table 5). Also, the maximum total draw values are lower, which gradually decrease in both fibre types with an increase in the as-spun draw ratio (Figure 6). It seems than that the effect of the TCP nanoadditive in alginate fibres is decreased susceptibility to deformation, mainly at the plasticisation drawing stage, the extent of which depending on the as-spun draw ratio value applied. At an extremely positive as-spun draw ratio, the total drawing values of both fibre types are very similar.

Strength properties are not only determined by the as-spun draw ratio and deformation applied at the drawing stage but also by the stress values used in the deformation processes. Furthermore, the stress value at which the structure is shaped at the solidification stage is vital. The nature of the structure determines its susceptibility to deformation at later drawing process stages. The increase in stress for both fibre types with higher as-spun draw ratio values to 110% (Figures 7 and 8) is noted. It seems that there is a critical stress value whose exceedance results in a much lower fibre tensile strength. For fibres without the nanoadditive, the difference in tenacity strength between the highest and lowest value is 3.86 cN/tex, while for those with TCP, it is 4.93 cN/tex (Table 5). The opposite direction of the total draw and stress values at the solidification stage, depending on the as-spun draw ratio, which occurs in both fibre types up to a ratio of 110%, may prove that the stress has a large influence on the resulting fibre tensile strength.

Furthermore, the resulting elongation at break value for fibres without the nanoadditive is higher than for those with the TCP nanoadditive (Table 5). An elongation at break value of approx. 5% for nanocomposite fibres is, as our studies of zinc alginate fibres prove [13], sufficient to ensure processability into flat textile products.

When analysing the strength properties of alginate fibres, one must allow for the fact that they largely depend on the number of primary bonds between macromolecules in the material (through zinc) and the capability of forming secondary bonds between unsubstituted OH groups. Within the defined solidification process parameters (bath composition and temperature), changes in the percentage of Zn ions, depending on the as-spun draw ratio values, are minor. The values are in the range of 10 - 11% at a theoretical value of 15.73%. The theoretical value was calculated assuming the complete substitution of sodium ions with zinc ions from the solidification bath. Therefore it may be assumed that changes in the parameter of ± 0.5% should not have a major impact on fibre strength properties. The potential for macromolecule linking by secondary bonds is determined by both their orientations, related to the longitudinal speed gradient, and the presence of the TCP nanoadditive between macromolecules. The first parameter contributes to their approaching one another and facilitates the
formation of secondary bonds, while the other hinders deformation processes and thus decreases the likelihood that macromolecules will be linked by secondary bonds. These effects of the nanoadditive in the fibre material may be attributed to increased internal friction in the system subjected to deformation processes. This is confirmed by lower maximum as-drawn spun ratio values possible in fibres with, rather than without, the TCP nanoadditive. This translates into lower strength properties of nanocomposite fibres, as discussed previously.

Furthermore, the susceptibility to deformation of zinc alginate fibres is higher than for calcium alginate fibres formed in similar conditions [12, 16]. This applies to fibres with the TCP nanoadditive as well.

Alginate fibre properties also depend on their supramolecular structure. This was investigated in our previous papers [12, 16] concerning calcium alginate fibres, which also contained various nanoadditives. The issue of the effect of forming conditions on changes in the degree of crystallinity of zinc alginate fibres with the TCP nanoadditive will be discussed in another paper.

The analysis of SEM images (Figure 9) of the surface of nanocomposite fibres reveals numerous scratches, cracks and sporadic protrusions related to nanoadditive clusters. The protrusions do not occur on the surface of fibres without the nanoadditive (Figure 10). However, their number in nanocomposite fibres is low.

SEM+EDS analyses showed that the protrusions are caused by the presence of tricalcium phosphate added to the material on the surface of zinc alginate fibres (Figure 11). This is proved by the intense peaks for phosphorus and calcium at point 1 in the fibre image subjected to X-ray microanalysis. A test carried out at point 2, or a fibre fragment without the protrusion, showed that the content of calcium and phosphorus in the spot was extremely low and proved that the nanoadditive was uniformly dispersed in the fibre material.

Apart from the peaks of the nanoadditive discussed above, the X-ray microanalysis plots also show peaks from carbon and oxygen (elements which make up the fibre material) as well as zinc (an element incorporated into the fibre material at the solidification stage).

Sporadic nanoadditive agglomerates can be found in images of cross sections of nanocomposite fibres (seen as lighter spots, Figure 12). The distribution of the nanoadditive throughout the fibre cross section can then be considered uniform.

Furthermore, the images (Figure 12) reveal, in the cross section, no pores larger than 1000 nm, which was the basis for the defined fibre porosity range.

**Summary**

1) The conditions for forming zinc alginate fibres with the TCP nanoadditive were selected. Preparation of nanocomposite alginate fibres with a tensile strength above 24 cN/tex and good sorption properties requires:
   - Solidification carried out in 5% ZnCl₂ bath at 40°C,
   - A two-stage drawing process in media of increasingly higher temperatures (7% ZnCl₂ plasticisation bath, superheated steam),
   - Moderately positive as-spun draw ratio values (approx. +30%) used at the forming stage. This provides adequate conditions for the deformation of the stream, which is still liquid, and the orientation of structural elements along the direction of the fibre axis.

2) The sorption properties and water retention values of zinc alginate fibres with the TCP nanoadditive are determined by the hydrophilic properties of the material. Apart from the hydrophilic properties of the material, water retention values are also affected by the porosity of the fibrous material.

3) The strength properties of nanocomposite fibres depend on the total draw values and also on the stress applied during deformation processes at successive fibre preparation stages.

4) The TCP nanoadditive in zinc alginate fibres decreases the susceptibility to deformation at the drawing stage, which results in a lower tensile strength compared to fibres without the nanoadditive.

**Acknowledgment**

The research funded by the Minister of Science and Higher Education in 2007-2010 as commissioned project no. PBZ-MNISW-01/II/2007.

**References**