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Wet Spinning of Dibutrylchitin Fibres from Ethanol Solution

Abstract

The possibility of obtaining dibutrylchitin porous fibres with a sufficiently high tensile strength for textile medical application by using the wet spinning method, was evaluated. Ethyl alcohol as a solvent for the polymer and as a component of the coagulation bath was applied. Boundary conditions for forming dibutrylchitin (DBC) fibres of the assumed porous structure and strength were determined.

Key words: biomaterials, dibutrylchitin fibres, wet spinning, wound dressings.

Introduction

Different types of wounds and the phases of their healing process have led to the creation and development of various wound dressing materials. However, traditional dressings have certain limitations when it comes to poorly healing and full thickness wounds. It has led to the development of biomaterials as significantly important products for improving wound healing. In 1970, Prudden et al. [1] demonstrated the high activity of chitin as a wound healing accelerator. From then on chitin as a biomaterial has been the focus of great attention. Chitin applications are strongly limited by its low solubility (and not only in the textile industry), and so the formation of fibres is very difficult. In contrast to chitin, its ester derivative dibutrylchitin (DBC) is easily soluble in several organic solvents, and it is therefore possible to manufacture high-quality shape materials. Clinical results of DBC nonwovens applications are very promising. In the majority of cases they have been observed to promote the process of wound healing [2,3].

Dibutrylchitin fibres for nonwoven manufacture can be formed in various ways [4-7]. Most commonly, the dimethylformamide (DMF) solvent has been used. However, bearing in mind the potential medical applications, solvents such as ethanol, N-methylpyrrolidone (N-MP) or dimethyl sulphoxide (DMSO) are preferred. Classical methods of manufacturing DBC nonwoven dressings required ready made fibres, although new techniques allow a web of fibres (fleece)

to be formed directly from a polymer solution. Both types of the fibres formed and the structure of their webs fulfil the very important properties of a dressing material, namely absorbability, water vapour and gas permeability. Thanks to its defined absorbability, the dressing is capable of removing the excess of exudates. If there is too much of it in the wound, the epithelium cells start to drown and swell. On the other hand, if the absorbability is too high it may result in evoking the exudates, leading to oedema. Active dressings for wounds healing in a wet environment should have a structure which permits inter- and intracapillary absorption of exudates. Their ability to transmit gases allows access to oxygen. This oxygen, dissolved in the exudates, is consumed by skin cells and improves the epithelialisation process. The ability to transmit water vapour will result in equilibrating the humidity inside the wound.

The application of hydrophobic fibres in close contact skin-dressing, prevents the adhesion of the growing granulation tissue, with the help of exudates rich in proteins. In this way, the atraumatic characteristic of the wound dressing is realised [8].

Potential ability of water sorption is a value characteristic for a given fibre, and depends on the sort of polymer from which it is made and its supramolecular structure, the degree of development of the external surface of the fibre, the total volume of pores and the porosity character. In turn, the effective sorptive capability is a variable quantity, which additionally depends on the parameters of the environment in which the fibre is placed.

It is known that in the case of hydrophobic material such as DBC, the main factor which decides sorptive abilities is its porous structure. This can be established

by applying the general rule of forming high-porosity fibres by correctly determining the fibre-forming parameters in the wet spinning process, such as the concentration, and temperature of the coagulation bath, the as-spun-draw ratio, and the draw ratio [9]. A general rule had earlier been determined and formulated for PAN fibres, and was then extended to other fibre-forming polymers.

The main aim of this study is to determine the possibility of applying ethyl alcohol as a solvent in order to obtain heighten the porosity of DBC fibres with sufficiently high tensile strength for textile medical application. It is expected that such fibres will be applied to manufacture new-generation wound-dressing materials including biologically active substances.

The results obtained and the analysis of them will form the basis for determining the range of parameters and boundary conditions for manufacturing DBC fibres with the desired properties.

Materials and experimental methods

Characteristics of the dibutrylchitin (DBC) and its spinning solutions

Di-O-butyrylchitin, known as DBC, is an ester derivative of chitin, which combines in itself biocompatibility and biodegradability with suitable physico-chemical characteristics.

In order to obtain different spinning solutions with the use of ethyl alcohol, we used DBC with the lowest possible molecular mass (evaluated on the basis of intrinsic viscosity) of $[\eta]=1.50$ dl/g (designated DBC-A1), and with the highest possible molecular mass of $[\eta]=2.75$ dl/g (designated DBC-A3).

Table 1. Dibutylchitin (DBC) and spinning solutions characteristics; *Intrinsic viscosity value $[\eta]$ was determined in DMAc solutions at the temperature 25°C by using Ubbelohde viscometer.

Symbol of dibutylchitin samples	*Intrinsic viscosity value $[\eta]$, dL/g	Concentration of DBC in spinning solution, %	Dynamic viscosity, Pa s	Rheological parameters	
				n	k
DBC-A1	1.50	17.5	41.75	0.93	41.74
DBC-A3	2.75	10.5	20.25	0.96	21.47
		11.5	35.70	0.93	35.46

Table 2. Conditions for wet spinning of dibutylchitin fibres with the use of ethyl alcohol; The temperature of solidification bath was constant and equal 7°C. The stage of plasticizing drawing was carried out in water plasticizing bath.

Symbol of sample	Dibutylchitin concentration in the spinning solution, %	Stage of solidification		Stage of plasticising drawing	
		Ethanol content in solidification bath, %	As-spun draw ratio, %	Temperature of the plasticising bath, °C	Draw ratio, %
E-1	17.5	0	-1.20	70	67.4
E-2	17.5	17	+18.5	70	70.4
E-3	11.5	5	-12.0	70	71.5
E-4	11.5	0	-12.0	70	54.5
E-5	10.5	0	-12.0	70	54.5
E-6	10.5	0	-4.27	70	86.4
E-7	10.5	5	-12.0	70	109.6
E-8	10.5	5	-2.2	70	96.0
E-9	10.5	12	-11.2	70	95.6
E-10	10.5	12	-11.2	55	55.9
E-W	10.5	0	-11.6	70	62.3

DBC was prepared in accordance with the patent [10]. Polish krill chitin from the Gdynia Sea Fisheries Institute was the basic substrate for this synthesis. The krill chitin was purified from proteins and calcium carbonate before synthesis. For both types of synthesised DBC the esterification degree of dibutylchitin was the same, and equalled almost 2. The solution concentration was selected so that its dynamic viscosity was appropriate for undisturbed processing by the wet-spinning method. The characteristics of DBC and spinning solutions given in Table 1 were presented for wet spinning fibres.

Rheological properties of spinning solutions

The rheological properties of dibutylchitin solutions in ethyl alcohol were determined by means of a Rheotest RV rotary rheometer at 20 °C using an H-type cylinder. The shearing rate reached 160 s⁻¹. The rheological parameters 'n' and 'k' of the Ostwald-de Wales equation were determined on the basis of flow curves. The detailed analysis of the rheological properties of the solutions with various concentrations of dibutylchitin in ethyl alcohol was presented earlier in the article [11].

Fibre formation

The DBC fibres were spun from solution in ethanol by the wet process, using a laboratory spinning stand equipped with exchangeable modules allowing the change of parameters over a very wide range, and their constant control and stabilisation on a given level. A 240-orifice spinneret with an orifice diameter of 0.08 mm was used. The solidification process was conducted in water or in a water bath with a changeable concentration of ethyl alcohol in the range from 0% to 17%. The stretching process was carried out in a single stage in hot water at 70 °C. After continuous rinsing, the fibres were dried under isomeric conditions within a temperature range from 20 °C to 40 °C.

Investigations of the fibres' structure and properties

The porous structure was determined via the mercury porosimetry method using a Carlo-Ebra porosimeter, combined with a personal computer. The following parameters were determined: total pore volume, percentage contents of pores sized between 4-7500 nm, and pores' total internal surface. The moisture absorption (RH) was determined in accordance with standard PN81/P-04635.

The water retention value (WRV) was determined by relating the mass of water stored by fibres after centrifuging the sample over 10 minutes at an acceleration of 10,000 m/s⁻², to the dry sample mass. Prior to centrifuging, the fibres were kept for 24 hours in water with a surface-active agent. A 1% water solution of Rocafeonl NX-3 was used as the surface-active agent.

The tenacity and elongation of the fibres were determined for monofilaments as the average value of fifty measurements carried out with the use of an Instron 4204 tensile tester, according to Polish Standard EN ISO 5079.

Results and discussion

Low susceptibility to deformation during the drawing stage is linked to the rigid structure of the DBC macromolecules. The result of this are rather poor strength properties in the fibres. The application of such forming conditions that increase the porosity may additionally cause a decrease in the above-mentioned factor. This might be the reason why a modification of the previously described [9] general rule for manufacturing highly porous fibres seems to be necessary, in order to reach a compromise between those two contradictory expectations.

Obtaining highly porous fibres requires the solidification process to take place in mild solidification baths (baths with an increased solvent content), in which the conditions were made more extreme due to an increase in temperature. Simultaneously, it is advisable to use positive values of the as-spun draw ratio [9].

Based on preliminary experiments concerning low molecular-mass polymer (DBC-A1), it has been determined that the suitable concentration of ethanol in the coagulation bath (to sustain the stability of the spinning process) must not exceed 17% at 7 °C. The application of higher temperatures causes disturbances in the wet-spinning process. It is also technically inadvisable, due to the solvent's high tendencies to evaporate.

For the two condition sets of extreme solidification – in water, and in a bath with the maximum contents of solvent (17%) – the upper limits of the as-spun draw ratio which would provide the stability of the wet spinning process were determined. These values are 32% and 22%

Table 3. Structure and properties of DBC fibres wet spun with the application of ethanol; Sample E-8 was not obtained. Solidification conditions resulted in creating a structure disabling its drawing process.

Symbol of DBC fibres sample	Total pore volume, cm ³ /g	Total internal pore surface, m ² /g	Moisture absorption at 65% RH, %	Moisture absorption at 100% RH, %	Water retention, %	Tenacity, cN/tex	Elongation, %
E-1				15.14	27.79	8.2	4.38
E-2				14.30	47.11	8.2	7.46
E-3			4.62	17.00	30.54	11.2	5.38
E-4			4.85	17.23	31.91	12.7	8.33
E-5	0.204	37.07	4.94	17.18	30.28	13.3	9.43
E-6	0.176	2.31	4.95	16.07	54.95	13.1	7.31
E-7	0.180	17.79	6.14	17.15	32.14	14.5	6.49
E-9	0.564	50.38	6.29	18.19	67.25	10.7	5.47
E-10			6.42	18.27	30.86	9.7	8.65
E-W			5.75	18.23	36.92	11.5	8.97

Table 4. Percentage content of capillary set with various radii for wet spun DBC fibres.

Symbol of DBC fibres sample	Small pores -	Midium pores -	Large pores -	Very large pores -
	capillary set with radii			
	4-12,3 nm, %	15-75 nm, %	50-150 nm, %	1875-7500 nm, %
E-5	47.06	13.72	1.96	37.25
E-6	0	18.18	2.27	79.54
E-7	31.11	15.55	13.33	40.01
E-9	20.58	22.69	4.26	52.48

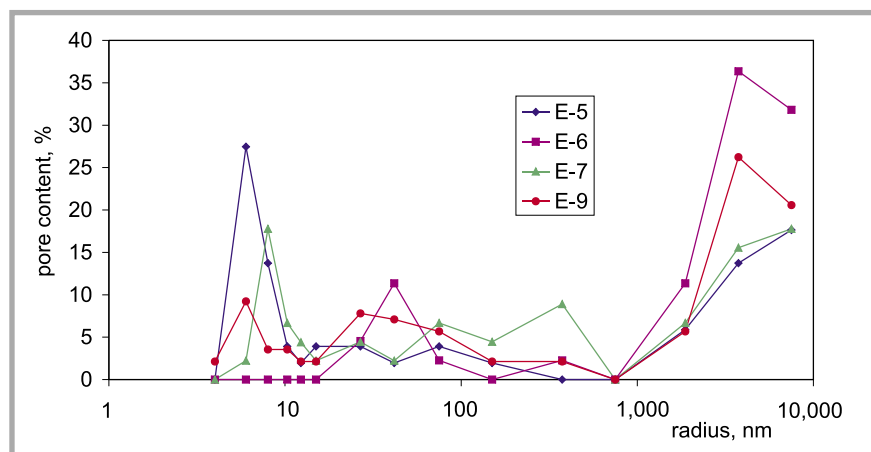


Figure 1. Dependences of percentage contents of distributions of pores as function of their radii for DBC fibres obtained. a capillary sets for dibutyrylchitin fibres spun with a variable conditions of solidification.

respectively. According to the conditions given in Table 2, the samples labelled as E-1 and E-2 were formed at lower values of the as-spun draw ratio, respectively -1.2% and +18.5%. The drawing process was carried out in a water plasticising bath at 70 °C. The fibres obtained, which showed similar susceptibility to deformation despite reduced as-spun draw ratio values being applied, were distinguished by a lower than assumed value of fibre tenacity of the order of 8 cN/tex (Table 3).

In an attempt to obtain higher values of this factor, the process of solidification was conducted at even lower as-spun

draw ratio values, which in theory would favour the production of stronger fibres. At the same time, DBC with a high molecular mass and symbol DBC-A3 was used. Its intrinsic viscosity value [η] was 2.75 dl/g. This resulted in obtaining better strength characteristics of the fibres, although this meant reducing the concentration of DBC in the spinning solution to 11.5%, maintaining the dynamic viscosity at an analogous level of 35.7 Pa.s. However, in this case the maximum value of the as-spun draw ratio was circa -2%.

The fibres obtained, labelled as E3 and E4 exhibited the tenacity at the level of

11.2 cN/tex to 12.7 cN/tex, and at the same time increased absorption capabilities (moisture absorption at 100% RH of the order of 17.2%, water retention value above 30%). In terms of hydrophobic material, these values signify that the fibres are more porous.

Next with the aim of obtaining better parameters for forming the porous structure of fibres, the concentration of the polymer in the spinning solution was slightly reduced, to 10.5%. Maintaining a constant temperature in the coagulation bath, the solidification process conditions were altered by increasing the concentration of solvent (ethanol) from 0% to 12% appropriately, for two values of the spun draw ratio (see Table 2, samples from E5 to E9).

Conducting the process of solidification in 'hard' conditions of the bath, which did not contain any solvent (Table 2, Table 3), results in obtaining fibres with strength above 13 cN/tex and a total volume of pores of about 0.2 cm³/g, although applying a higher value of as-spun draw ratio does not result in an increase in the porosity of the fibres. Making the solidification conditions less severe (at 5% ethanol concentration) leads to an increase in fibre strength to the level of 14.5 cN/tex (when applying larger negative values of the as-spun draw ratio at the level of -12.0%). However, together with the increase of the as-spun draw ratio, disturbances to the formation process start to occur. Under these conditions, the structure of the freshly solidified fibres were susceptible for deformation. This prevented obtaining a fibre sample of a proper quality after the drawing process (sample E8).

A further increase of the solvent content in the coagulation bath to 12% results in decreasing the strength properties of fibres to the level of 10.7 cN/tex. However, this is sufficient for nonwoven processing (sample E9). At the same time, the total volume of pores increases to 0.56 cm³/g. This range of values allows these fibres to be classified as fibres with increased porosity.

The obtained effect of lightening the coagulation bath is not typical, and reciprocal to what is usually observed in the case of fibres obtained from other fibre-forming polymers with the application of polar solvents [12]. The reason for this might be that in such conditions, a layer of external 'skin' with better permeabil-

ity is probably formed. This resulted in easier diffusion processes, and finally in the creation of a porous structure with a higher total pore volume.

The character of the porous structure obtained varies depending on the solvent contents in the coagulation bath. The curves of pore distribution versus their radii (Figure 1.) show a maximum within the range of capillary sets described as small pores, with the exception of fibre sample E6, which was solidified in a bath with no solvent and formed at a higher value of the as-spun draw ratio. Those fibres exhibit very high amounts of very large pores, even up to 80%, which are structural defects (Table 4, Figure 2). The low level of the content of small- and medium-size pores is about 18%, and the total volume of pores is 0.176 cm³/g. While fibres solidified in a bath containing 12% ethanol (E9) exhibit an increase in the total number of small and medium pores to 43%, at the same time their total volume is three times higher. The best pore character belongs to fibre sample E5 (Table 4). They were solidified in the same conditions as above, although the values of the as-spun draw ratio were more negative and smaller. With a large number of small pores and a fine-pored structure (where the total number of small and medium pores is above 60%), the number of large

pores is limited to 37%. The presence of very large pores in the cross-section view is visible in the SEM micrograph (Figure 2). On the surface of the fibres, we can observe crevices and scratches typical of the wet-spinning method.

The increased absorption properties of all the obtained fibres are connected with the character of the manufactured porous structure and the total volume of pores. Moisture absorption at 100% RH to the level to 18% and retention of the order of 30-67% should guarantee good penetration of biologically active substances into the fibre. Dressings made of such fibres should also exhibit the ability to absorb exudates from wounds, while at the same time providing a sufficiently moist environment.

As an alternative, it is possible to obtain fibres with a porosity enhanced to 0.5 cm³/g and high retention (above 60%) at a fibre strength of about 10.7cN/tex (which is assumed to be the lowest possible for processing nonwovens), or fibres with the strength of above 13 cN/tex but with the total volume of pores lowered to 0.2 cm³/g. In order to verify whether this total volume of pores is sufficient for introducing biologically active substances, suitable tests will be carried out.

In general, with the application of ethyl alcohol as a solvent for the wet-spinning process of DBC fibres, we have stated that there is a narrow scope for changes in parameters within which the process remains stable. The reasons for that may be found in the rather low polarity of the solvent used in comparison to dimethylformamide.

Tests carried out for other fibre-forming polymers showed [9] that the supramolecular structure depends upon the solvent and the character of the solvent-polymer interactions.

The most advantageous conditions for the solidification process, providing DBC fibres obtained from high molecular mass which have sufficient strength for processing, are as follows:

- the solvent (ethanol) content in a solidification bath not exceeding 12%;
- temperature of the solidification bath of 7 °C;
- the as-spun draw ratio negative of about -12%.

It is beneficial, due to the increased mobility of the macromolecules, to con-

duct the drawing process in hot water at about 70 °C, at deformations lower than maximal.

It has been stated that the increase in tensile stress due to reducing the temperature of the plasticising bath did not in this case result in higher fibre strength properties being obtained (sample E10). The main factor was the significantly decreased susceptibility to deformation, which resulted in a decrease in draw ratio value from 96% to 56%.

Under the selected conditions, which were favourable due to the desired character of the obtained porous structure and a tenacity of fibres greater than 11 cN/tex, fibres were spun (sample EW) which were designed for nonwoven dressing materials.

Our further investigations will be dedicated to the influence of the process conditions on the supramolecular structure, total orientation and strength properties of DBC fibres.

Conclusions

- The application of ethyl alcohol as a solvent enables us to obtain porous dibutylchitin fibres with the increased sorptive properties and sufficiently large strength parameters required in processing them into nonwoven dressing materials.
- The rather narrow scope of changes in the parameters for which the wet spinning process of dibutylchitin fibres is stable is connected with the use of ethyl alcohol as a solvent.
- The advantageous conditions for forming dibutylchitin fibres with the desired strength and porous structure were determined.
- For determining the relations between process conditions of wet spun DBC fibres on their supramolecular structure, total orientation, and strength properties, additional special programmed investigations will be carried out.

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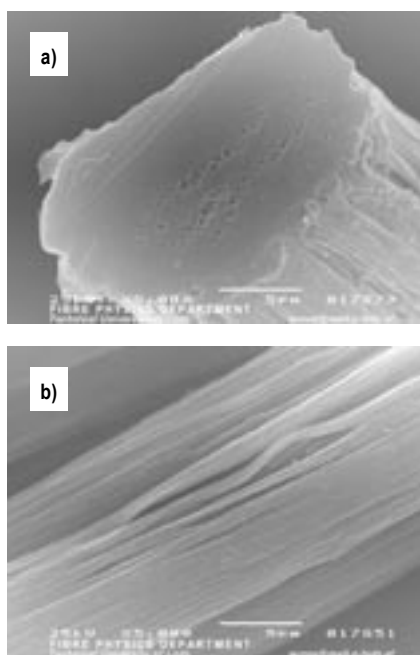


Figure 2. SEM micrographs of exemplary porous structure of dibutylchitin fibre; a) Cross-section view. Presence of very large pores is visible, b) Longitudinal view, with visible crevices and scratches on the surface.

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