Dariusz Wawro,
Włodzimierz Stęplewski,
***Agnieszka Komisarczyk,**
***Izabella Krucińska**

Institute of Biopolymer and Chemical Fibres,
ul. M. Skłodowskiej-Curie 19/27, 90-570 Łódź, Poland
E-mail: dariusz.wawro@ibwch.lodz.pl

***Department of Material and Commodity Sciences and Textile Metrology,**
Lodz University of Technology,
Łódź, Poland

Formation and Properties of Highly Porous Dibutyrylchitin Fibres Containing Nanoparticles

Abstract
The article gives an account of investigations on the preparation of highly porous dibutyrylchitin fibres containing tri-calcium phosphate (β-TCP) or nano-hydroxyapatite (nano HAp). Fibers were spun from 16% dibutyrylchitin (DBC) solutions in ethanol (content of ethanol: 67 - 78%). The fibers obtained showed a sheath/core structure; the sheath being a solid skin while the core presented itself as a macro-, micro- and nano-porous interior filled with air. DBC was used with an intrinsic viscosity [η] of 1.96, 2.19 & 2.42 dl/g and a content of β-TCP or nano HAp in the amount of 6 and 11.7% on DBC, respectively. The impact of ethanol concentration in the spinning solutions was investigated with respect to forming conditions: as-spun draw ratio, draw ratio, spinning speed and pH of the coagulation bath upon the morphology structure and mechanical properties of the fibers. Lab-scale wet spinning was applied, which produced highly porous fibers (DBC/HPCF) characterised by a tenacity of 4.0 - 10.5 cN/tex and elongation of 10 - 14.5% (conditioned state). The porosity of the fibres was assessed by mercury porosimetry, and as a comparison by digital analysis of SEM images of the fibre cross-section. The novel fibres may be used as material in the construction of bone implants, hygiene products and in various technical applications.

Key words: *dibutyrylchitin, nano-hydroxyapatite, highly porous fibre, mechanical properties, morphology.*

Introduction

Cellulose and chitin are biopolymers abundant in nature. Fibres prepared thereof are of importance for textile and hygiene applications as well as in the construction of bone implants [1]. A new domain of investigations and potential application is concerned with highly porous fibres prepared from biodegradable biopolymers like cellulose, chitin derivatives and blends of L-and D-polylactides [1 - 4]. The fibres can be prepared by wet spinning at proper parameters of the spin solution (concentration of the polymer, kind of solvent) and spinning conditions like the composition of the coagulation bath, as-spun draw ratio, draw ratio and drying temperature. Sheath/core fibres with a porous core were prepared by spinning in an ethanol bath from a mixture of poly-L-lactide and poly-DL-lactide dissolved in dichloromethane with the addition of bovine serum albumin (BSA) [4].

Known are wet-spun porous fibres with pores in the range of 0.1 μm, and voids and capillaries in the range of 5 - 10 μm that can be discerned under an optical microscope [5]. The porosity stands in close relationship with the spinning conditions: it augments with the increasing concentration of the coagulant and temperature of the coagulation bath, while an increasing concentration of the polymer in the spinning solution produces a lower porosity [6].

Tailored mechanical and biological properties may be conferred upon biocomposites containing tri-calcium phosphate $Ca_3(PO_4)_2$ (TCP) or hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HAp). Biocomposite materials are being applied in medicine in the form of biodegradable implants [7]. Porosity is an important feature of the implants, providing a proper distance between cells, the transportation of nutrition substances to the cells, and the disposal of the metabolism products. The size and amount of pores are crucial, particularly in the reconstruction of bone tissue [8, 9]. HAp manifests good biocompatibility and is well absorbed by the human organism, therefore it is used in the construction of medical composites [7]. Numerous clinical tests have confirmed the biocompatibility and positive action of composites with a 20 - 60% content of HAp in the process of wound healing and bone construction [10].

Hydroxyapatite ceramics combined with biopolymers like chitin/HAp offer the chance of preparing new composite materials fit for the tissue engineering of bone prostheses [11]. Investigations have given proof of the high efficiency of a bicomponent tube made up of chitosan and apatite, used in the regeneration of nerve tissue [12]. There are also known methods of preparing fibres containing chitosan and HAp/β-TCP, designed to serve as scaffolds in tissue culture [13, 14].

Chitin does not dissolve easily in typical organic and inorganic solvents, which is the reason why derivatives of the polymer are prepared by reacting with anhydrides of organic acids. A chitin ester which readily dissolves in solvents like aceton, ethanol, chloroform, ethylene-, and methylene chlorides: di-methylformamide, N-methylpyrolidon, and dimethylsulfoxide is obtained by the reaction with butyric acid anhydride, dibutyrylchitin (DBC) [15, 16].

Wound healing is stimulated on account of the biological properties of DBC like biocompatibility, bacteriostacity and susceptibility to the action of lysozyme as a result of degradation to oligoaminsaccarides [17, 18]. In alkaline solutions, DBC fibres are regenerated to chitin fibres [19]. Of the DBC- and regenerated chitosan fibres, wound dressings can be made that contribute to a quick regeneration of tissue and reduction of scare size [20, 21]. Products with bioactive and hemostatic properties can be made from aerated DBC solutions for easy use in surgery. Results of an investigation of hemostasis including biocompatibility and the assessment of the response to implantation indicate a dependence upon molecular mass. A lower molecular mass of the polymer is recommended [22].

Depending upon the solvent used, DBC fibres can be formed by dry, dry-wet, wet spinning, by the melt blown technique or electrospinning [23 - 26]. The wet spinning method offers the possibility of spinning fibres from DBC solutions in any of the known DBC solvents.

Porous DBC fibres have so far been prepared solely by wet spinning from DBC ethanol solutions at concentration of 10.5 - 17.5% [2, 3, 27, 28]. The porous fibres were formed in aqueous solidifying baths at 7 °C and an EtOH concentration in the range of 0 to 17 wt%. Highly porous composite DBC fibres have so far not been produced.

It was our aim to prepare a method for the manufacture of highly porous DBC fibres containing β-TCP or nano HAp offering potential use amongst other in bone implants. It was assumed that the effect could be attained by employing a solution with a lower ethanol concentration and by adopting conditions for the solidifying of the spinning solution in the bath which would enable the formation of a non-homogeneous porous system. We also investigated the influence of ethanol concentration in spinning solution containing β-TCP or nano HAp on morphology, as well as the mechanical properties of the fibre. Moreover we examined the influence of the as-spun draw ratio, draw ratio, composition of the coagulation bath and spinning speed on the morphology and mechanical properties of the DBC/HPCF fibre.

Materials

DBC polymer was synthesised according to the synthesis procedure described in [29] from krill chitin, supplied by HEPPE MEDICAL CHITOSAN GmbH, Germany. In the work presented, three different parts of synthetised dibutyrylchitin were used. The polymers differed in their molar mass. For the assessment of the molar mass, the intrinstic viscosity of the polymer solution in DMAc at 25 °C was measured. The polymers obtained were characterised by an intrinsic viscosity equal to 1.94, 2.19 and 2.42 dl/g, which corresponds to a molar mass equal to 148 600, 168 600 and 188 900 g/mol, respectively.

Reagents

Dimethyloacetamide (DMAc), analytically pure (POCh SA, Gliwice, Poland), ethanol 96%, pure (POCh SA, Gliwice, Poland), hydrochloric acid 37.8%, analytically pure (Fluka, Germany), β-tricalcium phosphate - β-TCP - (Sigma Aldrich Lab., Germany), nano hydroxyapatite - HAp - < 200 nm 97% (Sigma Aldrich Lab., Germany).

Methods

Spinning solutions of DBC with a content of β-TCP or HAp nanoparticles

Based on the authors' experience, solutions of DBC with a concentration of 16.0% were prepared in ethanol with a concentration in the range of 67 - 78%. DBC was put into a blending vessel equipped with a band agitator, and an adequate amount of ethanol was added. The content was agitated for 6 hours at 23 °C, producing a clear light yellow solution, to which a homogeneous suspension of β-TCP or HAp nanoparticles in ethanol was added at 30 °C to attain a concentration of 6 and 11.7%, respectively. β-TCP and HAp aqueous suspension was prepared by ultrasonic mixing with the use of a Hielsher UP 200S, at a power of 200 W and frequency of 24 kHz, for 15 minutes. The β-TCP-containing spinning solution was mixed for 60 minutes, then filtered, deaerated and used in the spinning of DBC/HPCF fibres.

Spinning of DBC/HPCF fibres

Ethanol solution of DBC with a content of β-TCP or HAp nanoparticles was fed by means of a gear pump to a 150-hole spinneret (hole diameter 80 μm). Fibres were formed at an as-spun draw ratio in the range of 0.2 - 1.74, draw ratio 1.43 - 2.74 and spinning speed 9 - 23.4 m/min. Water or a 5% aqueous solution of EtOH at 22 °C and pH 7.8 served as a coagulation bath. We also examined the impact of the bath pH in the range of 2.0 - 7.8, which was adjusted by HCl upon the fibre properties. The fibre cable was rinsed with water at 40 °C, drawn in water at 90 °C, washed again with water to entirely remove ethanol, and dried at 30 °C.

Analytical methods

Rheology of the spinning solutions

A Brookfield viscometer, model R/S-CPS+, with a Rheo 3000 V1.1 program, was used in the testing of the solutions' rheology at 20 °C. A procedure was employed that contained three testing blocks, the analysis time of which was 90 seconds: block I - with a linear increase in the shearing speed from 1 to 100 s^{-1}, block II -with a constant shearing speed of 100 s^{-1}, block III - with a linear decrease of the shearing speed of 100 to 1 s^{-1}. Basic rheology parameters were estimated by means of the program: time, shearing speed, shearing stress, apparent viscosity, temperature and thixotropy.

Assessment of solutions by means of an optical microscope

The spinning solutions were assessed under a polarising microscope - Biolar (made by ZPO Warsaw) with a photographic attachment. The program Basic 1.2 of MultiScan Co. was employed in the recording and digital data handling.

Assessment of fibres by means of scanning electron microscopy (SEM)

The fibre surface and cross-section were captured with the following apparatus:

Table 1. *Spinning properties of DBC solutions.*

Symbol of solution	Intrinsic viscosity of DBC	Concentration of EtOH in solution	Symbol of calcium phosphate	Concentration of β-TCP / HAp on DBC	Average viscosity			Thixotropy
					I block	II block	III block	
	dl/g	%		%	Pa·s			Pa/s
RDB 1	1.96	67	β-TCP	6.0	43.6	16.5	26.9	19.085
RDB 2		73			40.6	18.2	34.2	26.946
RDB 3		77			104.1	17.2	27.2	43.087
RDB 4		78			62.1	17.9	31.4	57.026
RDB 5					70.9	13.7	24.3	120.565
RDB 6	2.11	78	-	-	61.9	16.6	29.2	92.412
RDB 7			HAp	11.7	77.9	19.8	41.0	108.165
RDB 8	2.46	78	-	-	379.3	18.9	33.9	142.086
RDB 9			HAp	11.7	499.7	21.2	44.5	143.840

SEM/ESEM, Quanta 200 (W), FEI Co., USA.

Assessment of the porous structure of the fibres

Analysis of the porous structure of fibres was made using mercury porosimetry. Measurements were made on AUTOPORE IV apparatus, Micromeritics, USA for pores in the range from 3.0 to 400,000 nm. The average pore diameter as well as the total pore area were measured. Additionally, for each sample of fibres, curves of the dependence between pore size and pore volume were drawn. Samples of fibres before examination were cut to a length equal to 10 mm, which allowed the opening of pores inside the fibres.

For comparison purposes, the porosity of the fibres was assessed using image analysis, done on the basis of SEM images analysis employing the program Adobe Photoshop CS6, which enables estimation of the grey level and number of pixels of the darker (pores) and lighter (fibre polymer) regions. The porosity is given as the pore surface percentage of the total fibre cross-section. Images at 5000× magnification were analysed. The final result is an average of five measurements.

Mechanical properties of fibres

Mechanical properties of the fibres were tested according to Standards PN-ISO-1973:1997 and PN-EN ISO 5075:1999 [1].

Results of the investigation and discussion

Spinning properties of the DBC solutions with a content of β-TCP or nano HAp

Based on the authors' earlier experience, spinning solutions were prepared using 67 - 78% aqueous solution of ethanol as a solvent. The solutions prepared were inspected by means of an optical microscope. The impact of ethanol concentration in the said range upon the dissolution of DBC was up to the present not investigated. The addition of β-TCP or HAp nanoparticles to the DBC ethanol solution caused a change in the hue and transparency of the solution regardless of the amount or kind of additive. The concentration of β-TCP or HAp in the spinning solutions was 6% or 11.7% of the polymer, respectively. In the microscopic images only a few agglomerates of the calcium phosphate were discernible, which were expected not to disturb the fibre forming process. Properties of the ethanol DBC spinning solutions with a content of β-TCP or HAp are presented in ***Table 1***.

The average apparent viscosity (I block) and thixotropy of the solution (RDB 1 - RDB 5) goes up with an increasing ethanol concentration. The unexpected changes observed for RDB 3 solutions require further investigations. The authors also analysed the stability of the polymer solutions. For this purpose, the polymer solution denoted as RDB 4 was stored for 4 days. After this time, the rheology and thixotropy were analysed. The results obtained, presented in ***Table 1*** and denoted as RDB 5, show a sharp increase in thixotropy. Except for the residence time, there might also be an impact of nano HAp upon the increase in viscosity (RDB 7 and RDB 9). The use of DBC with a higher intrinsic viscosity caused an increase in viscosity by several times (***Table 1***). From the DBC solutions, fibres were spun at varying conditions. The influence of the spinning conditions on the formation of pores was assessed.

Impact of ethanol concentration in the spinning solution upon the properties of DBC/HPCF fibres (series 1 and 2)

Ethanol has so far been used as a DBC solvent. The authors adopted conditions for the preparation of DBC spinning solutions in diluted ethanol. It was assumed that the ethanol concentration affects the solidification ability and size and amount of pores in the DBC/HPCF fibres formed. From solutions (RDB 1 - RDB 5) with an ethanol content in the range of 67-78%, DBC/HPCF fibres (***Table 1***, (β-TCP)) were spun at the following conditions: as-spun draw ratio 1.36, draw ratio 1.69, spinning speed 17.1 m/min, coagulation bath - water (series 1, ***Figure 1.a***).

The influence of ethanol concentration in the spinning solution at defined conditions upon the spinning stability of fibres has never been studied before. However, we observed an increasing ethanol concentration, with a slight increase in the tenacity and a drop in fibre elongation. Ethanol concentration influenced the porosity of the fibres: porosity increases with increasing ethanol concentration.

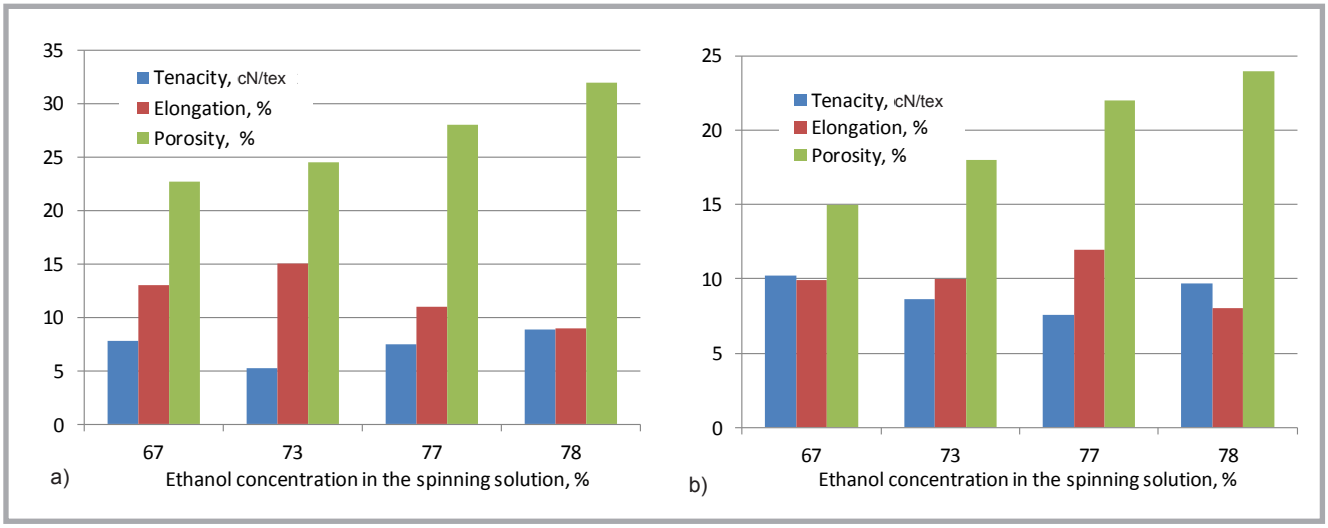

Figure 1. *Impact of ethanol concentration in the spinning solution upon DBC/HPCF fibre properties spun at the following conditions: a) series 1- as-spun draw ratio 1.36, draw ratio 1.69, spinning speed 17.1 m/min, b) series 2 - as-spun draw ratio 1.36, draw ratio 2.32, spinning speed 23.4 m/min.*

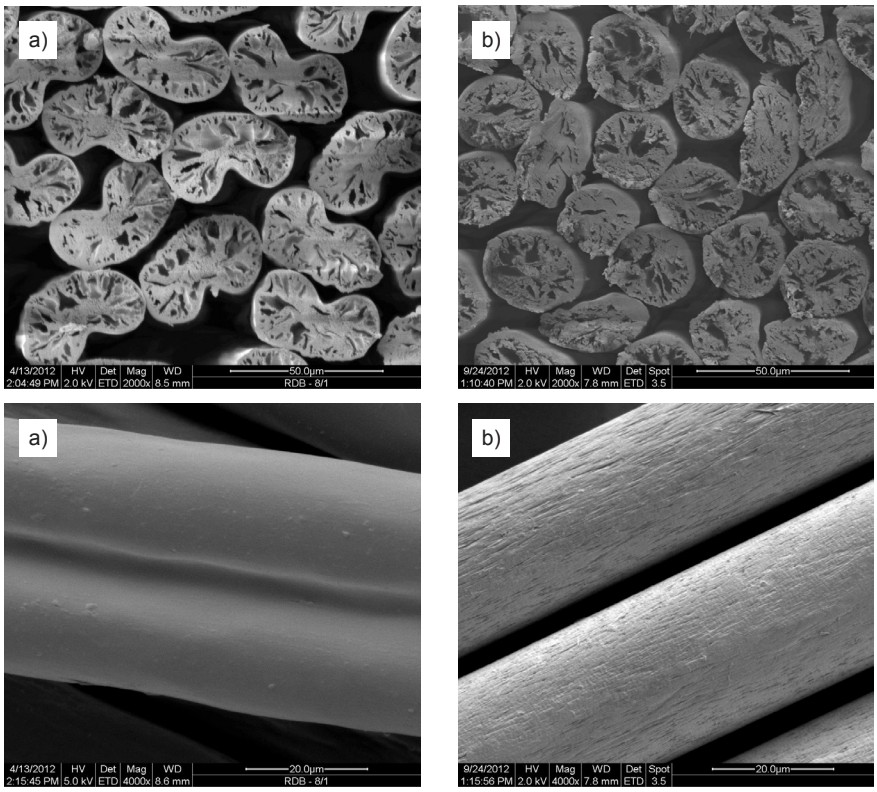

Figure 2. *SEM images of DBC/HPCF fibres spun at as-spun draw ratio 1.36, draw ratio 1.69, and spinning speed 17.1 m/min (series 1): a) - from a spinning solution with 73% of ethanol and pore surface of 25%, b) - from a spinning solution with 78% of ethanol and pore surface of 33%.*

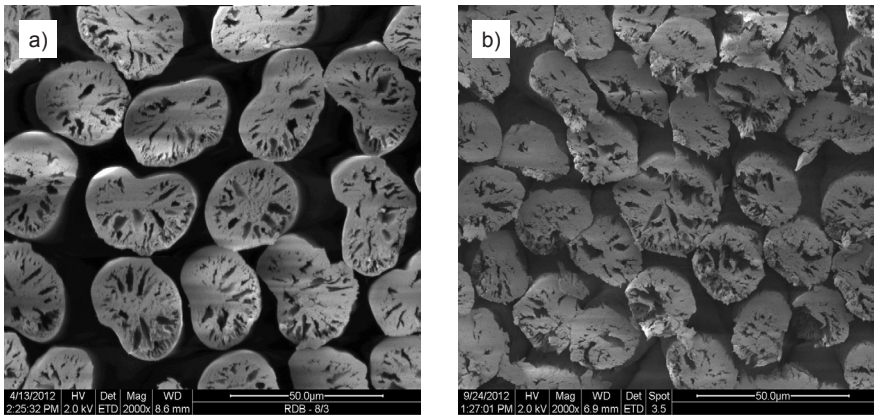

Figure 3. *SEM images of DBC/HPCA fibres spun at conditions: as-spun draw ratio 1.36, draw ratio 2.32, spinning speed 23.4 m/min (series 2), a) - from a spinning solution with ethanol of 73% content and porosity 18%, b) - from a spinning solution with ethanol of 78% content and porosity 24%.*

From the solution with a 73% ethanol concentration, fibres were obtained with a tenacity of 5.4 cN/tex and porosity of 25%, while at a 78% ethanol concentration the tenacity was 9 cN/tex and porosity 33%.

The fibre cross section (***Figure 2.a***), ethanol concentration 73%) is of a bean-like shape with pore divers in a shape arranged radially in the fibre interior, while the fibre surface is smooth, forming a solid skin.

The fibres (***Figure 2.b***), ethanol concentration 78%) are porous as well. The increase of ethanol concentration in the spinning solution influenced the morphological structure – the fibres are oval-shaped with very large radially arranged pores. The fibre surface is smooth with micro-cracks running along the fibre axis. The increase in porosity with the tenacity maintained at about 10 cN/tex is seen as positive having in mind the future application of the fibre. For the other two concentrations of ethyl alcohol, the same structure as presented in ***Figure 2.a*** was observed.

Gröbe et al. [30] proposed a mechanism for the forming of radially arranged capillaries: in the course of solidification of the spinning solution in a bath with a high precipitation potential, an inhomogeneous system is formed with pores filled with a mixture of the solvent and non-solvent. The larger of the pores act as nuclei for the forming of capillaries. The non-solvent is transported faster in the capillary than in the capillary-surrounding polymer, and a further precipitation of the polymer combined with the shrinkage and growth of the capillary proceeds in the direction of the concentration gradient, that is in the radial direction. The shape of the fibre cross-section depends largely on the proportion of the solvent and non-solvent streams [5]. A nearly circular cross-section appears if the proportion of the solvent to non-solvent stream falls below 1. If the proportion exceeds 1, the shape of the cross-section depends upon the diversified stiffness of the polymer on the fibre radius. With the increasing stiffness of the surface layer (a limited proneness to deformation) a flattening of the cross-section will occur along with a proceeding mass interchange. The proportion of the solvent to non-solvent stream was probably below 1 for the fibres in ***Figure 2.b***, (with 78% ethanol), with a circular shape of the cross section, while for the fibre in ***Figure 2.a***, (73% ethanol) the proportion was above 1 and a flattening of the cross-section occurred. In Series 2 with the same solutions (***Table 1***), the fibres were formed at a higher speed and draw ratio: as-spun draw ratio 1.36, draw ratio 2.32, spinning speed 23.4 m/min. The spinning had an uninterrupted run. An impact was found of the ethanol concentration in the spinning solution upon the tenacity, elongation and porosity of the fibre (***Figure 1.b***). With a higher draw ratio, fibres were obtained with a higher tenacity (around 10 cN/tex) and lower elongation. With an increased ethanol concentration in the spinning solution, the fibre porosity increases similar to that in Series 1, although at a lower level (max 24%). The change of spinning conditions (a higher draw ratio) influenced the fibre morphology. In ***Figure 3*** an oval, close to circular, shape can be seen. The pores are arranged radially and the fibre surface is smooth and even similar to Series 1 (***Figure 2.a***).

Analysis of pore structures using mercury porosimetry shows that the average pore diameter correlates with results obtained from the image analysis. In ***Figure 4***, the shape of the curve of differential pore volume versus pore size is presented. For all fibres assessed, the character of the curves was the same. Unfortunately the greatest pores visible on ***Figure 2*** and ***3*** were not determined by mercury porosimetry. For fibres formed from DBC solution in 73% of ethanol in conditions for series 1, the total pore area was equal to 59.7 m^2/g, while for series 245.7 m^2/g was noticed. Decreasing the total pore area is connected with an increase in the average pore diameter, which is equal to 256.1 nm for series 1 and 386.6 nm for series 2. The same relation was observed for other concentrations of ethanol.

Decrease in the alcohol concentration in the spinning solution caused a development of microporous phase, revealed by a peak at the diameter of 5 nm (***Figure 4***).

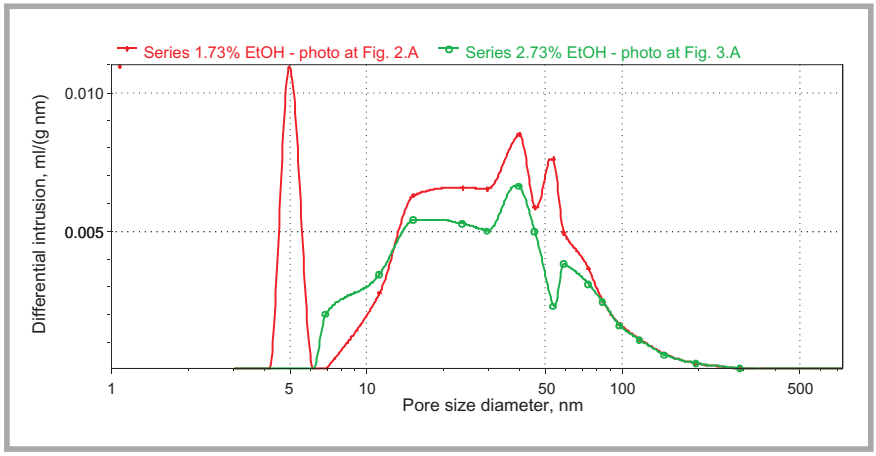

Figure 4. *Differential volume (pore volume) vs. pore size for two samples of fibres.*

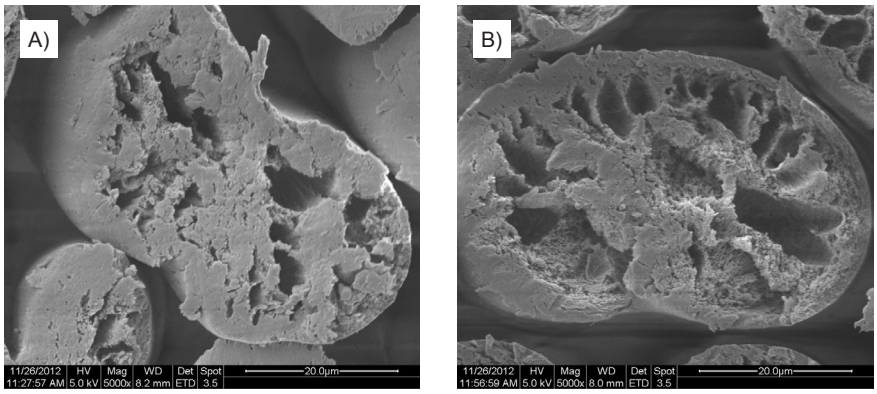

Figure 5. *SEM images of DBC/HPCF fibres spun at the following conditions: as-spun draw ratio 0.71, draw ratio 1.72, spinning speed 9.1 m/min. (series 3) from a spinning solution with a 78% ethanol concentration and 11.7% content of HAp; A - coagulation bath: water, B - coagulation bath: 5% aqueous EtOH.*

Impact of nano HAp in the spinning solution and spinning conditions upon properties of the DBC/HPCF fibres (series 3)

DBC with a higher intrinsic viscosity (2.19 dl/g) was used in the preparation of a solution with a 11.7% content of HAp on DBC (RDB 7, ***Table 1)***. The spinning of fibres was accomplished at the following conditions: as-spun draw ratio 0.71, draw ratio 1.72, spinning speed 9.1 m/min. Water was used as coagulation bath for fibres marked RDB 7/1 and a 5% aqueous ethanol for RDB 7/2 fibres. Spinning with 5% ethanol was more stable than with water as coagulant. DBC/HPCF fibres were obtained with properties presented in ***Figure 5*** and ***Table 2***.

A rather insignificant influence of the kind of polymer and nano HAp used was observed upon the tenacity of the fibre. A change of spinning conditions as well as a decrease in the draw ratio and spinning speed, in particular, had a direct impact on the decrease in fibre tenacity. The use of 5% ethanol as a coagulant caused a slight increase in the tenacity and a remarkable growth of fibre porosity (***Figure 5***).

An oval shape of the fibres appears regardless of the kind of coagulation bath used. The change from water to 5% aqueous ethanol affected the fibre morphology. The fibres obtained are characterised by very large radially arranged pores which occupy 21% and 33% of the cross-section surface, respectively, for water and 5% for ethanol coagulant. (***Figure 5***). The surface of both fibres is smooth and is even in the form of a solid skin, as in ***Figure 2.A***. It was demonstrated that the use of a 5% ethanol coagulant exerts a positive impact on the shape and size of pores in the fibre.

Impact of the coagulation bath pH upon the properties of the DBC/HPCF fibres (series 4)

For investigation of the spinning process, a solution was prepared of DBC with a higher intrinsic viscosity, and with a 11.7% content of HAp (RDB 9, ***Table 1***). The spinning was carried out at conditions like in series 3: as-spun draw ratio 0.71, draw ratio 1.72, spinning speed 9.1m/min. The impact of the coagulation bath pH (5% aqueous ethanol) was examined (***Figure 6***).

In spite of the fact that a polymer with a higher molecular mass was used with a comparable amount of HAp, the fibre tenacity was not improved as for fibres formed in 5% ethanol with varied pH. An impact was observed of the coagulation bath pH upon the porosity of the fibres. A low pH produced the maximal porosity of 42%. With such a high porosity of the fibre, the tenacity ranges at about 6 cN/tex. The lower coagulation bath pH did not result in a change in fibre tenacity.

The fibres reveal a regular, close to circular, shape, (pH 2 of the coagulation bath) and very large radially arranged pores which occupy 42 % of the cross-section

Table 2. *Mechanical properties of DBC/HPCF fibres.*

Parameter	Symbol of fibre	
	RDB 7/1 water	RDB 7/2 5% EtOH
Linear density, dtex	10.8	10.1
Breaking force conditioned, cN	7.24	7.18
Tenacity conditioned, cN/tex	6.7	7.11
Elongation at break, conditioned, %	12.0	9.0

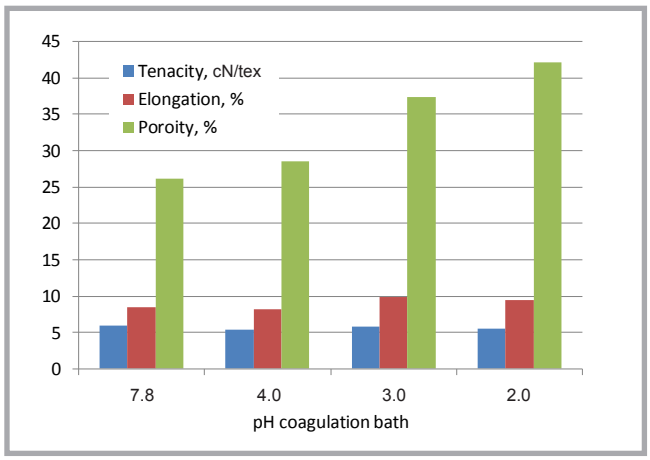

Figure 6. *Impact of the coagulation bath pH upon properties of the DBC/HPCF fibres formed at an as-spun draw ratio of 0.71, a draw ratio of 1.72, and spinning speed of 9.1 m/min (series 4).*

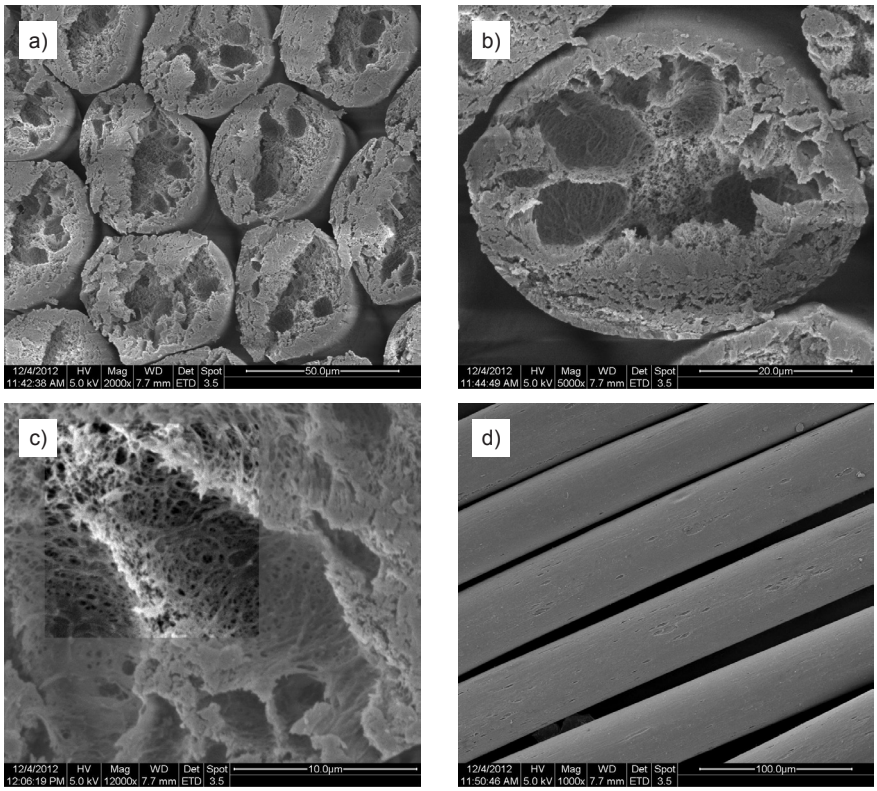

Figure 7. *SEM images of DBC/HPCF fibres formed at an as-spun draw ratio of 0.71, draw ratio of 1.72, spinning speed of 9.1m/min, and pH 2 of the coagulation bath (series 4).*

surface (***Figure 7***). The fibre surface is a smooth and even skin.

The change of the spinning solution composition (higher intrinsic viscosity of DBC, concentration of nano HAp-11.7% on DBC) and of the coagulation bath (aqueous 5% ethanol with pH below 7) had a beneficial impact on the fibre morphology. ***Figure 7.c*** presents the inner capillary wall with micro- and nanopores. The authors prepared conditions for the production of high porosity composite dibutyrylchitin fibres from spinning solutions with an ethanol concentration in the range of 66 - 78% [31].

Summary

Highly porous fibres were prepared from dibutyrylchitin containing β-TCP and nano HAp. The fibres reveal a smooth, even outer sheath, and inner porous macro-, micro- and nano structure. The DBC/HPCF fibres were spun from spinning solutions in aqueous 66 - 78% ethanol in a coagulation bath which was water or aqueous 5% ethanol. The properties of the spinning solution containing β-TCP or nano HAp varied in viscosity and thixotropy. The amount and size of pores formed was affected by varying the spinning conditions such as the as-spun draw ratio, draw ratio, spinning speed and pH of the coagulation bath. The tenacity of DBC/HPCF fibres which fell in the range of 5 - 10 cN/tex depended upon the concentration of ethanol in the solution as well as on the content of β-TCP or nano HAp, and spinning conditions. Based on SEM images, the porosity of the DBC/HPCF fibres was estimated, amounting to above 40% of the total fibre cross-section surface. The use of DBC/HPCF in the construction of bone implants can be envisaged. High porosity fibres can be obtained from DBC solution with a concentration of 78% ethanol at a low value of the as spun draw ratio, small drawing ratio and a coagulation bath of 5% ethanol.

Editorial notes

1) *Mechanical properties were tested at the Laboratory of Metrology of IBWCh acting under accreditation certificate PCA AB 388.*

Acknowledgement

This research was funded by the National Science Centre (NCN), Ministry of Science and Higher Education in 2009–2013 as research project No. N N507 446137 „Biodegradowalne implanty kostne", (Biodegradable bone implants).

References

1. Schulz B, Seide G, Gries T, Kayacan I, Milow B, Ratke L. Characterization and spinning of highly porous aero-cellulosic fibres for application in technical textiles, Achema 2012, 30 Word Exhibition Congress, Frankfurt am Main, 18-22 June 2012.
2. Wawro D, Stęplewski W, Ciechańska D, Krucińska I, Wesołowska E. "The Effect of Solvent Type on the Mechanical Properties of Dibutyrylchitin (DBC) Fibres", *Fibres & Textiles in Eastern Europe* 2007; 15, 3(62): 14-18.
3. Błasińska A, Mikołajczyk T, Krucińska I, Komisarczyk A. "Investigations on manufacturing of porous fibres made from dibutyrylchitin; Rheological properties of spinning solutions in ethanol and N-methylpyrrolidone", *Book of Proceedings of the 2nd International Textile, Clothing & Design Conference*, Dubrovnik, Croatia, 3-6 October, 2004.
4. Rissanen M, Puolakka A, Ahola N, Tonry A, Rochev Y, Kellomäki M, Nousiainen P. „Effect of Protein-Loading on Properties of Wet-Spun Poly(L,D-lactide) Multifilament Fibres", *Journal of Applied Polymer Science* 2010; 116: 2174–2180.

5. Ziabicki A, "Physics of the fibre formation from natural and artificial polymers") WNT, Warszawa, 1970.
6. Takahashi M, Nukushina Y, Kosugi S. *Text Res J* 1964; 34: 87.
7. Rosół P. "Estimation of durability of implants prepared from polymeric composites" (doctorate thesis) AGH in Kraków, 2006.
8. Błażewicz M. „Materials for tissue engineering", *Inżynieria Biomateriałów* 2001; 4, 15-16: 32-35.
9. Sosnowski S, Słomkowski S, Scaffolds for cell cultures produced from nano- and microparticles 2005; 8, 47–53: 214-216.
10. Di Silvio L, Dalby MJ, Bonfield W. *In vitro* response of osteoblasts to hydroxyapatite-reinforced polyethylene composites", *J Mater Science, Mater in Med* 1998; 9: 845–849.
11. Zigang Ge, Sophie Baguenard, Lee Yong Lim, Aileen Wee, Eugene Khor, "Hydroxyapatite–chitin materials as potential tissue engineered bone substitutes", *Biomaterials* 2004; 25: 1049–1058.
12. Isamu Yamaguchi, Soichiro Itoh, Masumi Suzuki, Akiyoshi Osaka, Junzo Tanaka, „The chitosan prepared from crab tendons: II. The chitosan/apatite composites and their application to nerve regeneration", *Biomaterials* 2003; 24: 3285–3292.
13. Yang D, Jin Y, Zhou Y,Ma G, Chen X, Lu F, et al. In situ mineralization of hydroxyapatite on electrospun chitosan-based nanofibrous scaffolds *Macromol Biosci* 2008; 8: 239–46.
14. Wawro D, Pighinelli L. Chitosan fibres with HAp/β-TCP nanoparticles, *International Journal of Molecular Sciences*, 2011; 12(11): 7286-7300.
15. Szosland L. Di-O-butyrylchitin. In: Muzzarelli RAA, Peter MG, editors. *Chitin Handbook*. European Chitin Society. Germany;1997, pp. 53–60.
16. Szosland L, Stęplewski W. Rheological characteristic of dibutyrylchitin semi-concentrated solutions and wet spinning of dibutyrylchitin fibres, in '*Advances in Chitin Science', vol II, Proceeding of 7th International Conference on Chitin and Chitosan*, Lyon, 3 – 5 Sept. 1997, 531-536, 1997, ed. A. Domard, G.A.F. Roberts, K.M. Varum, Jacques Andre Pub. Lyon 1997.
17. Chilarski A, Szosland L, Krucińska I, Kiekens P, Błasińska A, Schoukens G, Cisło R, Szumilewicz J. Novel Dressing Materials Accelerating Wound Healing Made from Dibutyrylchitin, *Fibres & Textiles in Eastern Europe* 2007; 15, 4 (63): 77-81.
18. Muzzarelli A, Guerrieri M, Goteri G, Muzzarelli C, Armeni T, Ghiselli R, Cornelissen M. The biocompatibility of dibutyryl chitin in the context of wound dressings, *Biomaterials* 2005; 26: 5844–5854.
19. Biniaś D, Boryniec S, Biniaś W, Włochowicz A. Alkaline Treatment of Dibutyrylchitin Fibres Spun from Polymer Solution in Ethyl Alcohol, *Fibres & Textiles in Eastern Europe* 2006: 14, 3(57): 122-18.
20. Krucinska I, Szosland L, Cisło R, Błasinska A, Komisarczyk A, Chilarski A, Bilska J, Pilas B. A wound dressing material of dibutyrylchitin and chitin reconstituted therefrom, EP1778303 A1, 2007.
21. Schoukens G, Kiekens P, Krucinska I. New Bioactive Textile Dressing Materials from Dibutyrylchitin Stimulating Wound Healing, V International Technical Textiles Congress 7-9 November 2012, İZMİR.
22. Krucinska I, Komisarczyk A, Paluch D, Szymonowicz M, Zywicka B, Pielka S. The impact of the dibutyrylchitin molar mass on the bioactive properties of dressings used to treat soft tissue wounds, *J Biomed Mater Res B Appl Biomater* 2012; 100(1): 11-22.
23. Szosland L, East GC. The dry spinning of dibutyrylchitin fibres, *J Appl Polym Sci*, 1995; 58: 2459-2466.
24. Szosland L, Stęplewski W. Method of obtaining fibre from chitin esters, PL 187224, 2004.
25. Krucińska I, Komisarczyk A, Chrzanowski M, Paluch D. Producing Wound Dressing Materials from Chitin Derivatives by Forming Nonwovens Directly from Polymer Solution, *Fibres & Textiles in Eastern Europe*, 2007; 15, 5-6 (64-65): 73-75.
26. Gliścińska E, Babeł K, Krucińska I. Activated Carbon/Dibutyrylchitin (DBC) as Fibrous Antibacterial Noncytotoxic Wound Dressing Material, *Fibres & Textiles in Eastern Europe*, 2012; 20, 2(91),: 84-90.
27. Błasińska A, Mikołajczyk T. Wet Spinning of Dibutyrylchitin Fibres from Ethanol Solution, *Fibres & Textiles in Eastern Europe* 2005; 13, 6 (54): 36-40.
28. Struszczyk H, Ciechańska D, Wawro D, Stęplewski W, Krucińska I, Szosland L, Van de Velde K, Kiekens P. Some properties of dibutyrylchitin fibres, H. Struszczyk, A. Domard, M. G. Peter, H. Pospieszny, ed., "*Advances in Chitin Science*" vol. VIII, EUCHIS'04, Institute of Plant Protection, Poznań, 2005; 279-283.
29. Szosland L, Janowska G. Method for preparation of dibutyrylchitin. Polisch Patent PL 169077B1, 1996.
30. Gröbe V, Mann G, Duwe G. *Faserforsch. Textiltech*, 1966; 17: 142.
31. Wawro D, Krucińska I, Stęplewski W, Komisarczyk A. Polish Patent Application P. 403200 (18.03.2013), Method of manufacture composites highly porous DBC fibres, 2013.

Received 24.12.2012 Reviewed 27.05.2013