

The Influence of Forming Conditions on the Properties of the Fibers Made of Chitin Butyryl-Acetic Copolyester for Medical Applications

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ABSTRACT: This work describes the impact of basic parameters of the forming process on the macroscopic structure, sorption properties, and strength of fibers made of chitin butyryl-acetic copolyester (BOC). Regardless of the chemical structure of chitin BOC and intrinsic viscosity of polymer, solutions used in the spinning industry are non-Newtonian fluids diluted by shearing without flow boundary. Obtained fibers have a high total pore volume; thus, they may be classified into the group of highly porous fibers. The nature of the porous structure and the total pore volume result in high sorption properties of this hydrophobic material and in very high values of water retention. At the same time, fibers made of chitin derivatives have a good tenacity exceeding 24 cN/tex. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Chitin is the second most abundant polysaccharide, next to cellulose. This naturally renewed polymer with excellent biological properties is composed of β -(1-4)-linked 2-acetamido-2-deoxy-D-glucopyranose units. Currently, main source of chitin production is focused on the chitin isolation from marine invertebrates such as crab, krill, shrimp, and lobster (79%) and fungi (21%); however, some insects are also perspective source of chitin.¹

Chitin, a natural polymer, and certain of its derivatives have been found to be nontoxic, biocompatible polymers, which do not lead to any allergic reactions in contact with tissues and blood, and their bioactivity involves macrophage activation, intense granulation tissue growth and tissue granulation, and growth of small blood vessels within a wound, that is, significant acceleration of wound healing.^{2–11}

A method for the preparation of soluble chitin copolyesters has been developed and described at the Department of Physical Chemistry of Polymers, Łódź University of Technology.¹²

The solubility of chitin copolyesters in typical organic solvents and chitin fiber-forming properties open up a possibility of application in the manufacture of wet-spun fibers.

The objective of this investigation has been to determine the effect of basic forming process parameters on the macroscopic

structure and sorption and strength properties of chitin butyryl-acetic copolyester (BOC) fibers.

Because of the role of the fibers in the polymer–fiber composite, the highest possible porosity was aimed at, because the fiber sorption properties of hydrophobic materials depend on the total pore volume and characteristics of the porous structure. These properties determine body fluid absorption and the subsequent resorption process of the fibrous composite component.

When osteoconductive or osteoinductive nanoadditives are introduced to the composite fibrous component, this accelerates bone tissue reconstruction. Another article will address a study of the preparation of nanocomposite fibers from the polymer.

The fiber strength properties also need to be at a level appropriate for the manufacture of an multi direction (MD)-type composite in which staple fibers are dispersed in a polymer matrix. We assumed that such fiber properties can be obtained by targeted selection of manufacturing process parameters. We aimed to obtain fibers that combined good tenacity properties and improved porosity. Given that the proposed implant solutions are materials that do not transmit stresses (MD-type composites), it is not desirable in this case for fibers to have a high intrinsic strength value. The fibers ought to have an intrinsic strength above 12 cN/tex. However, for applications of this

type, the fibers should feature higher porosity. This porosity will ensure easier penetration of body fluids into the fiber material and thereby accelerate the process of biodegradation. This in turn will enable the creation of a porous structure appropriate in terms of the proliferation of bone cells (pore sizes in the range of 15–200 μm) in the whole of the implant material.

MATERIALS AND TEST METHODS

Synthesis of Chitin BOC

Syntheses of the chitin co-(butyrate/acetates) were carried out according to a procedure described in our previous article.¹¹ Two polymer series differing in their content of acetyl groups were used to produce fibers: BOC 95/5 and BOC 90/10, containing 95 and 90% butyryl groups and 5 and 10% acetyl groups, respectively.

Determination of Rheological Properties of Spinning Solutions

The characteristics of spinning solutions were determined using an Anton Paar rotary rheometer. 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. N and k rheological parameters were determined based on flow curves.

Fiber Forming

BOC fibers were formed by a wet process from solution using ethyl alcohol as a solvent. A large laboratory spinning machine with exchangeable modules was used. The parameters of the respective process stages could be significantly varied, continuously monitored, and stabilized at a defined level. Spinning nozzles (240-hole) with a 0.08-mm diameter were used.

Solidification was carried out in a bath with a solvent (ethyl alcohol) and nonsolvent (water) with composition and temperature selected within the study. The drawing process was conducted in two stages in an aqueous plasticization bath at 25 or 65°C (depending on the process variant used) and subsequently in superheated steam at 135–140°C. In both drawing stages, the maximum possible deformation in the given conditions was applied. After washing, the fibers were dried in isothermal conditions at a low temperature.

Fiber Structure and Property Testing Methods

Fiber porosity was determined using mercury porosimetry with a Carlo-Erbe porosimeter coupled with a computer system for measuring pores with sizes between 3 and 7500 nm. The total volume of pores of respective sizes and their inside area were determined.

Moisture sorption for the fibers in 65% relative humidity (RH) and in 100% RH was determined according to Polish standard PN-P-04601:1991.

Water retention was determined after retaining the fibers in water with the surfactant Rokafenol for 24 h. The mass of the fiber sample after centrifugation at 10,000 m/s was compared with dry fiber mass. The average from five measurements was given.

Tenacity and elongation at break was determined using an Intron strength-testing machine according to Polish standard PN-EN-ISO-268:1997.

Microscopic structure was analyzed using a JSM 5400 JEOL scanning electron microscope (SEM) and an atomic force microscope (AFM), using MultiView 1000TM.

RESULTS AND DISCUSSION

Copolyesters Spinning Liquid Rheological Properties

Intrinsic viscosity of used chitin copolyesters was determined by viscometry method using dilute solutions of polymers in dimethyl acetamide (DMA) in range of concentrations from ca. 0.4 to 0.1 $\text{g}/100 \text{ cm}^3$.

Thin films of chitin copolyesters were prepared from solutions of polymers in formic acid (98%) as follows: after dissolution of polymer, 5 mL of solution with concentration of 10% was poured out on the Petri dish with diameter of 7.5 cm. The solvent was evaporated off and thin film was formed, and then the obtained film was washed with distilled water several times until no traces of formic acid were detected in water and dried. The prepared films served to confirm the chemical structure using the FTIR method.

The rheological properties of ethanol chitin copolyester solutions, which differed in their polymer chemical composition with similar intrinsic viscosity values of 1.83–1.93 dL/g , obtained directly after synthesis, were tested. The concentration of solutions was selected so that the apparent dynamic viscosity was at a relatively low level, which still ensured suitable processing into fibers in the wet process from solution and maintaining stability of the forming process. A low spinning solution concentration is favorable with regard to the porosity of the resulting fibers, even though stream discontinuity may occur. This is desirable because of the role of the fibers in the polymer–fiber composite.

When as low a spinning solution concentration as possible is to be used, the liquid's rheological properties are especially important. The rheological properties of the liquid also determine flow rate distribution during the flow in the spinneret channel (transverse gradient) and changes in the longitudinal speed gradient along the forming path. Its value, which is also related to the fiber reception force, determines the axial orientation of fiber structural elements in the gradually solidifying stream and related fiber strength properties.

The analysis of flow curves (Figure 1) shows that independent of the copolymer chemical composition and its intrinsic viscosity, both test solutions are non-Newtonian liquids diluted by shearing ($n < 1$) without a flow limit. Tangential stress increases less than proportionally with an increased shear rate, and flow curves cross the origin of the coordinate system.¹³ BOC 95/5 solution obtained from a copolymer with lower intrinsic viscosity and a concentration of 12.8% (see Table I) is more like a Newtonian fluid (higher n rheological parameter values). The rheological parameter k , a measure of solution consistency, has a slightly lower value of 22.76 compared with BOC 90/10 solution. The solution is more polymeric, which is consistent with the higher intrinsic viscosity value of the copolymer. Furthermore, the rheological parameter k is higher at lower spinning solution concentration.

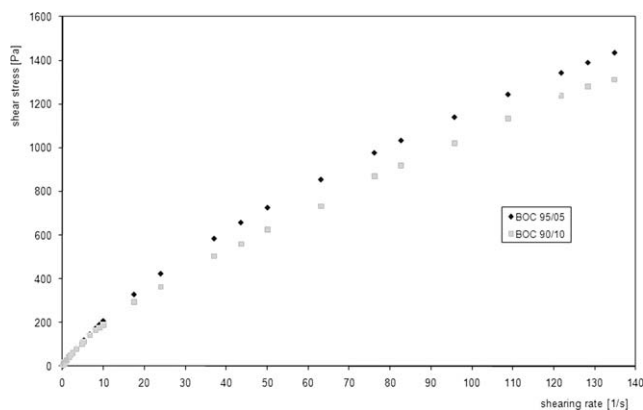


Figure 1. Shearing stress as a function of the shearing rate for chitin butyryl-acetic copolyester solutions BOC 95/05 and BOC 90/10.

Changes in the relationship between apparent dynamic viscosity and shear rate are shown in Figure 2. Reduced apparent dynamic viscosity with a higher shear rate is seen for both test solutions, which is typical for polymer liquids.

All the test solutions have stable rheological parameters over long periods of at least 72 h, which is favorable because of the fiber manufacturing process.

Analyzing the effect of the chemical structure of the BOC copolymer on the rheological behavior of the fluid, it can be assumed that the rise in the proportion of octane groups in the copolymer denoted BOC 90/10 leads to an increase in the dimensions of the tangled macromolecules¹¹ relative to copolymer BOC 95/05 (evidenced in its poorer solubility). According to the known explanation of the shear thinning mechanism,¹³ in an immobile liquid there is significant tangling of macromolecules with the continuous phase immobilized between them (solvent). During shearing, the macromolecules are straightened and untangled as the shear rate increases. This leads to a reduction in the internal friction of the system, as a result of the disintegration of those clusters, particularly when they are large (high tendency for macromolecules to become tangled).¹⁴ This is linked to the increase in the rheological parameter k for the copolymer BOC 90/10 compared with BOC 95/05, because in this case a higher value of the stress producing this effect is required. Also, the fluid becomes increasingly non-Newtonian, as is shown by the fall in the value of the rheological parameter n for the spinning solution containing the copolymer BOC 90/10.

This behavior of the copolymer BOC 90/10 solution may result in a lower. The lower orientation of macromolecules may lead

Table I. Characteristic and Rheological Parameters of Chitin Butyryl-Acetic Copolyester Solutions: BOC 95/05 and BOC 90/10

Type of solution	Rheological parameters	
	n	k
BOC 95/05	0.889	22.36
BOC 90/10	0.819	26.98

to reduction of intermolecular bonds that affect the strength properties. In spite of the greater deformability of the fiber made of copolymer BOC 90/10, the attainable value of R_c is significantly higher than in the case of fibers made of copolymer BOC 95/05. At the same time, the strength of the fibers obtained from copolymer BOC 95/05 is only slightly higher, by ~ 2.5 cN/tex, than that of the fibers made from copolymer BOC 90/10. This will be analyzed in detail in the next part of the work.

Selection of Solidification and Stretching Conditions in the Plasticization Bath

The structure and properties of the final fibers depend on the course of the solidification process and susceptibility of structures formed during the stage to deformation processes at successive stretching stages.

The essential parameters that determine the mass exchange rate during fiber solidification include the composition and temperature of the coagulation bath. It is known^{15,16} that when solidification occurs in so-called mild baths with increased solvent content at low temperatures, this is typical of solidification according to the diffusion mechanism. The structures formed in such conditions have high susceptibility to deformation, thus yielding increased fiber strength properties. When solidification conditions are more stringent because of reduced solvent content in the bath or increased temperature in a mild bath, solidification occurs according to a mechanism similar to the drop one, leading to increased porosity fibers.^{17,18}

As we aimed to obtain chitin copolyester fibers with as high a porosity as possible and simultaneously good fiber strength properties, the fiber solidification process was carried out at a low temperature of 15°C, also appropriate because of the properties of the solvent used.

The solvent content in the bath of between 5% and the upper limit of 25%, which ensured suitable solidification, was a parameter to be changed.

The process was conducted at a positive as-spun draw ratio value of +10%, which should result in fibers with increased porosity. The first stretching stage occurred in an aqueous

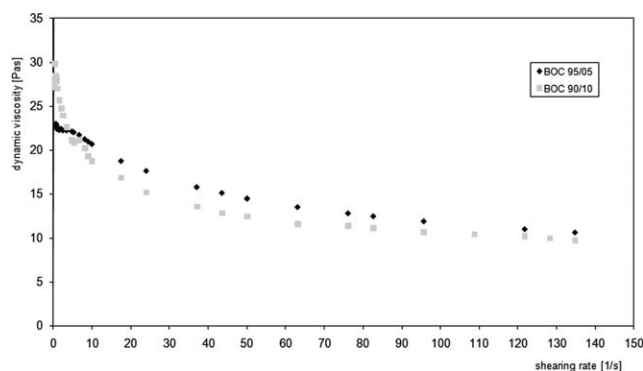


Figure 2. Apparent dynamic viscosity as a function of the shearing rate for solutions of chitin butyryl-acetic copolyester BOC 95/05 and BOC 90/10.

Table II. Molding Conditions for Fibers from a Polymer Designated BOC 95/05

Sample symbol	Content C ₂ H ₅ OH in coagulation bath (%)	Plasticization bath temperature (°C)	As-spun draw ratio (%)	Drawing process		
				Drawing in plasticization bath, R ₁ (%)	Drawing in stream, R ₂ (%)	Total draw ratio, R _c (%)
B1	5	25	+10	38.50	379.38	563.95
B2	10	25	+10	54.72	347.33	592.14
B3	15	25	+10	43.06	404.46	621.64
B4	20	25	+10	57.97	359.07	625.20
B5	25	25	+10	49.76	365.82	597.62
B6	20	25	+30	26.17	319.41	429.17
B7	10	65	+10	88.76	228.53	520.13
B8	10	65	+10	One-stage process R ₁ = R _c = 88.76%		
B9	15	65	+10	139.05	132.62	456.08

Constant conditions of the forming process:

^a Temperature of coagulation bath at 15°C.

^b First stretch stage—water and second stretch stage—superheated steam at 135–140°C.

plasticization bath at 25°C, and the second stage in superheated steam at 135°C with deformation close to maximum values. Both stretching process media were selected in preliminary tests.

It follows from the analysis of susceptibility to deformation of the structure formed in fiber solidification in baths with various compositions (Table II) that solvent content increased to 20% leads to higher maximum total stretch values (up to 625%). However, this does not significantly affect fiber strength properties, being between 16 and 18 cN/tex (Table III).

The fibers solidified in a bath with 15% solvent content have the highest tenacity of 18 cN/tex. This is due to the fact that in such a case, at lower deformation in the plasticization bath, the stretch value in the second process stage was the highest (>400%).

A further increase of solvent content in the solidification bath to the limit of 25% leads to reduced susceptibility to deforma-

tion in the second stretching stage and reduced total stretch values. This leads to fiber tenacity reduced to 14.5 cN/tex. In addition, for the bath with 20% solvent content, fiber forming was attempted at a higher as-spun draw ratio value (+30) (sample B6). The resulting fibers had lower susceptibility to deformation, especially at the first stretching stage, and the total stretch value was at a level of 430%. This resulted in a fiber tenacity of 14 cN/tex. Therefore, the selection of plasticization bath temperature was carried out for fibers formed at an as-spun draw ratio of +10%. A plasticization bath temperature increased to 65°C had a positive effect on susceptibility to deformation at the process stage because of increased macromolecule mobility in the material. For fibers solidified in baths with 10% solvent content, this led to tenacity increased to 21.1 cN/tex (sample B7). However, for fibers solidified in a bath with 15% ethanol concentration and stretched in a plasticization bath at both 25 and 65°C, the tenacity level was similar (~ 18 cN/tex) (samples B3 and

Table III. Strength Properties of Fibers Formed from a Polymer Designated BOC 95/05 Formed with a Changing Solvent Content in the Solidification Bath

Sample symbol	As-spun draw ratio (%)	Total draw ratio (%)	Tenacity (cN/tex)	Elongation at break (%)	Young's modulus (N/tex)
B1	+10	563.95	16.31 ± 2.61	2.50 ± 0.58	10.27 ± 0.74
B2	+10	592.14	16.13 ± 2.08	2.17 ± 0.49	10.74 ± 0.91
B3	+10	621.64	18.41 ± 2.18	2.42 ± 0.51	10.47 ± 0.73
B4	+10	625.20	16.45 ± 1.75	1.93 ± 0.38	10.38 ± 0.62
B5	+10	597.62	14.51 ± 1.71	1.86 ± 0.46	10.06 ± 0.87
B6	+30	429.17	14.63 ± 1.55	2.18 ± 0.61	8.85 ± 0.64
B7	+10	520.13	21.11 ± 2.25	3.42 ± 0.57	10.57 ± 0.67
B8	+10	88.76	11.23 ± 1.63	4.54 ± 1.17	4.53 ± 0.73
B9	+10	456.08	17.96 ± 2.26	3.87 ± 0.59	8.15 ± 0.80

Table IV. Molding Conditions for Fibers from a Polymer Designated BOC 90/10

Sample symbol	Content C ₂ H ₅ OH in coagulation bath (%)	As-spun draw ratio (%)	Drawing process		
			Drawing in plastification bath, R_1 (%)	Drawing in stream, R_2 (%)	Total draw ratio, R_c (%)
C1	5	-20	77.18	408.37	800.75
C2	10	-10	82.04	434.07	872.33
C3	15	0	91.37	297.26	660.07

Constant conditions of the forming process:

^a Temperature of coagulation bath at 15°C.

^b First stretch stage—water at 25°C and second stretch stage—superheated steam at 135–140°C.

B9). This is due to the fact that with fibers solidified in mild conditions having a high susceptibility to deformation in the first drawing stage ($R_1 = 139.0\%$), the draw ratio value in superheated steam is considerably reduced to a value comparable to that in the first stage. In consequence, this leads to a total draw ratio value as much as 165% lower than for fibers stretched in a plasticization bath at 25°C. Therefore, it is appropriate to conduct the first stage of fiber drawing in a 65°C bath when the solidification process occurs in a bath with 10% solvent content. As its concentration is relatively low, this should contribute to the formation of porous fiber structure. The need for the two-stage stretching process was confirmed by the fact that after drawing in a 65°C plasticization bath the fibers had a tenacity of 10 cN/tex (sample B8) lower compared with those subjected to additional stretching in superheated steam (sample B7).

Studies of the selection of solidification and plasticization stretching conditions were also carried out for BOC 90/10 copolymer fibers. These proved that the stability of the fiber-forming process is greatly reduced when spinning solutions of the polymer are used. It is only possible to conduct the forming process with a narrow range of negative as-spun draw ratio values. Depending on the solvent content of the solidification bath, this ratio is between 0 and -20% (Table IV).

This behavior may result from increased acetyl group content in the macromolecule of the material, which in turn affects the properties of the gel formed during solidification and the phase transition process. This, however, does not exclude the possibility of obtaining fibers with a tenacity of 21–22 cN/tex (Table V), favorable sorption properties for a hydrophobic material, and water retention at a level of up to 50%. The values of the

parameters may indicate increased fiber porosity. It is noteworthy that the properties are obtained when the first stretching stage occurs in a 25°C plasticization bath. The second stretching stage is carried out in superheated steam, exactly the same as for BOC 95/05 copolymer fibers.

Effect of As-Spun Draw Ratio and Deformation during Stretching Stages on BOC Fiber Structure and Properties

The as-spun draw ratio is the essential parameter that determines the fiber structure after the solidification stage and the susceptibility to deformation processes at successive stretching stages. When the macromolecule structure is rigid, the deformation of building blocks in a still liquid stream is important (as proved for alginate fibers).^{19,20} This is related to the longitudinal velocity gradient value that changes along the forming path, depending on the as-spun draw ratio value.

When positive as-spun draw ratio values are applied, alginate fibers are formed²¹ with good strength properties.

A wide range of as-spun draw ratio changes (-20 to +50%) was used for BOC 95/5 chitin copolyester fibers. The detailed forming conditions were consistent with those selected in the previous section (see Table VI).

Changes in as-spun draw ratio from negative to slightly positive values (at a level of +10%) lead to fiber specific strength higher by ~ 2 cN/tex (Table VI). Fibers formed at an as-spun draw ratio of +10% have a maximum value of 24.77 cN/tex. This is due to the fact that in such cases the maximum achievable stretch values in the second process stage were the highest (at a level of 200.6%) with small differences in total stretch values (sample B10 compared with B13). A further increase in as-spun draw ratio values leads to reduced maximum achievable

Table V. Properties of Fibers from a Polymer Designated BOC 90/10

Sample symbol	As-spun draw ratio (%)	Total draw ratio (%)	Moisture sorption at 65% RH (%)	Moisture sorption at 65% RH (%)	Water retention (%)	Tenacity (cN/tex)	Elongation at break (%)	Young's modulus (N/tex)
C1	-20	800.75	6.08	10.10	49.90	21.01 ± 0.50	3.64 ± 0.78	9.58 ± 0.54
C2	-10	872.33	5.98	12.04	48.53	21.34 ± 1.09	4.09 ± 0.51	9.93 ± 0.88
C3	0	660.07	5.23	11.21	50.86	21.36 ± 2.22	4.40 ± 0.44	9.32 ± 0.66

Table VI. Forming Conditions and Strength Properties of Fibers Formed from a Polymer Designated BOC 95/05, Prepared with Changing As-Spun Draw Ratios

Sample symbol	As-spun draw ratio (%)	Drawing process			Tenacity (cN/tex)	Elongation at break (%)	Young's modulus (N/tex)
		Drawing in plastification bath, R_1 (%)	Drawing in stream, R_2 (%)	Total draw ratio, R_c (%)			
B10	-20	133.41	194.23	586.77	22.73 ± 1.71	4.06 ± 0.59	9.70 ± 0.56
B11	-10	135.80	155.99	503.63	23.37 ± 1.72	4.51 ± 0.32	9.41 ± 0.57
B12	0	141.30	163.11	534.88	23.49 ± 1.42	4.22 ± 0.38	9.60 ± 0.48
B13	+10	122.88	200.61	570.00	24.77 ± 1.97	3.91 ± 0.46	11.03 ± 0.69
B14	+30	121.72	168.31	494.90	19.47 ± 1.65	3.93 ± 0.41	8.18 ± 0.43
B 15	+50	109.30	151.54	426.48	21.64 ± 1.19	4.20 ± 0.30	8.84 ± 0.57

deformation, both in the first and in the second stages of the stretching process, and the total draw ratio value is reduced by $\sim 144\%$. This results in fiber tenacity reduced from 3.13 to 5.3 cN/tex. The elongation at break of fibers formed in the above conditions is between 3.9 and 4.2%. Fibers formed at an as-spun draw ratio of +10% have the maximum value of Young's modulus (11.03 cN/tex). This Young's modulus value and high tenacity of over 24 cN/tex may be considered as predisposing it for use as a fibrous component in polymer-fiber composites not only as staple fibers but also as fiber bundles. Furthermore, the fibers will be capable of absorbing body fluids. This is a necessary condition for the gradual resorption of the composite fibrous component. As a result of the process, an additional pore system with a micrometre size corresponding to the fiber diameter will be formed. This will support bone cell migration and growth throughout the composite material. It follows from the analysis of BAC fiber sorption that moisture sorption at 65% RH is between 7.2 and 4.7% (high values for a hydrophobic material) (Table VII).

Moreover, with as-spun draw ratio changes from negative to positive values, an untypical tendency of reduced ratio values occurs. A similar changing tendency is seen for moisture sorption at 100% RH and water retention. The values of both parameters are also high between 13.8 and 10.0% and between 35.5 and 30%, respectively. This order of magnitude of moisture sorption at 100% RH and water retention results both from fiber porosity and from the properties of the resulting porous struc-

ture. The pore system that occurs in the fibers was assumed (according to previous results^{20,21}) to be pores with a size of 3–1000 nm, and the corresponding total pore volume was labelled as P_1 . This porosity range includes small pores (4–15 nm), medium pores (15–75 nm), and large pores (75–1000 nm).

However, the porosity of the fibrous material labelled as P includes pores with sizes of up to 7500 nm. This also includes gaps in the fiber surface. It should be noted that the existence of a porous structure, and principally of pores in the large and very large ranges, causes a reduction in the intrinsic strength of the fibers. However, this phenomenon applies to all of the analyzed fiber samples and is difficult to estimate. Therefore, it was decided not to examine the effect of total pore volume and pore size on the strength properties obtained.

In general, both total pore volume P and volumes of pores with a size of up to 1000 nm may be considered high, at a level of 0.9–0.5 and 0.17–0.25 cm³/g, respectively. Therefore, the resulting BOC fibers may be considered highly porous. If so, this would explain the high moisture sorption at 100% RH and water retention values. These are also associated with the nature of the resulting porous structure. The curves for the relationship between the percentages of pores and radii (Figure 3) have a number of successive maxima located within respective pore sizes (small, medium, large, and very large).

Their height differs depending on the as-spun draw ratio values at which the fibers were formed. The high maxima at the pore

Table VII. Porous Structure and Sorption Properties of Fibers Formed from a Polymer Designated BOC 95/05, Prepared with Changing As-Spun Draw Ratios

Sample symbol	As-spun draw ratio (%)	Moisture sorption at 65% RH (%)	Moisture sorption at 65% RH (%)	Water retention (%)	Total pores volume, P (cm ³ /g)	Volume of pores (3–1000 nm), P_1 (cm ³ /g)	Total internal surface of pores (m ² /g)
B10	-20	7.20	13.80	35.49	0.913	0.197	9.58
B11	-10	7.05	13.49	32.42	0.810	0.415	37.41
B12	0	6.73	10.88	32.74	0.490	0.184	17.87
B13	+10	5.93	11.74	31.43	0.739	0.253	36.90
B14	+30	6.03	10.99	30.02	0.620	0.168	16.63
B15	+50	4.79	10.01	29.99	0.650	0.246	28.39

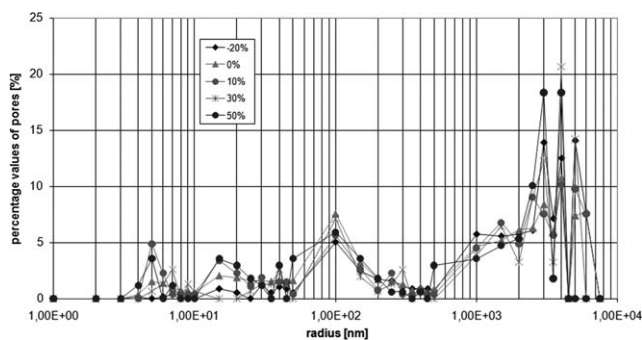


Figure 3. Porous structure of BOC 95/05 fibers.

distribution curve in the range of the pores with the highest sizes (up to 7500 nm) are related to fibrous material porosity. It is assumed in the analysis of fiber sorption properties related to porous structure¹⁶ that for hydrophobic materials with moisture sorption values of 100% RH the percentage of pores with sizes sufficiently small for moisture absorption by capillary condensation is crucial. Usually, the first two maxima in the pore distribution curve correspond to this. However, pores large enough for water to penetrate them and small enough to retain water when it is mechanically removed are responsible for the water retention value. This is usually applicable to large pores, with sizes of 300–1000 nm. Their percentages are mainly related to the third maximum in the plot (Figure 3).

It is noteworthy that BOC fibers formed at an as-spun draw ratio of 10% have the highest tenacity value of 24.77 cN/tex and also have one of the highest total pore volume values of 0.25 cm³/g and very high pore internal surface; this is consistent with the first maximum in the pore distribution curve.

The presence of pores with various dimensions in BOC fibers is seen in fiber cross-sectional scanning microscope photographs (Figure 4).

The fiber surface has numerous scratches and slots, being typical of fibers wet spun from solution. The heterogeneity of fiber surface is clearly visible in AFM photographs (Figure 5).

The fiber surface has numerous scratches and slots with different depth, being typical of fibers wet spun from solution (Figure 6).

The finely porous nature of the structure typical of solidification in mild conditions and the solidification process according to the diffusion mechanism is seen in the scanning microscope photograph (Figure 4). There are none of the radially distributed pores and empty spaces typical of the drop mechanism.

It follows from the analysis of cross sections of final fibers formed at different as-spun draw ratios, −10% (B11), +10% (B13), and +30% (B14), that changes in as-spun draw ratios from negative to positive values result in a certain flattening of the fiber cross section. This is demonstrated by the cross section

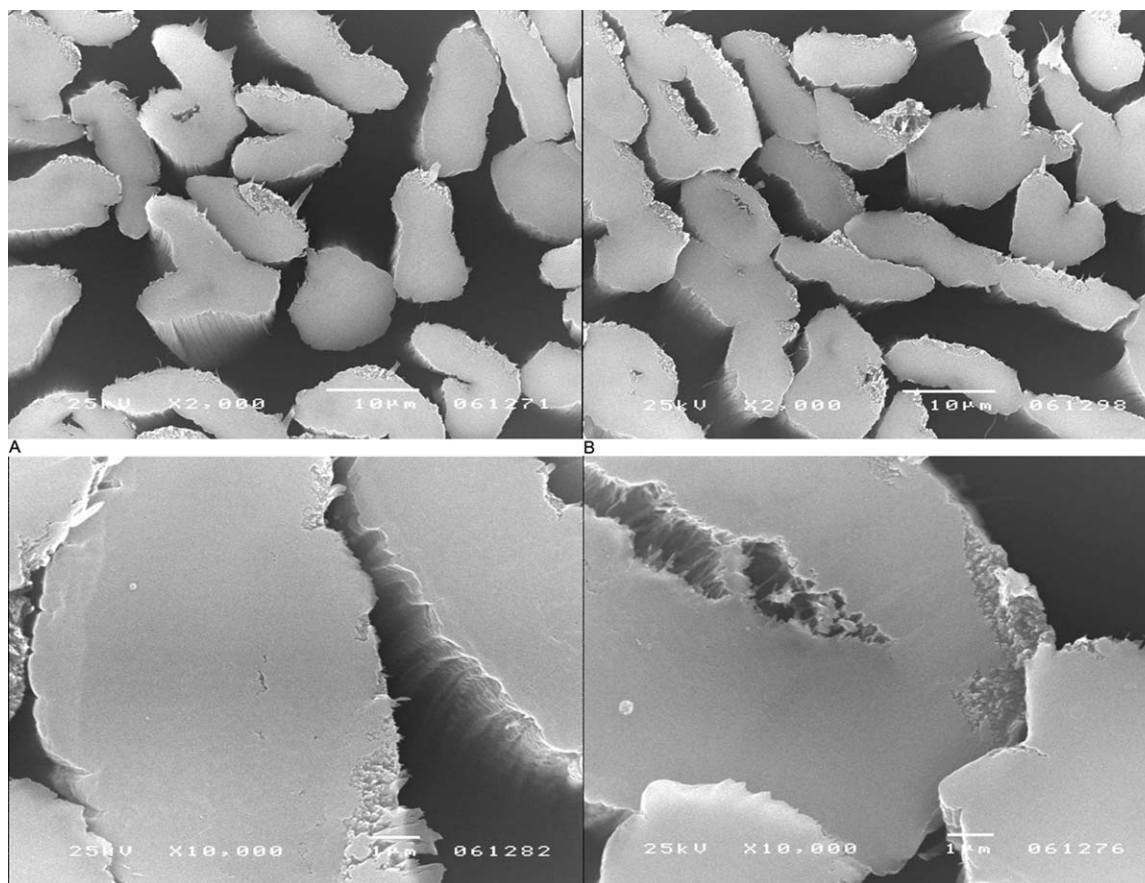


Figure 4. SEM cross section of the fibers: (A) as-spun draw ratio of −10% (B11) and (B) as-spun draw ratio of +30% (B14).

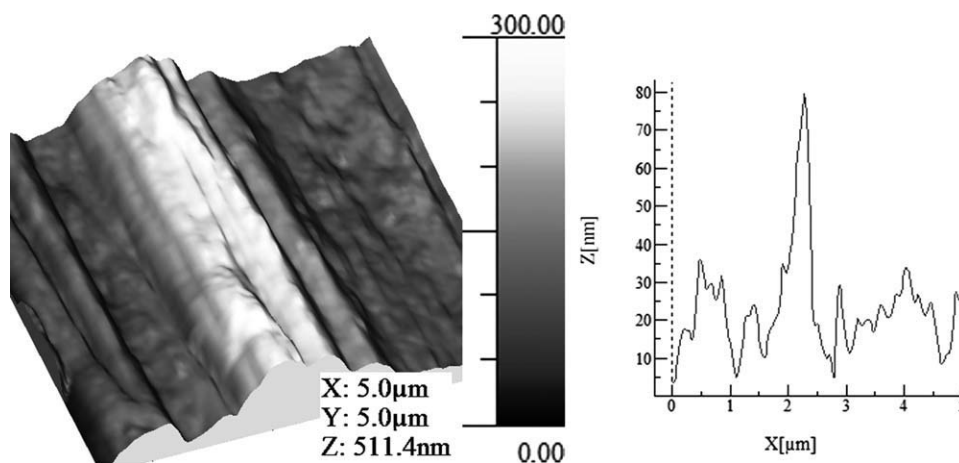


Figure 5. Fiber surface of AFM photographs.

shape development index changing in a range of 2.34–2.70, defined as the ratio of the radius of a circle circumscribed on a cross section to the circle inscribed in it. A similar tendency was also observed for calcium alginate fibers.²² However, BOC 95/5 fibers have highly heterogeneous cross sections. Fiber bundles contain both fibers with a bean-like cross section and those with a nearly circular or flattened cross section. The latter prevail for fibers formed at an as-spun draw ratio of +30%. However, fibers formed at an as-spun draw ratio of –10% have a higher percentage of bean-like fibers in the bundles. Moreover, the shape dominates for fibers formed at an as-spun draw ratio of +10%, which have the highest tenacity.

CONCLUSIONS

Owing to the modification of the process for the preparation of chitin copolyester, postreaction solutions could be used directly for forming wet fiber from solution.

Irrespective of the chemical structure of chitin BOC and polymer intrinsic viscosity, the spinning solutions are non-Newtonian liquids diluted by shearing without a flow limit. The

reduced percentage of acetyl groups in the copolymer leads to resulting spinning solutions, which are closer to Newtonian liquids.

Despite the differences in total stretch values and stretches at the respective process stages (related to the as-spun draw ratio changes in a wide range from negative to positive values), the strength properties of BOC fibers are quite similar. The fibers formed at a moderately positive as-spun draw ratio of +10% have the highest tenacity value of 24.77 cN/tex. This results from the positive effect of deformation of the still liquid stream during fiber solidification.

Throughout the range of as-spun draw ratio changes, the resulting BOC fibers have high total pore volume, and they can be included in the group of highly porous fibers. Fiber sorption properties high for a hydrophobic material and very high water retention values are related to the nature of the resulting porous structure and total pore volume.

A unique combination of high porosity and good tenacity above 24 cN/tex has been achieved in chitin-derivative fibers.

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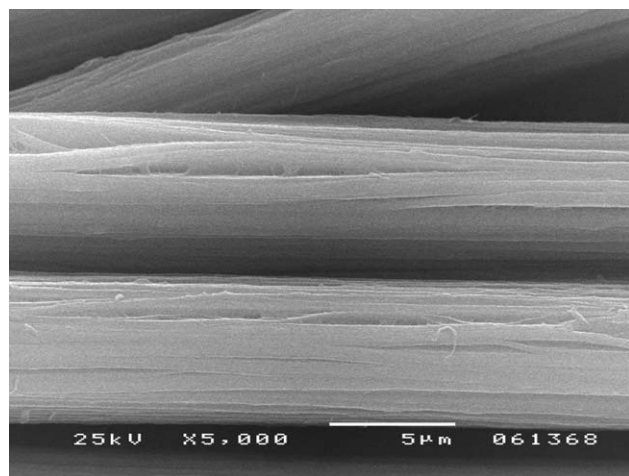


Figure 6. Fiber surface of SEM photographs.

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