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The Effect of Solvent Type on the Mechanical Properties of Dibutyrylchitin (DBC) Fibres

Abstract

This paper concerns the manufacture of fibres from dibutyrylchitin (DBC) using the wet spinning method. Special attention was paid to exploring the effect of solvent type on the mechanical properties of DBC fibres. Dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), *n*-methyl-2-pyrrolidone (MP) and ethyl alcohol (EtOH) were used for preparing the DBC spinning solutions. Additionally, more detailed investigations were carried out on the DMF spinning dope, such as the effect of polymer content in the solution, as well as that of the spinning conditions (temperature of coagulation bath, fibre take-up speed and stretching ratio) on the mechanical properties of DBC fibres. The conditions of DBC fibre spinning on a semi-technical scale were defined for the DMSO and DMF spinning dopes. DBC fibres from DMSO and DMF solutions were characterised by a tenacity of 10.5 to 14.6 cN/tex and elongation at break from 10% to 22%. Batches of DBC fibres (from DMF and DMSO solutions) were prepared for further processing into nonwovens for medical use.

Key words: dibutyrylchitin, solutions DBC, wet spinning fibres, mechanical properties of DBC fibres.

Introduction

Chitin (poly-(1-4)-2-acetamine-2-acetamine-2-deoxy-D-glucopyranose) is the second most abundant biopolymer on earth, after cellulose. This polysaccharide is formed in a biosynthesis process characterised by high molecular weight and a high degree of crystallinity. Its advantageous biological properties, such as biocompatibility, biodegradability, haemostatic activity and the ability to stimulate the wound-healing process are well known, which means that this biopolymer could be useful material for medical applications as a wound dressing. However, the use of chitin for higher technology products such as fibres is limited because of its lack of solubility in common solvents. Therefore, the practical application of chitin in chemical fibre technology requires suitable methods of modification to increase its reactivity and solubility. Much effort has been made to modify chitin by chemical methods and create chitin derivatives which would be easily soluble in common solvents. Modification of chitin by butyric anhydride treatment produces dibutyrylchitin (DBC), a chitin derivative which is soluble in organic solvents such as dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), *n*-methyl-2-pyrrolidone (MP), ethyl alcohol (EtOH) and others. DBC solutions distinguished by high stability and suitable rheological properties can be used for spinning DBC fibres [1, 2].

Depending on the type of solvent used to prepare the DBC spinning dope, various methods of fibres spinning can be applied: the dry, dry-wet or wet methods. A DBC spinning solution containing

20-22 wt% of polymer in acetone was used for forming fibres by the dry method [3].

The DBC fibres were spun (from EtOH solutions) using a dry-wet method [4, 5]. When the fibres were partly solidified, they were then introduced into a water bath and taken up on a bobbin device, stretched twice and next dried in air.

The most frequently method used for spinning DBC fibres is the wet method, which allows spinning solutions based on all known solvents for DBC to be prepared [6 - 8].

At the Institute of Biopolymers and Chemical Fibres (IBWCh), the studies of DBC fibres spinning process were conducted as part of the CHITOMED European Project (No. QLK5-CT-2002-01330), and the results of this research have been presented at conferences [9, 10].

The subject of this particular research work concerned the manufacture of fibres (staple fibres, multifilament yarn) from dibutyrylchitin (DBC) using the wet spinning method. Special attention was paid to selecting suitable solvents for DBC; DMF, DMSO, EtOH and MP were used as solvents for preparing the DBC spinning solutions. The properties of each solution were studied carefully

in terms of dissolution parameters and dynamic viscosity, in order to increase our knowledge of the behaviour of these solutions, and to optimise the dissolution conditions. We determined the effect of polymer content in solution, as well as that of spinning conditions such as temperature of coagulation bath, fibre take-up speed and stretching ratio, on the mechanical properties of DBC fibres. The optimal conditions for DBC fibre and yarn spinning on a semi-technical scale were defined.

Experimental data

Materials

Dibutyrylchitin (DBC), characterised by the properties presented in Table 1, was prepared by the Institute of Dyes and Organic Products (IDOP), Zgierz, Poland.

The following solvents were used in the research work: dimethyl formamide (DMF), 1-methyl-2-pyrrolidone (MP), dimethyl sulphoxide (DMSO) and ethyl alcohol (EtOH). All were pure, and were produced by POCh, Gliwice, Poland.

The special avivage agents such as Span 20 pharma, Tween 20 pharma (produced by I.C.I., Great Britain) were used to avoid the sticking of fibres. These agents

Table 1. Some properties of polymer used for spinning of DBC fibres; * intrinsic viscosity value was determined at 25 °C using the viscometry method; solutions of DBC in DMAc were within the range of 0.4 to 0.1 g/100 ml.

Symbol of the sample	Intrinsic viscosity [η], dl/g	Moisture, %	Colour	Form
DBC 1	1.83	3.00	cream-coloured	powder
DBC 2	2.03	1.74	beige	powder

meet the pharmaceutical requirements according to the Pharmacopea (catalogue producer edited by the I.C.I.).

Methods

Due to the individual properties of solvents used, the conditions for preparing the spinning dopes required different temperatures for dissolving the DBC, various times of swelling and total times of solution preparation. Depending on the type of solvent and the dynamic viscosity, spinning dopes with polymer content from 10 wt% up to 19.5 wt% were prepared.

Preparation of DBC spinning solutions in DMF

A suitable amount of DBC (DBC 1) was introduced into a tank equipped with an agitator containing DMF. The swelling process was carried out for 30 min, then dissolution took place over 4 hours using a mixer running at 120 r.p.m.. Next, the solution was stored for 24 hours at room temperature, and after filtration on a plate filter and de-aeration, it was used to manufacture the fibres. The DBC content in the solution was within the range of 15 wt% to 19.5 wt%.

Preparation of DBC spinning solutions in DMSO

A suitable amount of DBC (DBC 2) was introduced into the reactor equipped with a jacket and agitator; next, the DMSO solvent was added. The swelling process was carried out for 30 min at 20 °C; next, the temperature of the suspension was increased to 60 °C. At this temperature, the dissolving process was conducted for 4 hours at 1250 r.p.m.. After dissolving, the spinning solution was filtered on a plate filter, de-aerated for 24 hours, and then used to manufacture fibres. The DBC content in the solution was 10-12 wt%.

Preparation of DBC spinning solutions in MP

A suitable amount of DBC (DBC 1) was introduced into the reactor equipped with a jacket and agitator; next the MP solvent was added. The swelling process was carried out for 30 min at 20 °C; next, the temperature of the suspension was increased to 40 °C. After dissolving, the spinning solution was filtered onto a plate filter, de-aerated for 24 hours and then used to manufacture fibres. The DBC content in the solution was 14 wt%.

Preparation of DBC spinning solution in EtOH

A suitable amount of DBC (DBC 2) was introduced into the reactor equipped with

a jacket and agitator, and next the EtOH solvent was added. The swelling process was carried out for 120 min at 20 °C. Next, the dissolving process was continued for 2 hours using a mixer at 120 r.p.m. In order to de-aerate the solution, it was stored until the next day. After filtration, the solution was used to manufacture fibres.

Wet spinning of DBC fibres

The DBC fibres were spun using the wet method on a pilot spinning machine at IBWCh. The DBC fibres were manufactured in the form of multifilament yarn or in a staple state, during the process of wet spinning carried out on an apparatus commonly used for preparing different multifilament fibres. The dope was extruded through a Pt-Au spinneret with 300 holes with a hole diameter of 80 µm into a water coagulation bath. The filaments taken from the coagulation bath were stretched in a water bath, washed and finished using avivage agents and next dried. The fibres were taken-up on a roller at a rate of 20 to 40 m/min. The total stretching ratio was within the range from 80 to 180%.

A part of the fibres cut into 60-mm lengths was been used for manufacturing non-woven textile fabrics. The other part of fibres was used to manufacture knitted objects.

Analytic methods

Determining the polymer content in the spinning solution

About 3 ± 0.0002 g of DBC spinning solution were introduced onto the glass plate. The film of DBC solution on the glass plate was soaked with a water bath. The removed DBC film was washed in distilled water and dried at 105 °C to a constant weight. The polymer content was determined from the following equation:

$$X = m_2/m_1 \times 100, \%$$

where:

m_1 – the DBC spinning solution sample weight, g

m_2 – the dry DBC film weight, g.

Determining the dynamic viscosity of DBC solutions

The dynamic viscosity of the DBC solutions was measured using a Brookfield Dial Viscometer. The method consists in measuring the torque necessary to overcome the resistance of viscous fluid at 6, 12, 30, or 60 r.p.m. using an appropriate spindle.

Determining the DBC fibres' mechanical properties

The mechanical properties of the obtained DBC fibres were determined according to Standards PN-ISO 1973:1997 and PN-EN ISO5079:1999.

Microscopic assessment of the DBC fibres

The surface and cross-section of DBC fibres were assessed using a Quanta 200 scanning electron microscope (FEI, USA).

Results and discussion

Study of the DBC fibres spun from the DMF solutions

Preliminary studies of DBC fibre and yarns spinning process were carried out with the use of DBC solutions in dimethylformamide (DMF). The spinning solutions were characterised by assessing the polymer content and dynamic viscosity of the solutions used for forming fibres (Table 2).

The DBC fibres were spun using the wet method. The spinning line consisted of a spinning solution tank, a coagulation bath, 3 godets, a stretching bath, two washing baths and a finishing bath. The study included the impact of polymer content in solution, titre, take-up speed and stretching ratio on the mechanical properties of the DBC fibres. The results of the influence of these parameters are shown in Tables 2 to 5.

From economic perspectives, it is common to prepare spinning solutions with the highest possible polymer content. When DMF was used as a solvent, it was possible to prepare a spinning solution with a DBC content of about 19 wt%. This solution was characterised by a dynamic viscosity of 37,000 cP at 20 °C. Solutions prepared within such a range of polymer concentrations were easily filtrated and de-aerated. The effect of the polymer content in spinning solution on the mechanical properties of DBC fibres was also investigated; the results are presented in Table 2.

On the basis of these results, it was found that DBC fibres with an assumed linear density of 2.0 dtex spun into water bath at 20 °C with a take-up speed of 30 m/min and a stretching of 130% were characterised by a tenacity of 12-14 cN/tex and elongation at break of 7-9%. Because the maximum values of mechanical parameters were achieved for fibres spun from a solution containing 18.3 wt% of

polymer, it seems that this concentration is optimal. The suitability of this solution for fibre spinning has also been proved by the relatively lower dynamic viscosity. Manufacturing fibres from a solution containing 19.3 wt% of DBC was more complex; a part of the spinneret head's holes became clogged, which increased the linear density of fibres up to 2.89 dtex. The fibres' mechanical properties can also depend on their linear density. The influence of linear density within the range of 1.64 - 4.20 dtex has been examined. The recommended range of fibres' linear density include values presently used for manufacturing medical dressings. The results obtained are shown in Table 3.

The highest values of tenacity and elongation at break were indicated for linear density within the range of 1.85 to 2.37 dtex. That is why this range of linear density was selected for further studies of fibre formation. Below 1.85 dtex, the elongation at break decreases (more fragile filaments); and above 4.0 dtex, the tenacity of filaments also decreases.

A very important parameter affecting the fibres' properties as well as the economy of the process is take-up speed. The effect of raising the take-up speed from 20 m/min to 30 m/min at stretching of 86% was studied, and the results are given in Table 4.

On the basis of the results presented, it was concluded that take-up speed has an insignificant effect on the fibres' mechanical properties. The spinning process runs most stably at a take-up speed of 20 or 30 m/min, while at the same time the fibres are characterised by higher mechanical properties than those spun at a take-up speed of 40 m/min.

The main parameter of fibre spinning which directly affects their mechanical properties is the stretching process. It has been observed that DBC fibres are prone to stretching during spinning. The influence of the stretching ratio of DBC fibres within the range of 130-185% was studied (Table 5).

The results presented in Table 5 indicated the dependence of the fibres' mechanical properties and the stretching ratio.

The most advantageous stretching range of DBC fibres is from 139 to 185% at a take-up speed of 30 m/min. At higher take-up speeds and higher stretching values, the tenacity of fibres decreases, or the breakage of fibres may even be observed.

Table 2. The effect of polymer content in spinning solution on mechanical properties of DBC fibres.

DBC content in spinning solution, wt%	Dynamic viscosity at 20 °C, cP	Linear density, dtex	Tenacity, cN/tex	Elongation at break, %
15.0	22 000	1.94	11.8	6.7
17.0	25 300	2.04	13.7	8.4
18.3	28 500	2.15	14.1	8.7
19.3	37 000	2.89	12.9	8.1

Table 3. The effect of linear density on DBC fibres properties (DBC content in spinning solutions – 18,3%, take up speed 30 m/min, stretching 130%).

Linear density, dtex	Tenacity, cN/tex	Elongation at break, %
1.64	11.8	6.7
1.85	13.6	7.5
2.04	13.7	8.4
2.37	13.3	9.1
3.44	12.8	9.3
4.20	9.5	9.1

Table 4. The effect of take-up speed on mechanical properties of DBC fibres.

Take-up speed, m/min	Linear density, dtex	Tenacity, cN/tex	Elongation at break, %
23	1.94	13.6	7.9
30	2.04	13.7	8.4
40	2.06	12.6	7.8

Table 5. Influence of stretching ratio on mechanical properties of DBC fibres.

Stretching ratio, %	Take-up speed, m/min	Linear density, dtex	Tenacity, cN/tex	Elongation at break, %
130	23.0	2.14	12.9	7.1
130	30.0	2.30	14.1	7.6
185	30.0	2.18	14.1	6.1
170	35.0	2.53	11.0	5.5
185	37.5	break of fibres		

On the basis of the results presented, we selected the conditions of fibre spinning from DBC solutions in DMF, and a larger batch of fibres in the form of multifilament or staple fibres was manufactured.

The staple fibres and multifilament yarn spun in these conditions on a high lab scale were characterised by properties listed in Table 6.

Figure 1 shows a SEM photo cross-section and the surface of the DBC fibres being spun from DMF.

Most of the fibres have an oval shape, and a few possess cross-sections of close to circular shape. The fibre edges are slightly deformed, due to the sticking of the elementary fibres. Small furrows and hollows are visible on the fibres' surface.

Spinning DBC fibres from DMSO solutions

For further studies of the DBC dissolution process and the preparation of spinning baths, more ecological solvents than DMF, such as dimethyl sulphoxide

(DMSO), n-methyl-2-pyrrolidone (MP) and ethyl alcohol (EtOH), were used.

The conditions of fibre spinning were optimised separately for each spinning solution. They varied depending on the type of DBC solvent and the properties of the DBC solution.

The DBC fibres prepared were characterised by determination of their mechanical properties and morphological parameters, mainly by SEM.

As mentioned before, DBC is also soluble in DMSO. The conditions of preparing a solution differ substantially from those used for dissolving DBC in DMF, including the temperature of dissolution and the polymer concentration. Temperature has a fundamental effect on the dissolving process: the higher the temperature, the more quickly the polymer dissolves. In spite of the lower polymer content (10 - 12 wt%), the dynamic viscosity of solutions is high, up to 27,000 cP.

The data presented in Table 7 show the mechanical properties of DBC fibres

spun from DMSO solutions under selected conditions.

On the basis of the results presented in Table 7, it can be stated that the DBC fibres obtained from DMSO solutions are characterised by a tenacity of 11.6 cN/tex, although the elongation at break depends on the type of fibre. An elongation of 21% was noted for the staple fibres which were cut in a wet state and then dried freely at 25 °C. Fibres in the form of multifilament yarn were characterised by a value of elongation lower by half, which could have been caused by drying them in a stressed state on hot godets. It seems that the manufacture of staple fibres is more profitable, due to the higher values of elongation of break. Figure 2 shows an SEM photo of the DBC fibres spinning from the DMSO solution.

DBC fibres have round, regular cross-sections, but their surface is smooth with visible cracks. Batches of DBC staple fibres and multifilament yarn were designed for further processing into nonwovens for medical applications.

Spinning DBC fibres from MP solutions

The next selected solvent was 1-methyl-2-pyrrolidone (MP). The spinning solution was prepared according to the description presented in methodology, and was characterised by suitable parameters for fibre spinning: dynamic viscosity of 18,000 cP at 20 °C, and a polymer content of 14 wt%. Table 8 presents the conditions of the DBC fibres spun from MP solutions.

DBC fibres spun from MP solutions show tenacity at the level of 12.6 cN/tex and an elongation of 14.5%. The mechanical parameters of these fibres classify them at the medium level. The SEM photo of these fibres is presented in Figure 3.

The cross-sections of DBC fibres spun from MP solutions are irregular with deep cracks, which are also visible on the surface.

Spinning DBC fibres from EtOH solutions

Ethanol seems to be most interesting as a DBC solvent, from the medical and ecological point of view. A DBC spinning solution was prepared according to the description given in the methodology. Solutions with a polymer content of 13.2 wt% and a dynamic viscosity of 16,300 cP were clear and spinnable. DBC fibres from EtOH solutions were

Table 6. Some mechanical properties of DBC fibres spun from DMF solutions in selected conditions; temp. of 20 °C, take-up speed 30 m/min and stretching 130%.

Type of fibres	Spinning solutions		Fibres properties		
	Polymer content, wt%	Dynamic viscosity at 20 °C, cP	Titre, dtex	Tenacity, cN/tex	Elongation at break, %
Staple fibres	18,26	22500	2.49	14.3	9.9
Multifilament yarn	18,34	29000	2.40	14.6	8.0

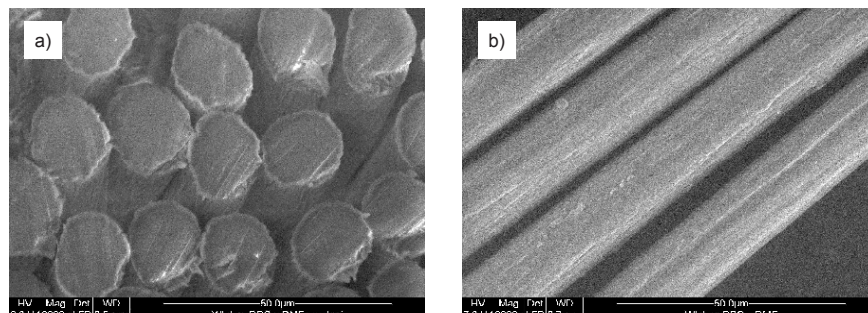


Figure 1. SEM photos of DBC fibres solvent - DMF; a) cross-section, b) surface.

Table 7. Some mechanical properties of DBC fibres spun from DMSO solutions in selected conditions; symbol of polymer: DBC 2, stretching ratio - 80%, take up speed - 23 m/min.

Type of fibres	Spinning solutions		Fibres properties		
	Polymer content, wt%	Dynamic viscosity at 20 °C, cP	Titre, dtex	Tenacity, cN/tex	Elongation at break, %
Staple fibres	10.4	8 500	3.14	10.7	21.0
Multifilament yarn	12.1	27 000	2.53	11.6	12.0

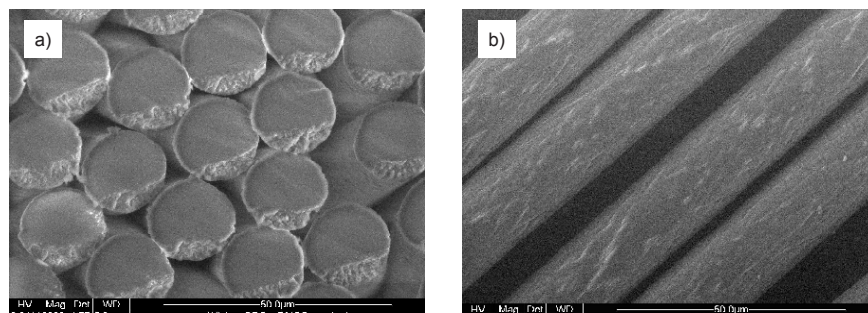


Figure 2. SEM photos of DBC fibres solvent - DMSO; a) cross-section, b) surface.

Table 8. Some mechanical properties of DBC fibres spun from 1-Methyl-2-Pyrrolidone (MP) solution. stretching ratio - 80%, take up speed - 23 m/min.

Type of fibres	Spinning solutions		Fibres properties		
	Polymer content, wt%	Dynamic viscosity at 20 °C, cP	Titre, dtex	Tenacity, cN/tex	Elongation at break, %
Staple fibres	14.0	18 000	2.58	12.6	14.5

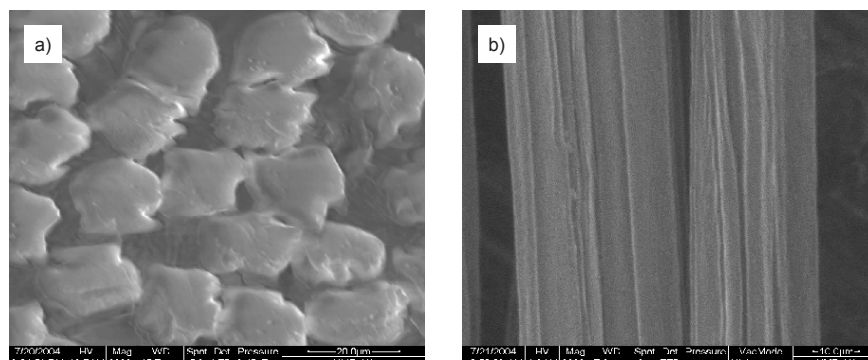


Figure 3. SEM photos of DBC fibres solvent - MP; a) cross-section, b) surface.

Table 9. Some mechanical properties of DBC fibres spun from EtOH; solution. stretching ratio - 80%, take up speed - 23 m/min.

Type of fibres	Spinning solutions		Fibres properties		
	Polymer content, wt. %	Dynamic viscosity at 16.5 °C, cP	Titre, dtex	Tenacity, cN/tex	Elongation at break, %
Staple fibres	13.3	14 800	2.13	8.12	9.8

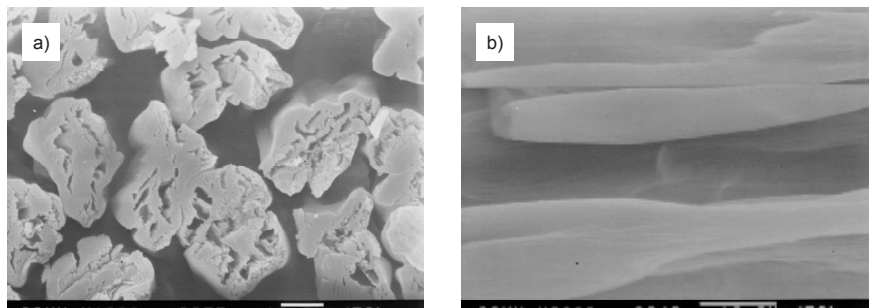


Figure 4. SEM photos of DBC fibres spun from solvent EtOH: a) cross-section, b) surface.

formed at a take-up speed of 30 m/min at a stretching ratio of 130% into a water coagulation bath. The properties of the solution and the mechanical properties of the fibres are shown in Table 9.

The DBC fibres were characterised by a tenacity of 8.12 cN/tex. This was probably caused by the large porosity of fibres, as is seen on the SEM photo of the surface and cross-sections (Figure 4).

The fibres in cross-section look like a sponge with different pore sizes; the shape of fibres is somewhat flat, which was probably caused by the collapse of the pores under the weight or strain existing while the fibres were being spun. The image of the fibres' surface can confirm this hypothesis.

Summary

On the basis of the results obtained, the following conclusions could be drawn:

- It is possible to spun DBC fibres using various solvents such as DMF, MP, DMSO, EtOH. The fibres obtained demonstrate different mechanical properties depending on the type of solvent used and the spinning conditions.
- The DBC solution in DMF was characterised by the highest polymer content with viscosity suitable for forming fibres, as well as an ability to dissolve at 20 ± 2 °C and good filterability. The fibre spinning process was stable at a take-up speed of 30 m/min.
- The DBC fibres spun from DMF solutions have shown the best tenacity, and it is possible to spin both staple and multifilament yarns from the DMF solutions.

- The DBC solution in DMSO is characterised by large viscosity at relatively low polymer content; preparing these fibres requires higher temperatures of polymer dissolution, but on the other hand they make it possible to spin both staple fibres and multifilament yarn. Staple fibres dried freely have the highest elongation, at a level of 20%.
- DBC solutions in EtOH allow the manufacture of unique, spongy form high-porous fibres. For this reason they are very interesting, although only staple fibres can be manufactured from EtOH solutions.
- Within the study of DBC fibres spinning conditions, samples of DBC fibres in the form of staple fibres and multifilament yarns were prepared and transferred to our Partner (Technical University of Łódź) for the production of knitted materials: bandages, dressing gauze, nets for supporting and/or isolating internal organs under surgery.

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References

1. Szosland L., Janowska G., 'The method of preparation of dibutylchitin', 1996, PL 169077 (B1).
2. Szosland L., Stęplewski W.: 'Rheological characteristic of dibutylchitin semi-concentrated solutions and wet spinning of dibutylchitin fibres', in 'Advances in Chitin Science', volume II, 7th ICCS (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.
3. Szosland L., East G.C.: 'The dry spinning of dibutylchitin fibres', J. Appl. Polym. Sci. 58, 2459-2466, 1995.
4. Biniś W., Włochowicz A., Biniś D., Boryniec S.: Polish Patent Application, No. P 359883.
5. Biniś D., Boryniec S., Biniś W., Włochowicz A.: 'Alkaline Treatment of Dibutylchitin Fibres Spun from Polymer Solution in Ethyl Alcohol', Fibres & Textiles in Eastern Europe July / September 2006, Vol. 14, No. 3 (57).
6. Szosland L., Stęplewski W.: "Method of obtaining fibre from chitin esters", 2004, PL 187224 (B1).
7. Błasińska A., Mikołajczyk T., Krucińska I., Komisarzyk A.: 'Investigations on manufacturing of porous fibres made from dibutylchitin; 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 (ISBN 953-7105-05-9).
8. Błasińska A., Mikołajczyk T.: "Wet Spinning of Dibutylchitin Fibres from Ethanol Solution", Fibres & Textiles in Eastern Europe January / December 2005, Vol. 13, No. 6 (54).
9. Struszczyk H., Ciechańska D., Wawro D., Stęplewski W., Krucińska I., Szosland L., Van de Velde K., Kiekens P., 'Some properties of dibutylchitin fibres' w H. Struszczyk, A. Domard, M.G. Peter, H. Pospieszny, ed., 'Advances in Chitin Science' vol. VIII, EUCHIS'04, Institute of Plant Protection, Poznań, p. 279-283, 2005.
10. Gillet D., Contandriopoulos Y., Kopczacki P., Rutkowska-Olma E., Szuster L., Muszynski M., Krucińska I., Szosland L., Szumilewicz J., Kornobis E., Kiekens P., van de Velde K., Schoukens G., Wawro D., Stęplewski W.: 'Dibutylchitin as a raw material for new bioactive textile dressing materials': Results of the CHITOMED European Project', World Textile Conference, 4th AUTEX Conference, Roubaix, France, 22-24 June 20, 2004.

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