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# Dibutrylchitin Nonwoven Biomaterials Manufactured Using Electrospinning Method

## Abstract

*The world market of dressing materials is being systematically enriched with new products. The raw materials used for dressing manufacture have been modified, the structure of products has been changed, and new kinds of finishes have been applied. A great number of research works have been devoted to demonstrating that chitin, a natural polysaccharide which is a waste material in seafood processing, has many features suiting it for the manufacture of excellent dressing materials. As chitin is characterised by limited processing possibilities, a range of chitin derivatives has been developed. One of them is an ester chitin derivative named dibutrylchitin, which can be easily dissolved in common solvents. This paper presents a new method of manufacturing nonwoven products made from dibutrylchitin, which will be applied with the aim of obtaining dressing materials. The technology proposed is based on fleece manufacturing directly from the polymer solution using electrospinning (e-spinning) technology. The proposed method allows fibres of transverse dimensions of below 0.4 μm to be obtained.*

**Key words:** electrospinning, dibutrylchitin, biomaterials.

## Introduction

A great number of research works have been devoted to demonstrating that chitin, a natural polysaccharide which is a waste material in seafood processing, has many features suiting it for the manufacture of excellent dressing materials. Numerous experiments have proved that chitin is a biocompatible and biodegradable polymer which demonstrate bacteriostatic and analgesic effects, which in addition shorten the time of wound healing and the rebuilding of connective tissue. The only disadvantage of natural chitin application is its insolubility in the common solvents generally available, and the enormous related difficulties connected with chitin processing.

For that reason, only a few research and production centres have been able to master appropriate dressing materials with use of chitin. One such producer, which manufactures the dressing materials known as beschitin, is the Japanese enterprise Unitika Co. This company offers its products at very high prices; for example, the cost per piece for a dressing with the dimensions of 10 cm × 8 cm is 25 USD. The Mycoton dressing produced in Ukraine is another chitin dressing material available on the market. Mycoton is manufactured by means of the hand-made paper technique from a pulp which includes fungi chitin in a complex with glucan and melamine. The main disadvantages of this kind of dressing are its fragility and dark colour.

Independently of the Unitika Co. product described above, a dressing with the name of Beschitin-W is also available on the market. This dressing is manufac-

tured in the form of a nonwoven from crab chitin. Information has recently appeared concerning attempts to spread a membrane which includes chitin of fungi origin in its structure on a fibrous material. The sacchachitin membrane is manufactured on the basis of an extract from the *Ganoderma Tsuage* fungus, which includes about 40% chitin in its composition.

As chitin is characterised by limited processing possibilities, a range of chitin derivatives have been developed. An original, novel method of manufacturing one of them (an ester chitin derivative which can be easily dissolved in common solvents) was developed at the Technical University of Łódź [1-2]. This derivative, known as dibutrylchitin, has film- and fibre-forming properties, and the DBC fibres can be manufactured by means of traditional methods. Dibutrylchitin is also a raw material for manufacturing yarn and a broad range of textile dressing materials. These latter materials can be processed by means of relatively simple methods, and transformed into materials containing regenerated chitin (RC) without any damage to their own structure. Dibutrylchitin and regenerated chitin fulfil all the requirements considering dressing materials formulated by European Standard EN ISO 10993 [3-7].

As a conclusion to the investigations carried out recently, a proposition was formulated to manufacture the dressing products in two stages. The first stage should consist in fibre and yarn formation from dibutrylchitin, whereas the second should consist in manufacturing flat textile products.

These multi-stage technological processes increase the cost of the final product obtained in a form that demands high polymer consumption. The most sensible and economically reasonable way of applying such dressings would be their use for long-healing wounds, which require the regeneration of the connecting or bone tissue without rejecting the dressing before the wound has been totally healed, or before the total biodegradation of the dressing occurs. In the case of dirty and purulent wounds, when the dressings should be changed frequently with the goal of rejecting both the matter and the bacteria colonies, the use of the above-mentioned dressings would be inexpedient, because it would be connected with the loss of such valuable raw material as dibutrylchitin.

Nonwoven technologies of dressing material production create the opportunity of manufacturing thin flat textile products directly from the polymer, without the stage of fibre formation. This method is certainly more economical in comparison to that mentioned above, as it enables the manufacture of a product of an intended thickness directly from the polymer. The products obtained in these technologies, in general known as nonwovens, can be manufactured by means of the following four methods: by spinneret formation, by the melt-blown method, by the blow-about polymer solution, and by electrospinning. Some installations designed for nonwoven production from polymer melts are operational in Poland, although there is a lack of any stand that would enable nonwoven manufacture by blowing about polymer solution. Unfortunately, in the case of dibutrylchitin, the nonwoven

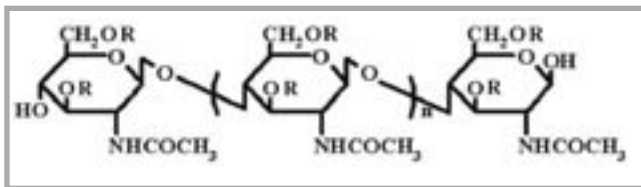


Figure 1. Chemical structure of dibutrylchitin;  $R = \text{COC}_3\text{H}_7$ .

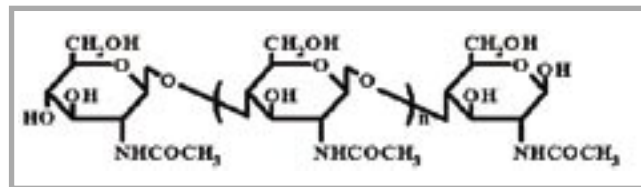


Figure 2. Chemical structure of chitin.

production directly from melt is impossible, as the melt temperature of dibutrylchitin is near the destruction temperature of the polymer. Research works aimed at achieving nonwovens directly from a polymer solution by means of the blow-about method and by electrospinning were commenced at the Department of Textile Metrology of the Technical University of Łódź.

The electrospinning method is based on fibre formation, as the effect of a reaction of a polymer solution drop on the forces of an electric field. Transformation from a drop to a stream in an electric field is known as a Taylor cone [8-11]. Taylor proved in 1964 [10,11] that for a given kind of liquid, a critical value of the applied voltage exists, at which the liquid drop, flowing out from the nozzle, is transformed into a cone under the influence of the electric field. The electric charges, which diffuse in the liquid influenced by the electric field, cause strong deformation of the liquid's surface and minimise the total system energy. Within the region of the maximum field strength and the maximum charge density, the electric forces exceed the forces of surface tension, and the liquid creates a cone at the nozzle outlet. A thin stream of liquid particles is torn off from the end of the cone.

The foundations for electrospinning were created in 1882 by Rayleigh [12] and Zeleny [13,14] who described the behaviour of a liquid jet in an electric field. Patents for electrospinning were created by Formhals in the years 1934-1944 [15-19]. Up to now, this process has been examined in several important studies, although not everything is yet fully understood. Theoretical research, dealing with the problem of fully describing the phenomena accompanying the electrospinning, e.g. that of Yarin and co-workers from the University of Akron in the years 2001-2003, developed the theory of the bending instability of jets [20,21,22]. Electrospinning has gained much attention recently since it offers the manufacture of fibres with transverse dimensions of nanometers.

Taylor's investigations has been an inspiration for many researchers who

conducted observations of the behaviour of different kinds of polymers in electric fields, and which were the basis for the development of manufacturing technologies of a new generation of nanofibres made from about fifty various polymers [23] such as polylactic acid (PLA) [24], polyacrylonitrile (PAN) [25], polyvinyl alcohol (PVA) [23], poly(ethylene oxide) (PEO) [26], polyamide (PA) [27], polyethylene (PE) [28,29], and polypropylene (PP) [29]. It can be expected that over fifty more samples will appear in the future.

At this point we would like to present some preliminary research on the manufacture of dibutrylchitin fibres by means of electrospinning. The aim of the research was to investigate the influence of selected parameters, such as polymer concentration in solution and voltage applied, on fibre formability.

## Materials and Methods

### Characteristics of dibutrylchitin (DBC)

Dibutrylchitin (Figure 1) was prepared from krill chitin (Figure 2) with a degree of acetylation of 0.97 and intrinsic viscosity value of 17.9 dl/g, determined at 25°C in a solvent consisting of N-MP (N-methylpyrrolidone) containing 5% LiCl. The krill chitin was purchased from the Sea Fisheries Institute, Gdynia, Poland. It was purified from proteins and calcium carbonate before processing. The esterification procedure and conditions were the same as those worked out by Lidia Szosland and described earlier [1,2]. The final DBC product was characterised by an intrinsic viscosity value determined for its solution in N,N-dimethylacetamide (DMAc) at 25°C. The intrinsic viscosity values were equal to 1.07 dl/g and 1.5 dl/g.

### Electrospinning process

An experimental laboratory stand for manufacturing nonwoven materials by means of the electrospinning technique was designed and constructed. A schematic drawing of this stand, a photograph of its main parts and a photograph of the electrically driven bending instability of the jet, are presented in Figure 3.

The stand is composed of three basic elements: a high voltage generator, an upper and a lower electrode. The upper electrode serves for extruding the polymer and enables the polymer drops to achieve a suitable electric potential. The second (lower) electrode is the take-up electrode, in relation to which the electric potential of the polymer is applied, and on which the fibres are deposited during the process of manufacturing the nonwoven. The shape and dimensions of both the lower and the upper electrode may differ; for example, we changed the diameter of the metal tip from 0.8 to 1.2 mm respectively.

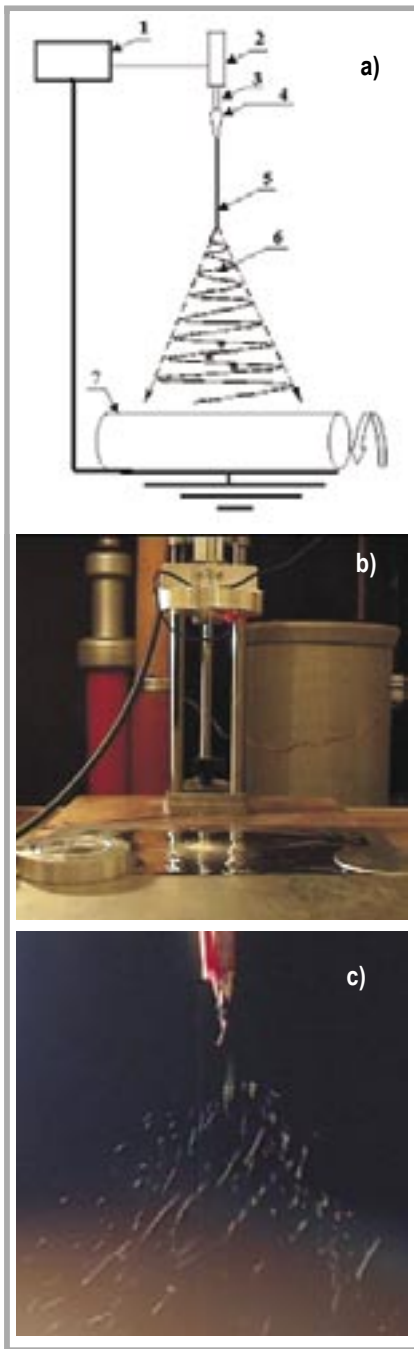
In the first stage of research, our interest was concentrated on determining the influence on fibre formability of technological parameters such as polymer concentration in solution and the applied voltage. The applied values of both parameters are specified in Table 1.

### Characteristics of dibutrylchitin nanofibres

In the second stage of the research, the characteristics of DBC nanofibres were established. The transverse dimension of dibutrylchitin nanofibres was determined by means of a Scanning Electron Microscope. Since dibutrylchitin belongs to the group of biodegradable polymers, the supermolecular structure of fibres is the one of the important parameters which influence the degradation ability of fibres. Therefore this kind of investigation fell within the range of our interest. The supermolecular structure of the DBC nanofibres was analysed by wide angle X-ray scattering (WAXS). The investigations were made by means of a Seifert USD 63 diffractometer. The X-ray diffraction pattern was recorded within an angle range of 3 to 60° with a

Table 1. Specification of the technological parameters applied during the electrospinning process.

Technological parameter	Values of technological parameter
DBC concentration in ethanol, % wt/v	6, 8, 9, 10, 15
Voltage, kV	6, 8, 10, 12, 14, 16 up to 25



**Figure 3.** Laboratory stand for manufacturing nonwovens by electrospinning: a) schematic drawing of apparatus: 1 - high voltage source, 2 - polymer container, 3 - tip of metal tube, 4 - droplet of polymer solution in the conical shape known as Taylor cone, 5 - rectilinear part of jet, 6 - electrically-driven bending instability of the jet (instability region), 7 - collector a-lower electrode (grounded); b) photograph of the main parts of the apparatus, front view; c) photograph of the electrically-driven bending instability of the jet.

step of  $0.1^\circ$  using  $\text{CuK}\alpha$  radiation. The impulse counting time was 10 s, the current intensity was 30 mA, and the accelerating voltage was 40 kV. Deconvolution of peaks was performed by the method proposed by Hindeleh & Jonson and im-

proved and programmed by Rabej [30]. The degree of crystallinity was calculated as the ratio of the integral intensity from crystalline regions to the integral intensity scattered by the whole sample (total domain from the crystalline and the amorphous regions).

## Experimental Results

### Influence of the dibutylchitin concentration in ethanol on the fibre formability

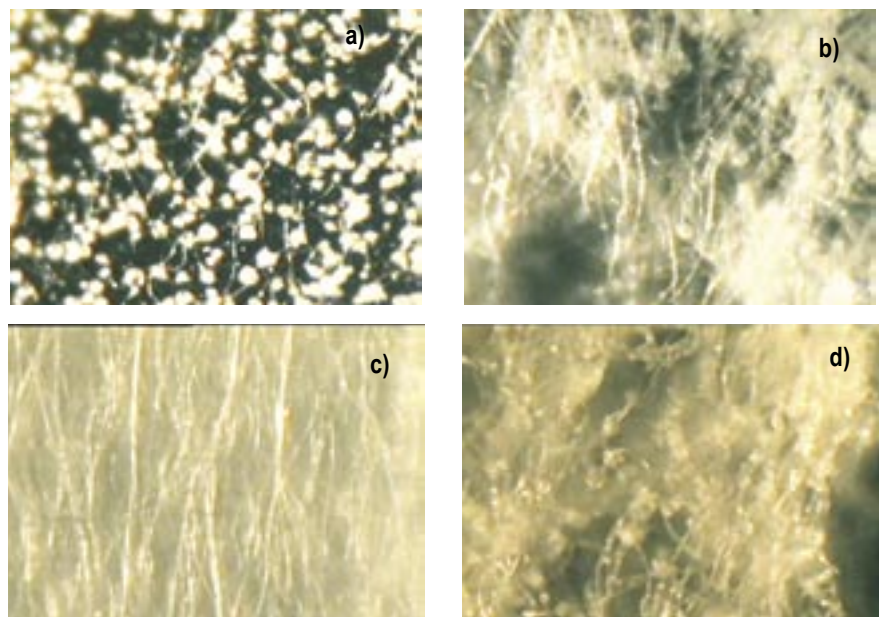
The fibres were electrospun at the voltage of 25 kV using five variants of polymer solution as described in Table 1. The obtained results are illustrated in Figure 4.

The influence of dibutylchitin contents in solution of ethanol on the fibre formability was examined on the basis of light microscope images of electrospun fibres. There are no scale bars in the photographs in Figure 4 because only a quali-

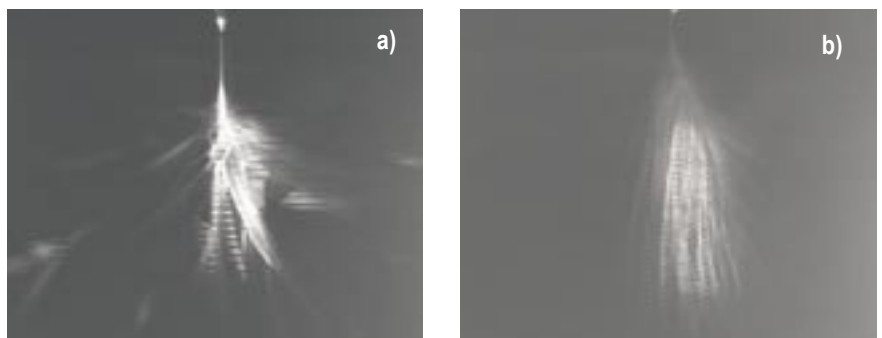
tative assessment was carried out. The images presented in Figure 4 indicate that the best results were obtained using a polymer concentration in ethanol equal to 9% wt/v. Such a concentration ensures the formation of fibres without any disturbances. Polymer concentration at the level of 6% wt/v resulted in droplets forming instead of fibres. In the case of polymer concentrations greater than 10% wt/v, the formation of a film was observed. Therefore the concentration of 9% wt/v was selected as the basis for further investigation.

### Influence of applied voltage on the mechanism of fibre formation

The electrical field is produced by a high-voltage source between the tip of the metal tube and the fibre collector. Potential difference plays an important part in the formation of the bending instability of the jet, as can be seen in Figure 5 as well as stated on the basis of the parameters



**Figure 4.** Light microscope images for qualitative examination of electrospun DBC fibres: a) 6% wt/v, 25kV; b) 8% wt/v, 25 kV; c) 9% wt/v, 25kV; d) 10% wt/v, 25 kV.



**Figure 5.** Influence of voltage on the fibre-forming region for 9% wt/v DBC solution in ethanol at a distance between electrodes of about 21 mm, applied voltage equal to 6 kV (a) and 12 kV (b).

measured, which are presented in Table 2. This confirmed that the formation of ultra-thin fibres is the result of electrostatic-type interactions. The jet of the polymer was stretched in the electrostatic field as far as possible, as an effect of the repulsion of the charges flowing on the surface of the jet.

A preliminary evaluation of the dimensions of the fibre formation region was carried out. Specifically, the length of the rectilinear part of the jet region and the vertex angle of the cone was tested on the basis of the recorded images, as is schematically presented in Figure 6. The values of the geometrical parameters measured are given in Table 2. We believe that these parameters will be useful for verifying the theoretical model of the electrospinning process.

### Characteristics of the DBC nanofibres

The transverse dimensions of nanofibres formed from DBC ethanolic solution under the chosen conditions was determined on the basis of micrographs taken by a scanning electron microscope (SEM),

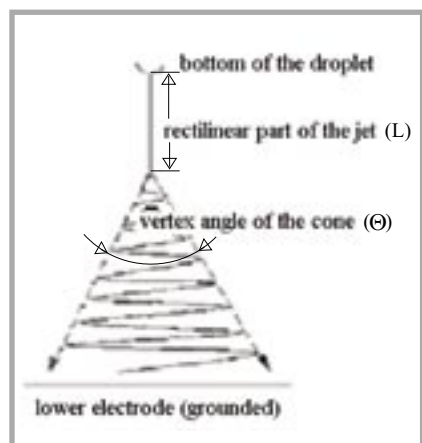


Figure 6. An illustration of the fibre-forming region and its characteristics.

Table 2. Relation between the rectilinear part of jet, the vertex angle of the cone and the applied potential in fibre forming region.

Measured parameters	Voltage, kV				
	6	8	10	12	14
Rectilinear part of the jet L, mm	24.6	15.1	15.8	11.1	18.8
Vertex angle of the cone $\Theta$ , deg	116	101	81	41	56

Table 3. Characteristics of supermolecular structure of the DBC fibres (\*all fibres were spun using ethanol).

Type of sample	Crystallinity index X, %	Dimension of crystalline regions $D_{(100)}$ , Å
Chitin	80.3	69.3
DBC polymer	24.1	17.8
DBC classical fibres*	32.7	18.2
DBC nano fibres*	39.8	15.5

as illustrated in Figure 7. The average value of the transverse dimension of DBC nanofibres which were electrospun under these conditions was equal to 0.3  $\mu\text{m}$ , with a coefficient of variation of 18.9%. The application of the electrospinning technique allows us to reduce the transverse dimensions of fibres by two orders of magnitude in comparison to the fibres spun by classical methods, as shown in Figures 7 and 8.

The results of an analysis of the supermolecular structure of the DBC nanofibres by wide angle X-ray scattering (WAXS) are presented in Table 3. In addition, the crystallinity of initial chitin, DBC polymer and the crystallinity of DBC fibres manufactured using the classical wet spinning method was assessed.

The analysis of the results presented in Table 3 demonstrates that the value of the crystallinity index of DBC nanofibres is higher by about 21%, compared with those of the DBC fibres formed using the classical wet method. The average dimensions of crystalline regions for nanofibres are smaller by about 15% when compared to DBC wet spun fibres.

### Conclusions

The results of our investigations allow us to draw the following conclusions:

- The experiments carried out proved the possibility of forming nonwovens from a dibutylchitin solution by means of electrospinning.
- Applying the electrospinning technique allows us to reduce the transverse dimensions of fibres which compose the nonwovens by two orders of magnitude, i.e., down to dimensions within the range of nanometers.
- The supermolecular structure of fibres

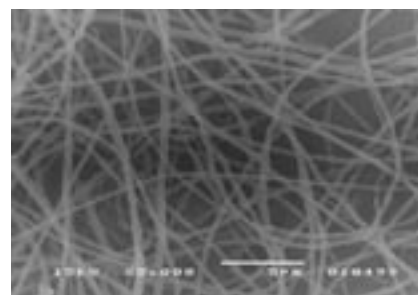


Figure 7. The example of SEM micrograph of non-woven from dibutylchitin nanofibres manufactured by means of electrospinning.

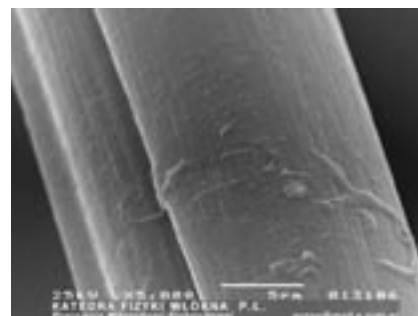


Figure 8. A view of DBC fibres spun by means of the wet classical method.

manufactured by means of the electrospinning technique does not differ significantly from the supermolecular structure of those fibres obtained using the classical wet spinning technique.

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### Editorial note

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The Conference is organised by the Textile Department of the Faculty of Mechanical Engineering, University of Maribor, Slovenia. AUTEK stands for the Association of Universities for Textiles ([www.autex.org](http://www.autex.org)), founded in 1994, which groups together universities with established international reputations in textile education and research, and consists of members within Europe and beyond, including the USA. The association aims at playing a leading part in the future development of textile education and in basic, strategic and applied research.

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### Important dates:

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|---------------------------------------|--|
| <b>November 30<sup>th</sup>, 2004</b> | - extended abstract                    |
| <b>January 31<sup>st</sup>, 2005</b>  | - notification of acceptance           |
| <b>April 20<sup>th</sup>, 2005</b>    | - final papers - camera ready          |
| <b>May 31<sup>st</sup>, 2005</b>      | - payment of registration fee deadline |

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