Maciej Boguń

Department of Man-Made Fibres
Faculty of Material Technologies
and Textile Design
Technical University of Lodz
ul. Żeromskiego 116, 90-924 Lodz, Poland
E-mail: maciek.bogun@wp.pl

Rheological Properties of Sodium Alginate Spinning Solutions with Ceramic Nanoadditives

Abstract
The effect of ceramic nanoadditives, such as nanosilica, montmorillonite, hydroxyapatite, calcium triphosphate and bioglass, on the rheological properties of aqueous sodium alginate solutions was studied. The influence of the nanoadditives on changes in rheological parameters n and k was determined. The mechanism of the rheological behaviour of spinning solutions containing the nanoadditives is explained. Furthermore, the effect of the rheological properties on the formation process of nanocomposite alginate fibres is described.

Key words: *rheological properties, nanoadditives, montmorillonite, bioglass, nanosilica, hydroxyapatite, sodium alginate, calcium triphosphate.*

Introduction

Regenerative medicine provides new opportunities for the development of many areas of science and industry, including the textile industry. The manufacture of new types of composite materials may largely reduce the time of in-patient treatment and, thus, treatment costs. Based on this aim, a concept was developed for the manufacture of alginate fibre biocomposites with a bioactive nanoadditive dispersed in the material. The addition of various ceramic nanoadditives such as hydroxyapatite, calcium triphosphate, silica, bioglass and montmorillonite to alginate fibres is meant to confer the osteoconductive or osteoproductive properties desired to the fibre. All the nanoadditives in question have specific biological properties; therefore, they have been widely used in contemporary medicine [1 - 11]. In the future the resulting nanocomposite alginate fibres will be used to manufacture bone implants.

However, as our previous studies showed [12 - 14], the addition of a non-fibre-forming nanoadditive to the fibre leads to a reduction in the deformation capacity of the material, therefore affecting the resulting structure and final properties of the fibres. The properties of nanocomposite alginate fibres that result from the moulding process also depend on the properties of the spinning solution. A concentration should be chosen so that the apparent dynamic viscosity is at a level that ensures suitable processing properties from the solution in the wet process, moulding process stability and no tears of elementary fibres at the spinneret. The use of excessively high concentrations of the spinning solution, beneficial due to the fibre strength properties, is limited by the associated increase in apparent dynamic viscosity, whose bottom limit is the occurrence of stream discontinuity due to capillary disintegration or brittle (cohesive) rupture [15], which also depends on the fibre reception force.

The rheological properties of spinning solutions also determine flow rate distribution during the flow of the spinning liquid in the spinneret channel (transverse gradient), as well as changes in the longitudinal speed gradient along the moulding path, because the latter value affects the orientation of structural blocks along the fibre axis and strength properties of finished fibres. In the case of alginate fibres with a quite rigid macromolecule structure of the material, the properties, as our studies showed [12], largely depend on the as-spun draw ratio and stress, which leads to the formation of the structure during solidification and its transformation in deformation processes at the subsequent fibre manufacturing stages. All these parameters are closely related to the properties of spinning solutions used to manufacture fibres. The presence of various nanoadditives in the solutions affects their rheological properties and leads to a reduced deformation capacity and, in consequence, fibre strength properties.

The aim of our work was to determine the effect of the quantity and type of ceramic nanoadditive on the rheological properties of sodium alginate spinning solutions. Comparative analysis of the effect of the presence of various quantities and types of ceramic nanoadditives may also contribute to explaining the differences in the strength properties of fibres obtained from such solutions.

The analysis is based on the strength properties [12 - 14] of fibres with 3% of the phosphorus peroxide nanoadditive, formed at an optimum as-spun draw ratio. The optimum as-spun draw ratio was selected based on our earlier results [12 - 14].
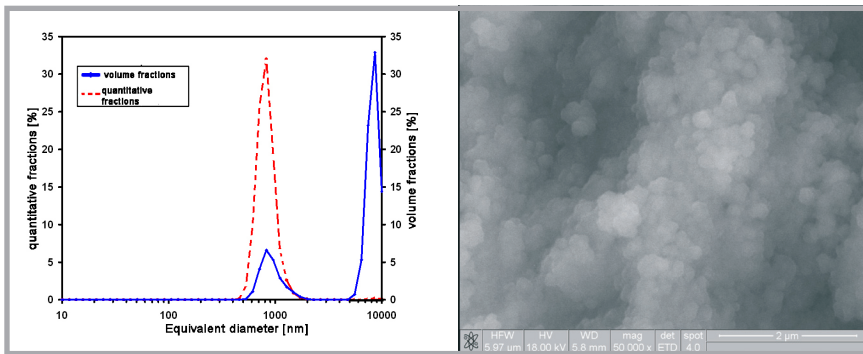
## Experimental

Materials and methods

Protanal LF 10/60LS sodium alginate from FMC Biopolymer (Norway) with an intrinsic viscosity $\eta = 3.16$ dL/g was used for the preparation of the spinning solutions. The percentage of mannuronic acid blocks in the polymer is higher (65%) than that of guluronic acid blocks.
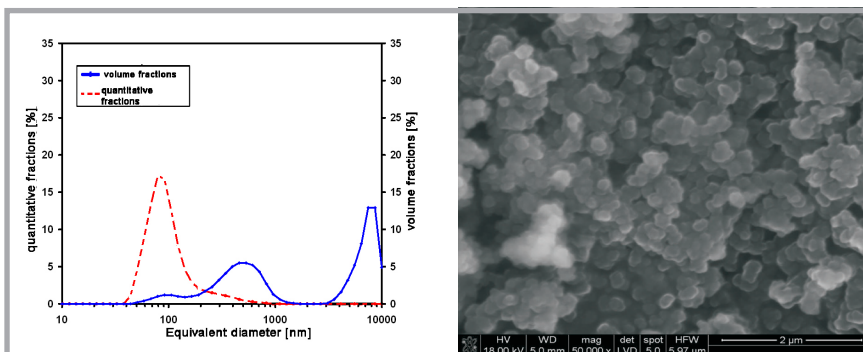
Table 1. Characteristics of nanoadditives used.

Nanoadditive type	Specific surface, BET, m²/g	Average particle size range, nm	Location of the quantitative fraction peak maximum, nm
HAp	73.6	100 – 800	825
TCP	570.9	80 – 110	80
SiO$_2$	563.5	60 – 100	80
bioglass	220.2	100 – 200	190
MMT	-----	20 – 1000	100

Boguń M.; Rheological Properties of Sodium Alginate Spinning Solutions with Ceramic Nanoadditives.
FIBRES & TEXTILES in Eastern Europe 2009, Vol. 17, No. 5 (76) pp. 17-22.

17

Figure 1. *Characteristics of the volume and quantitative fractions, and SEM image of the HAp nanoadditive.*
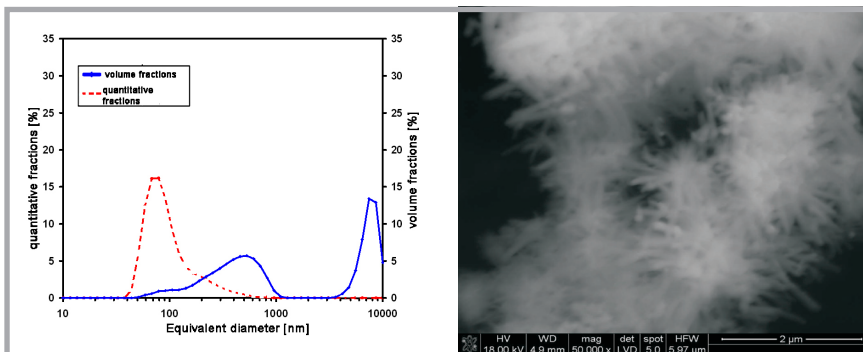
Figure 2. *Characteristics of the volume and quantitative fractions, and SEM image of the TCP nanoadditive.*

Figure 3. *Characteristics of the volume and quantitative fractions, and SEM image of the SiO₂ nanoadditive.*

The following nanoadditives were used in our studies:

- hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$, obtained at the AGH University of Science and Technology in Kraków according to a patent [16];
- calcium β-triphosphate (TCP), $Ca_3(PO_4)_2$, commercially available at Chempur Polska;
- silica (SiO_2), commercially available at Sigma Aldrich;
- bioglass, obtained at the AGH University of Science and Technology in Kraków, with the following oxide

composition: CaO- 16%mol, SiO_2 - 80%mol, P_2O_5 - 4%mol; and,
- montmorillonite (MMT), obtained at the AGH University of Science and Technology in Kraków from bentonite (Jelesovy Potok deposit).

The nanoadditives were characterised at the AGH University of Science and Technology in Kraków. The analysis included the measurement of surface development by gas adsorption (BET), particle size determination (DLS), and particle microscopic observation (SEM). Specific surface measurements were carried out using a Nova 1200e from Quantachrome Inst. by the BET adsorption isotherm

method. Particle size was analysed with a Nano-ZS Zetasizer from Malvern Inc., which uses dynamic laser light scattering technology. Before being added to the spinning solution, the aqueous nanoadditive suspensions were sonicated using an ultrasonic probe with a 100 W power output for 15 min.

Nanoadditives in the amounts of 1%, 3%, or 5% with respect to polymer weight were added to the aqueous sodium alginate spinning solution during its preparation. The polymer concentration in the solution was 7.4%.

The results are shown in ***Table 1*** (see page 17) and ***Figures 1 - 5***.

For determination of the rheological properties of the spinning solutions, an Anton Paar rotary rheometer was used. According to the manufacturer, the error of Newtonian fluid viscosity measurement (used as standard) is 0.32%. The measurements were carried out at a shear rate of $0.2 - 100 \ s^{-1}$ and shear stress of $12 - 1200 \ N/m^2$ at 20 °C. Rheological parameters *n* and *K* were determined based on flow curves. Their fitting to the measurement results expressed by determination coefficient R^2 exceeds 0.97.

■ Discussion of results

The rheological properties of spinning solutions are determined by mutual interactions between the polymer and solvent. The addition of a ceramic nanoadditive broadens the range of such interactions, which depend not only on the nanoadditive chemical structure but also on the grain size, internal surface and agglomeration capability.

Differences in the chemical structures of respective nanoadditives lead to different interactions with polymer macromolecules and solvent molecules. This determines whether the formation of secondary bonds in the system is possible.

Analysis of the rheological properties of all the solutions studied shows that, irrespective of the quantity and type of nanoadditive used, they are non-Newtonian fluids thinned by shear (n < 1) without a flow limit. The tangential stress increases less than proportionally to an increase in the shear rate and flow curves cross the origin of the coordinate system, an example of which is shown in ***Figure 6*** (see page 20) for a 3% content of respective nanoadditives in the solution. According
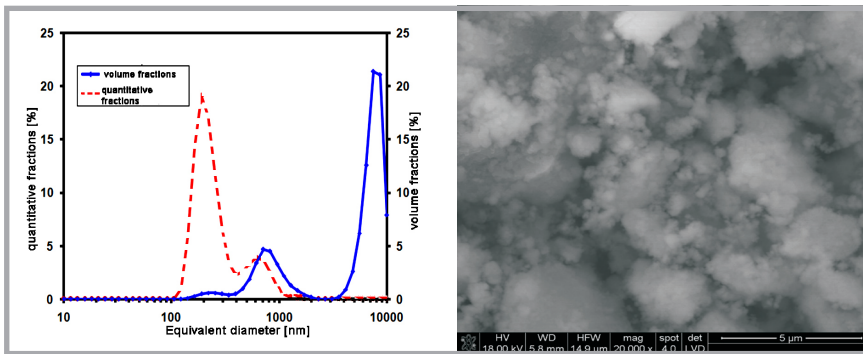
Figure 4. *Characteristics of the volume and quantitative fractions, and SEM image of the bioglass nanoadditive.*
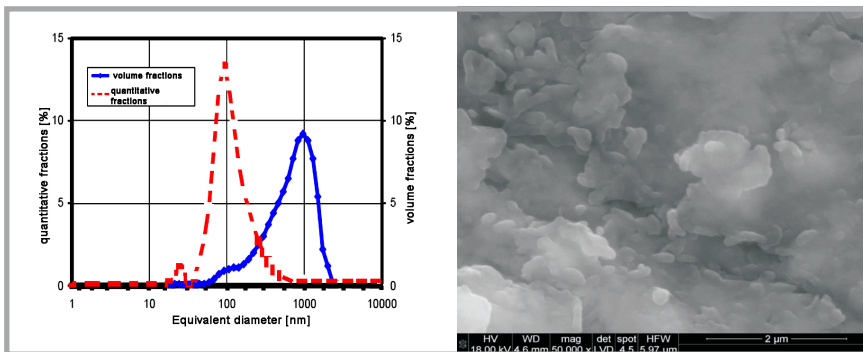
Figure 5. *Characteristics of the volume and quantitative fractions, and SEM image of the MMT nanoadditive.*

Table 2. *Rheological properties of aqueous sodium alginate spinning solutions.* ***Remark.*** *Reological parameters n and k were determined on the basis of flow curves in the logarithmic scale, which were correlated with the measured results by the factor R^2 of value which was greater than 0.97. The accuracy of of the dynamic viscosity measurement of newtonian standard fluids was 0.32% according to the viscometer's producer.*

Solution type	Content of nano-additive, %	Rheological parameter	
		n	k
Sodium alginate without nanoadditive	----	0.72	36.35
Sodium alginate with HAp	1	0.65	40.88
	3	0.64	43.78
	5	0.66	43.96
Sodium alginate with SiO$_2$	1	0.70	33.94
	3	0.67	36.02
	5	0.68	38.77
Sodium alginate with TCP	1	0.65	44.71
	3	0.68	35.36
	5	0.72	33.30
Sodium alginate with MMT	1	0.67	41.72
	3	0.64	45.18
	5	0.62	54.30
Sodium alginate with bioglass	1	0.62	46.75
	3	0.55	68.30
	5	0.55	70.25

to our earlier observations, which also included solutions of other fibre-forming polymers [17, 18], the presence of nanoadditives did not lead to changes in the rheological properties of the liquid, but it affected the value of rheological parameters *n* and *k* in the Ostwald-de Waale equation [19] (***Table 2***). It is concluded from the analysis of changes in the rheological parameter *n*, depending on the type of na-

noadditive used, that the properties of the solution are substantially different from Newtonian in the case of bioglass added, which is true irrespective of its quantity in solutions. Solutions containing TCP- or SiO$_2$ are more like Newtonian fluids; however, solution containing SiO$_2$ has a higher value of rheological parameter *n* for a 1% solution. The sequence of solutions with respect to decreasing values of

rheological parameter *n* (3% nanoadditive content) is as follows:

TCP > SiO$_2$ > MMT > HAp > bioglass

It is of some interest that the sequence is consistent with the nanoadditive particle sizes. Two groups are distinguished: 60 to 110 nm for TCP and SiO$_2$ and up to 1000 nm for MMT, HAp and bioglass (***Table 1***). Even though most bioglass particles are smaller (within 100 to 200 nm), the properties of its solutions are the most non-Newtonian, which may be related to its high agglomeration potential (***Figure 4***). This is confirmed by the highest values of rheological parameter *k*, which is a measure of the consistency of solutions compared to those containing other nanoadditives. Furthermore, values of rheological parameter *k* are the highest for all bioglass contents in solutions; it is k = 70.25 for a 5% concentration. This indicates that the apparent dynamic viscosity is almost twice as high as in solutions containing identical amounts of TCP or SiO$_2$ (***Table 2***).

In general, the sequence of changes in values of rheological parameter *k* for respective nanoadditives (3% concentration in solution) is as follows:

bioglass > MMT > HAp > SiO$_2$ > TCP

The sequence is generally opposite to changes in values of rheological parameter *n*. The apparent dynamic viscosity, presented as an example for a 3% nanoadditive concentration in ***Figure 7*** (see page 20), changes accordingly depending on the shear rate.

The solution containing bioglass is the most polymeric (the lowest value of rheological parameter *n*), which may be related not only to the bioglass agglomeration capacity but also to the formation of secondary bonds with the –OH groups of polymer macromolecules. Solutions containing SiO$_2$- or TCP are the least polymeric (***Table 2***).

The analysis of the effects of quantities of respective nanoadditives on changes in values of rheological parameter *n* shows that the content increased from 1 to 5%, leading to more non-Newtonian properties of the liquid. Solutions containing TCP are an exception, because the highest value of rheological parameter *n* is observed at a 5% concentration. This is also associated with a different pattern of changes in values of rheological parameter *k*, since the highest value is found for
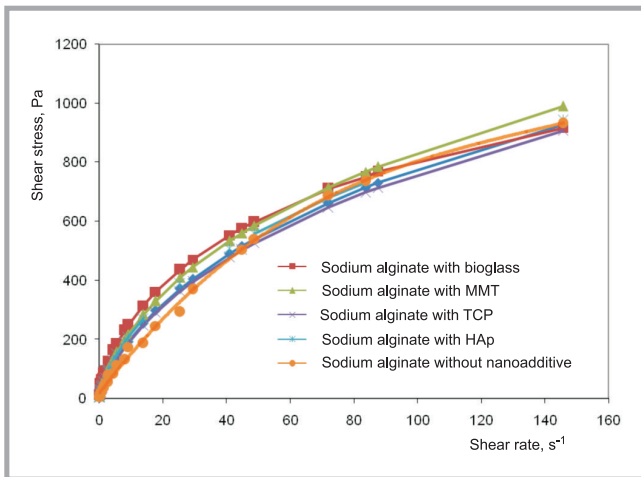
Figure 6. *Relationship between the shear stress and shear rate for 7.4% LF 10/60/LS sodium alginate solutions with a nanoadditive (3%) and without a nanoadditive. Determination coefficient R2 for the experimental curves is within 0.977-0.988.*
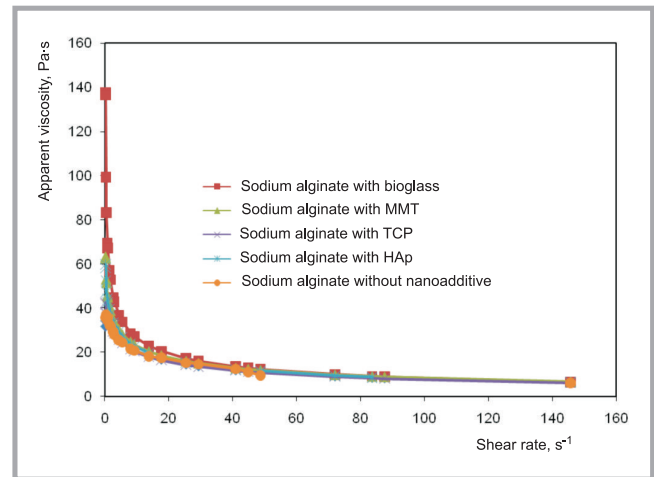
Figure 7. *Relationship between the apparent dynamic viscosity and shear rate for 7.4% LF 10/60/LS sodium alginate solutions with a nanoadditive (3%) and without a nanoadditive.*

5% solutions. It is interesting that that the value of rheological parameter *k* for solutions with 3% of the TCP nanoadditive is similar to that for a solution without the nanoadditive. The value of rheological parameter *k* for a 3% SiO_2 solution is similar. However, in this case, increased nanoadditive concentration in the solution leads to thicker solution consistency. In view of this, the different behaviour of solutions containing TCP observed is hard to explain. The causes of such effects of TCP and SiO_2 nanoadditives may be related to their impact on the solidification process during fibre formation; it was found [20] that the presence of ceramic nanoadditives in spinning solutions of fibre-forming materials slows diffusion processes down (including ion diffusion), especially in the near-spinneret area. A similar effect can be expected for ion diffusion occurring during the solidification of alginate fibres. The effect is more pronounced for additives with smaller particle sizes. In consequence, the structure produced at the solidification stage is formed at lower stress and is more porous. Furthermore, the structure is less susceptible to deformation processes at the stretching stage. Moreover, the process occurs at lower stress. This accounts for the lower strength of SiO_2- or TCP-containing fibres [13, 14]. This effect of ceramic nanoadditives was also observed in the formation of nanocomposite fibres from other fibre-forming materials [17, 18].

Changes in values of rheological parameter *k* for solutions with other nanoadditives are opposite to changes in the rheological parameter *n*. An increased content

of such nanoadditives in the solution (from 1 to 5%) leads to thicker solution consistency, which is most pronounced for solutions containing bioglass, for which an approximately 1.5-fold increase in the parameter is observed. Different values of rheological parameters *n* and *k* may be related not only to the varied grain sizes of the nanoadditives used but also to their agglomeration capacity and nature of quantitative and volume distribution (***Figure 4*** - see page 19), depending on the equivalent particle diameter. The occurrence of a high maximum at the highest equivalent diameters of 10,000 nm in the volume distribution curve may be interpreted as being a significant agglomeration capacity of a nanoadditive.

The analysis of curves of quantitative and volume fractions of respective nanoadditives shows that the similar location of TCP and SiO_2 nanoadditives in the sequence of changes in rheological parameters *n* and *k* is consistent not only with the particle size but also with the nature of the quantitative and volume distribution of their equivalent diameters.

The distribution of quantitative fractions is identical for SiO_2 and TCP. It is unimodal with a maximum at the equivalent diameter of approx. 80 to 100 nm. For the bimodal volume distribution, the contribution of particles with sizes up to 7000 nm is limited, which proves the agglomeration potential of these nanoadditives. It is much higher for hydroxyapatite, for which the height of the maximum for a range up to 10,000 nm is more than 32%. Furthermore, HAp particle sizes are much higher (within 100 to 800 nm),

and the maximum is at approx. 800 nm. Bioglass has a similarly high agglomeration potential; however, much smaller particles (approx. 200 nm) constitute the major fraction. They have a different layered structure because the quantitative distribution of MMT grain sizes has a maximum at an equivalent diameter of slightly more than 100 nm. The agglomeration capacity of MMT is at the same time much lower, which is proved by the location of the maximum volume fractions at the 1000 nm level. This explains its intermediate location in the sequence of changes in the rheological parameters *n* and *k* of the nanoadditives, because differences in particle sizes and their agglomeration capacity affect the rheological properties of liquids at shear. According to the well-known explanation of the shear thinning mechanism in stationary fluid, macromolecules are largely entangled by the continuous phase (solvent) immobilised between them. If, for example, a HAp nanoadditive of relatively large size is present in the system, the effective size of such clusters increases. During shear, macromolecules are straightened and disentangled at an increased shear rate, which leads to lower internal friction of these clusters if the clusters are large (high agglomeration capacity of HAp and bioglass). This relates to a higher value of rheological parameter *k*, because a higher stress value, which leads to this effect, is then needed. Simultaneously, the properties of the liquid are more non-Newtonian, which is proved by reduced values of rheological parameter *n*, compared to the liquid without the nanoadditive. In the case of solutions with a 3% nanoadditive content, if its size is

between 10 and 100 nm (nano-SiO$_2$ and TCP), the stress needed to strengthen chains is lower because of smaller cluster sizes and lower values of rheological parameter k, similar to values for the liquid without any nanoadditive. Simultaneously, the rheological parameter n increases, but its values are still lower than for the liquid without any nanoadditive.

Nanoadditive sizes and their agglomeration capacity also affect the shear thinning mechanism related to solvation, whichentails the binding of continuous phase (solvent) particles by dispersed polymer macromolecules or solid molecules (nanoadditives). The removal of the solvation sheath from the system at an increased shear rate depends on the interaction between polymer macromolecules and the solvent, as well as on interactions with any nanoadditives present in the system. The size, particle size, and agglomeration capacity of the nanoadditives determine the intensity of the removal of the solvation sheath. As a result, the system's internal friction decreases, depending on the type and quantity of the nanoadditive and interactions with the polymer and solvent.

The rheological properties of spinning solutions not only determine their processability and moulding process stability but also the stress at which the structure forms at the solidification stage, which is reconstructed at further stages of the deformation process, consequently affecting the fibre strength properties.

The results obtained by us in our earlier investigations are of interest here [12 - 14], some examples of which are presented in *Table 3*.

The analysis of correlations between the rheological properties of spinning solutions (containing 3% of various nanoadditives), the course of the moulding process, and the strength properties of nanocomposite alginate fibres leads to the following conclusions: The use of solutions containing TCP or SiO$_2$ with similar and the lowest values of rheological parameter k (35.3 and 36.0, respectively) produces fibres with the lowest specific strength properties as well (*Table 3*). The analysis was based on the strength properties of fibres with 3% nanoadditive, moulded at the optimum as-spun draw ratio and selected according to our previous studies [12-14].

*Table 3. Strength properties of nanocomposite alginate fibres, source - [12-14]; *fibres with 3% nanoadditive.*

Fibre type	As-spun draw ratio, %	Total draw ratio, %	Stress in plasti- cisation, cN/tex	Tenacit, cN/tex
Calcium alginate with HAp	+70	103.58	2.628	26.03
Calcium alginate with TCP	+70	89.27	1.850	24.39
Calcium alginate with MMT	+70	100.66	2.113	25.95
Calcium alginate with SiO$_2$	+70	88.09	1.625	22.86
Calcium alginate with bioglass	+110	79.06	2.160	24.73
Calcium alginate	+70	120.40	2.719	28.07

With an identical polymer content in the solutions, their least polymeric properties (the value of rheological parameter n closest to 1) are related to the presence of TCP or SiO$_2$ nanoadditives. Furthermore, despite the lowest particle size of both nanoadditives (no higher than 110 nm) and low agglomeration capacity, the highest deformation possible at the plasticisation drawing stage is the lowest (approx. 88 to 89%). The process also occurs at similarly low stress values of 1.6 to 1.8 cN/tex compared to fibres with other nanoadditives. Considering the fact that fibre strength properties depend not only on the total stretch values but also on the stress applied during deformation processes, it is noted that the low values of both parameters compared to others is due to the least polymeric nature of the liquid. On the other hand, the nature of such liquids is more polymeric compared to solutions without any nanoadditive, from which higher strength fibres are obtained. It may then be concluded that fibre strength properties are determined by an array of frequently contrasting effects (total stretch, stretching stress, presence of a nanoadditive) which occur in the system in question. We also have to consider the fact that the nanoadditive may affect the intensity of polymer-solvent or polymer-polymer interactions not only in the solution but also in the solidifying stream and fibre material. Despite their inferior particle size characteristics, spinning solutions containing MMT or HAp with higher values of rheological parameter k show a higher deformation capacity at the drawing stage, the total stretch being from 100 to 103%. Simultaneously, the process occurs at higher stress values of 2.1 to 2.6 cN/tex, which leads to the formation of fibres with a specific strength of approx. 26 cN/tex, that is, approx. 3 cN/tex higher than fibres containing TCP and SiO$_2$ (*Table 3*). It is also interesting that, given the resulting strength properties, it was favourable to conduct the moulding process at an as-spun draw ratio of +70% for the nanocomposite

fibres in question. However, for fibres containing bioglass, the moulding process had to be carried out at a more positive as-spun draw ratio of +110%. The different behaviour of materials containing bioglass may also be related to the rheological properties of the spinning solution and the high agglomeration capacity of the nanoadditive. With the most polymeric characteristics of the solution (a value of rheological parameter n of 0.55), the highest total draw possible was 79%; the process was conducted at the high stress of 2.16 cN/tex, which resulted in a specific strength of 24.73 cN/tex. This value was undoubtedly influenced by the orientation of structural elements that occurred in the still liquid stream, related to the high positive as-spun draw ratio. Considering the above, it may be concluded that the rheological properties of spinning solutions (classified into two groups of TCP and SiO$_2$ vs. MMT, HAp and bioglass nanoadditives) determine their behaviour during moulding, the total stretch values and the stress in deformation processes, related to the strength properties of various nanocomposite alginate fibres.

■ Conclusions

Irrespective of the quantity and type of ceramic nanoadditive added, aqueous sodium alginate spinning solutions are non-Newtonian fluids thinned by shear without a flow limit.

An increased content of respective nanoadditives (except for TCP) in the spinning solution results in more pronounced non-Newtonian properties of the liquid depending on particle size, agglomeration capacity and interactions with the solvent and polymer.

Rheological properties of the liquid, determined by the type of nanoadditive, its particle size and agglomeration capacity, affect the moulding process (total stretch values and stress in deformation proc-

esses). In consequence, this influences differences in the strength properties of calcium alginate nanocomposite fibres.

❏

References

1. *Katti K. S.; Colloid Surface B 39, 2004, 133.*
2. *van Blitterswijk C. A., Grote J. J, Kuijpers W., Daems W. T., de Groot K. A.; Biomaterials 7, 1986, pp. 553.*
3. *Chen Q. Z., Wong C.T., Lu W. W., Cheung K. M. C., Leong J. C. Y., Luk K. D. K.; Biomaterials 25, 2004, pp. 4243.*
4. *Le Geros R. Z.; Clin Mater 14, 1993, p. 65.*
5. *Weiner S., Wagner H. D.; Annu Rev Mater Sci 28, 1998, p. 271.*
6. *Ogata N., Jimenez G., Kawai H., Ogihara T.; J Polym Sci B 35, 1997, p. 389.*
7. *Bandyopadhyay S., Chen R., Giannelis E. P.; Polym Mater Sci Eng 81, 1999, p. 159.*
8. *Sinha Ray S., Yamada K., Okamoto M., Fujimoto Y., Ogami A., Ueda K.; Polymer 44, 2003, p. 435.*
9. *Hench L. L.; J Am Ceram Soc 74, 1991, p. 1487.*
10. *Hench L. L.; J Am Ceram Soc 81, 1998, p. 1705.*
11. *Yilmaz S., Efouglu E., Kilic A. R.; J Clin Periodontol 25, 1998, p. 832.*
12. *Boguń M., Mikołajczyk T., Rabiej S.; J. Appl Polym Sci. 114, 2009, p. 70.*
13. *Boguń, M.; Rabiej, S. The influence of fibre formation conditions on the structure and properties of nanocomposite alginate fibres containing tricalcium phosphate or montmorillonite. Fibres & Textiles in Eastern Europe – in press.*
14. *Boguń M.; „Nanocomposite Calcium Alginate Fibres Containing SiO$_2$ and Bioglass" Express Polym Lett. – in press.*
15. *Ziabicki A.; „Fizyka procesów formowania włókien z polimerów naturalnych i syntetycznych", Wydawnictwa Naukowo-Techniczne, Warszawa 1970.*
16. *Haberko K., et.al; Polish Patent No. P-359960, 2003.*
17. *Mikołajczyk T., Olejnik M.; Fibres & Textiles in Eastern Europe 13(1), 2005, p. 24.*
18. *Mikołajczyk T., Boguń M.; Fibres & Textiles in Eastern Europe 13(1), 2005, p. 28.*
19. *Ferguson J., Kembłowski Z.; ,,Reologia stosowana płynów", Wydawnictwo Marcus sc, Łódź, 1995.*
20. *Boguń M "New Generation Precursor PAN Fibres Containing Ceramic Nanoaddition" Doctoral Thesis, Technical University of Lodz, 2007.*

UNIVERSITY OF BIELSKO-BIAŁA
Faculty of Materials and Environmental Sciences

The Faculty was founded in 1969 as the Faculty of Textile Engineering of the Technical University of Łódź, Branch in Bielsko-Biała. It offers several courses for a Bachelor of Science degree and a Master of Science degree in the field of Textile Engineering and Environmental Engineering and Protection. The Faculty considers modern trends in science and technology as well as the current needs of regional and national industries. At present, the Faculty consists of:

■ **The Institute of Textile Engineering and Polymer Materials,** divided into the following Departments:

■ Physics and Structural Research

■ Textiles and Composites

■ Physical Chemistry of Polymers

■ Chemistry and Technology of Chemical Fibres

■ **The Institute of Engineering and Environmental Protection**, divided into the following Departments:

■ Biology and Environmental Chemistry

■ Hydrology and Water Engineering

■ Ecology and Applied Microbiology

■ Sustainable Development of Rural Areas

■ Processes and Environmental Technology

University of Bielsko-Biała
Faculty of Materials and Environmental Science

ul. Willowa 2, 43-309 Bielsko-Biała
tel. +48 33 8279 114, fax. +48 33 8279 100