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Alkaline Treatment of Dibutrylchitin Fibres Spun from Polymer Solution in Ethyl Alcohol

Abstract

Dibutrylchitin (DBCH) was obtained from native krill chitin by its esterification with butyric anhydride. In this study, DBCH was the initial material for the fibre formation. DBCH fibres were manufactured from a polymer solution in ethyl alcohol by extrusion. Because a dry-wet formation method was applied, the fibres obtained had a porous core. The microporous DBCH fibres were then treated with aqueous KOH solutions. By applying various parameters of the alkaline treatment, DBCH fibres can be transformed into fibres from the regenerated chitin or even into chitosan fibres. The use of a potassium hydroxide solution as an alkaline medium enables a total reconstruction of the original supermolecular structure of chitin. When transforming DBCH fibres into the regenerated chitin fibres, diluted KOH solutions were applied, whereas treatment at an elevated temperature with saturated KOH solutions obtained chitosan fibres with various values of deacetylation degree. At every stage of the treatment, the structural changes in the fibres were examined using IR spectroscopy (FTIR), wide-angle X-ray diffraction and scanning electron microscopy (SEM).

Key words: dibutrylchitin fibres, alkaline treatment, regenerated chitin fibres, chitosan fibres.

Introduction

Chitin poly-(1-4)-2-acetamido-2-deoksy-D-glucopyranose) is a natural polymer formed in the biosynthesis process. Like cellulose, chitin is a polysaccharide with a ring-structure polymer chain. Chitin is present in the shells of sea crustacea (shrimps, crabs, krill, lobsters). It can also be found in insects, as well as in some microorganisms and fungi [1 - 3].

The interest in chitin and its derivatives mainly results from the fact that these materials possess specific properties such as biocompatibility, bioactivity and biodegradability, which makes them useful for biomedical purposes.

Chitin is characterised by a high molecular weight and a high degree of crystallinity. However, its low solubility makes it difficult to process, and thus significantly limits the application of chitin, despite its unique properties. Therefore different physical and chemical modifications have been carried out in order to obtain chitin derivatives with considerably better solubility, while at the same time maintaining its biological activity [3, 4].

The most important chitin derivatives are dibutrylchitin (DBCH) and chitosan. Both are characterised by good solubility; DBCH is soluble in popular organic solvents, whereas chitosan can be dissolved in aqueous solutions with low pH values, which makes it quite easy to process them into fibres. The most convenient forms of biomedical materials are fibres, fibrous materials and textiles.

Materials

One of the components of krill shells (*Euphasia superba*) is calcium carbonate. In order to get rid of it, the shells were treated with a 2M aqueous solution of a hydrochloric acid. The reaction was carried out at 25 °C for 2 hrs. The formed calcium chloride and the excess of hydrochloric acid were removed by repeated rinsing of the material with water. The

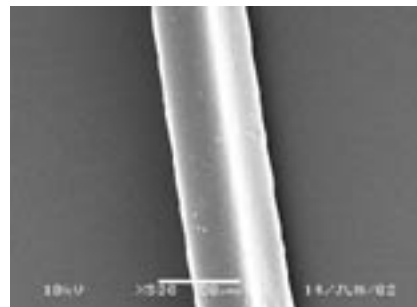


Figure 1. SEM micrograph of the surface of DBCH fibres spun into air and water, magnification 500×.

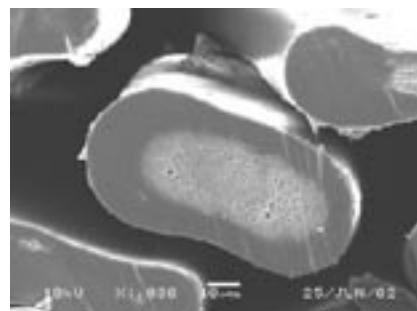


Figure 2. Cross-section of DBCH fibres spun into air and water. SEM micrograph, magnification 1000×.

chitin thus purified was then esterified with a butyric anhydride in the presence of hyperchloric acid used as a catalyst.

The reaction was carried out at temperatures from 0 °C to 17 °C for 7 hrs. To remove the by-products of the esterification, the DBCH was rinsed several times, with ethyl ether and then with distilled water [4].

The dibutylchitin obtained in this way was next dissolved in an anhydrous ethyl alcohol, and 15%, 18%, 20%, 25% spinning solutions were prepared. Using such a solvent made it possible to replace the acetone or dimethylformamide which has been applied up to now, and to eliminate their toxic action on organisms.

The prepared spinning solutions were heated at temperatures ranging from 50 °C to 75 °C for a period from several hours to several days to ensure the total dissolution of the polymer, deaeration, and finally to obtain fully homogeneous spinning solutions which did not require any additional filtration. In this study, higher polymer concentrations of spinning solutions required higher temperatures and longer dissolution periods.

Before spinning, the solutions were additionally heated at 60 °C for 1 hr. and then extruded through orifices of 0.2 mm diameter.

The DBCH fibres were spun using a wet-dry method. When the fibres were partly solidified, they were then introduced into a water bath and taken on a bobbin device, stretched twice and next dried in air [8, 12, 13].

This method of fibre formation was applied for all the prepared spinning solutions. As a result, the microporous DBCH fibres of different linear densities (1.7 to 5.6 dtex) and diameters (35 - 75 µm) were obtained (Figures 1, 2).

Experimental

The DBCH fibres were treated with 5% KOH aqueous solutions at 20 °C – (series A), 50 °C – (series B), 70 °C – (series C), and 90 °C – (series D). During the process, the mass loss of the fibres and their linear densities values were determined. It should be noted that the application of NaOH to the DBCH hydrolysis led to the total decomposition of the fibres. Therefore further trials with NaOH were given up [12].

The FTNIR spectra of the remaining N-deacetylation products for both hydroxides are shown in Figure 3.

The height of the band at 6547 cm⁻¹ corresponding to the –NH₂ group is much greater for KOH than for NaOH at the same temperature and the same duration of treatment. This means that KOH is a much better deacetylation medium. It was established that the treatment with KOH causes no decomposition of the chitin fibres even under more severe temperature and concentration conditions. Therefore only KOH solutions were used in the experiments.

N-deacetylation was applied to fibres made of the regenerated chitin obtained at the first stage of the experiments, as well as for the initial fibres made of DBCH. N-deacetylation reactions were

carried out in solutions of potassium hydroxide saturated at specific temperatures, i.e. at 70 °C (series N C), 100 °C (series N F), 120 °C (series N G), and 140 °C (series N H).

When the reaction was complete, the fibres were rinsed several times with ethyl alcohol.

Measurements and equipment

Spectroscopy determinations were performed in the medium-IR range for DBCH fibres which underwent debutyrylation and in the near-IR range (NIR) for the fibres that were N-deacetylated.

Measurements in the medium-IR range of 4000-400 cm⁻¹

All the measurements were carried out using a Magna-860 type FTIR spectrometer, a product of Nicolet.

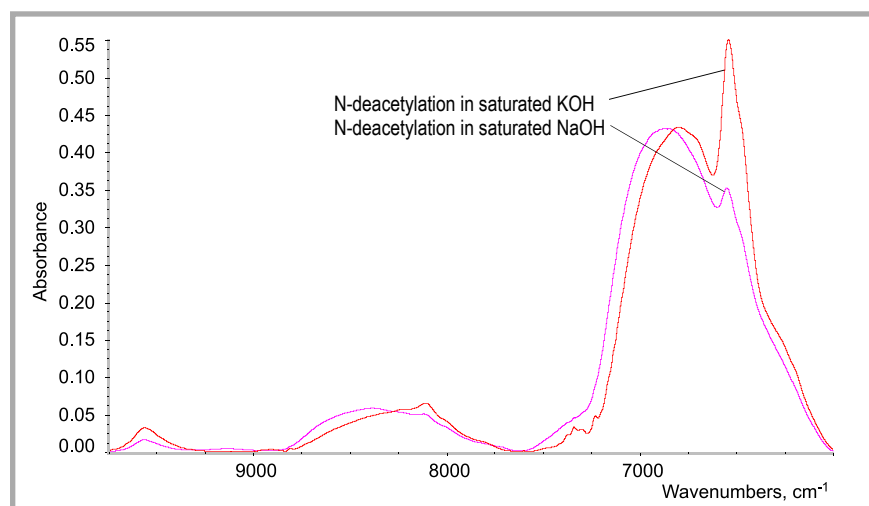


Figure 3. FT NIR spectra ranging from 9750 cm⁻¹ to 6000 cm⁻¹ for regenerated chitins fibres after N-deacetylation at 70 °C in saturated KOH and NaOH solution after 240 min.

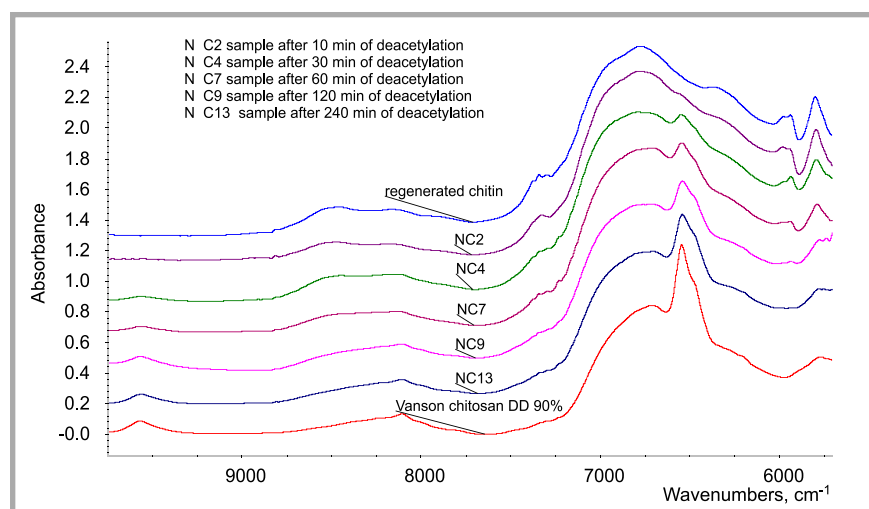


Figure 4. FT NIR spectra ranging from 9750 cm⁻¹ to 5700 cm⁻¹ for Vanson chitosan (DD 90%) for fibres from regenerated chitin, and the same fibres after alkaline treatment at 70 °C in saturated KOH solution.

Table 1. Deacetylation degree (DD) values for chitin and chitosan fibres (series NC - N - deacetylation) obtained from the regenerated chitin deacetylated at 70 °C.

Sample	Alkaline treatment, min	Total area spectrum	Area of peak -N-H at 9559 cm ⁻¹	Area of peak -N-H at 8110 cm ⁻¹	Area of peak -N-H at 6547 cm ⁻¹	Area of peak -N-H at 6483 cm ⁻¹	Spectral coefficient F	Deacetylation degree (DD), %
N C1	5	815.00	1.52	-	2.98	2.54	0.00869	3.8
N C2	10	774.97	2.15	-	4.63	3.56	0.01343	5.9
N C3	20	810.35	2.94	-	9.58	9.58	0.02743	12.0
N C4	30	865.78	6.50	-	12.64	5.39	0.31970	14.0
N C5	40	823.95	6.17	-	15.27	12.10	0.04739	20.7
N C6	50	836.26	7.70	0.79	22.26	18.37	0.04859	21.3
N C7	60	848.66	6.76	0.82	24.95	21.40	0.06387	27.9
N C8	90	853.36	10.96	3.21	36.09	30.26	0.09483	41.5
N C9	120	871.67	15.12	3.44	50.25	40.75	0.12627	55.2
N C10	150	861.72	14.48	3.33	46.63	44.45	0.12723	55.7
N C11	180	840.95	12.12	3.26	51.48	46.81	0.13541	59.2
N C12	210	879.03	15.96	4.12	57.33	54.21	0.15048	65.8
N C13	240	882.22	16.87	4.76	58.02	59.21	0.15891	69.5
Vanson	-	566.00	13.41	6.70	51.40	44.93	0.20573	90.0

Table 2. Deacetylation degree (DD) values for the chitosan fibres (series NH - N - deacetylation) obtained from the regenerated chitin deacetylated at 140 °C.

Sample	Alkaline treatment, min	Total area spectrum	Area of peak -N-H at 9559 cm ⁻¹	Area of peak -N-H at 8110 cm ⁻¹	Area of peak -N-H at 6547 cm ⁻¹	Area of peak -N-H at 6483 cm ⁻¹	Spectral coefficient F	Deacetylation degree (DD), %
N H1	10	652.66	16.39	3.05	55.70	40.64	0.17845	78.0
N H2	20	658.16	13.24	3.08	60.23	42.32	0.18115	79.2
N H3	30	622.16	13.11	3.12	52.24	45.65	0.18342	80.2
N H4	60	644.41	12.78	3.11	61.33	46.65	0.19224	84.1
N H5	120	611.12	13.56	3.25	63.25	45.22	0.20501	89.7
N H6	180	604.00	13.78	3.41	65.32	44.32	0.21000	91.8
N H7	240	625.53	15.11	3.52	67.22	46.32	0.21130	92.9
Vanson	-	566.00	13.41	6.70	51.40	44.93	0.20573	90.0

The fibres were cut into 1-3 mm pieces, and then blended with powdered sodium chloride (spectrally pure). The samples were then pressed at 200 MPa to obtain a tablet. The tablet was placed in a measuring chamber of the spectrometer equipped with a mirror beam collimator (focused 16x). As a reference, a tablet made of NaCl (without fibres) was used.

The following measuring parameters were applied: range: 4000 - 400 cm⁻¹, resolution: 4 cm⁻¹, number of scans: 128, source of radiation: IR, detector: DTGS, beamsplitter: KBr

Measurements in the near-IR range (FTNIR) 1600-5600 cm⁻¹

The measurements were carried out for those fibres which had not been mechanically processed. The fibres were placed in a measuring tube in such a manner as to ensure the whole sample's homogeneous exposition to radiation.

The following measuring parameters were used: range: 1600-5600 cm⁻¹, resolution: 8 cm⁻¹, number of scans: 512,

source: halogen lamp, detector: InGaAs, beamsplitter: CaF₂.

Calculated deacetylation degree

For all the samples examined, as well as for the standard commercial chitosan (prod. Vanson) with a definite deacetylation degree (the value calculated from the data of potentiometric titration), FTIR spectra (from the range of near infrared) were obtained (FTNIR) [12].

A set of spectra (as an example) is shown in Figure 4. As a result of the mathematical treatment of the spectra (using "GRAMS" software), spectral coefficients for particular spectra were calculated from the following formula:

$$F = \sum S_{-N-H} / S_w$$

where:

S_{-N-H} – the total area determined by the distribution of the -N-H, band for the following positions; 9559 cm⁻¹, 8110 cm⁻¹, 6547cm⁻¹ and 6483 cm⁻¹;

S_w – the total area spectrum.

Based on the calculated value of a spectral coefficient for standard commercial chitosan (Vanson), the deacetylation degree values for the samples examined were calculated from the following formula:

$$DD [\%] = F \times 90\% / 0.20573$$

where:

F – the spectral coefficient for the adequate spectrum; 0,20573 – the coefficient calculated for the commercial chitosan (Vanson).

Table 3. The results of DD obtained by the ¹³C NMR method.

Sample	Absorption			Deacetylation degree (DD), %
	-CH ₃	-C ₁	-CH ₃ /C ₁	
N C7	19.60	24.65	0.795	20.5
N C9	10.46	24.86	0.421	57.9
N C13	7.54	24.62	0.306	69.4

Some examples of DD values for the chitosan fibres (the N C and NH – N series; deacetylation obtained from the regenerated chitin deacetylated at 70 °C and 140 °C) are given in Tables 1 and 2.

Additionally, the deacetylation degree was calculated on the basis of the results from ¹³C NMR spectroscopy. Several spectra for the N C series (deacetylation at 70 °C) were prepared. Using the intensity proportion of CH₃ to the C₁ group (C₁ being the first atom of the glycoside ring), the DD value was calculated from the following equation [14]:

$$DD = 1 - A_{CH_3}/A_{C_1} \times 100\%$$

where:

A_{CH₃} – the absorption intensity of the CH₃ group,

A_{C₁} – the absorption intensity of the C₁ group.

The results are presented in Table 3.

X-ray diffraction measurements

The measurements of wide-angle X-ray diffraction (WAXS) for all the samples examined were carried out in the reflection mode at a room temperature using a Seifert URD-6 diffractometer with a scintillation counter connected to a computer. Ni-filtered Cu K α radiation was applied. The accelerating voltage value was 40 kV, and the plate current intensity 30 mA. The diffraction scans were collected between 2 θ values from 2° to 60° with a step of 0.1°.

Microscopy

The examination of the surface topography as well as of the selected cross-sections for the initial DBCH fibres and the fibres after successive stages of the alkaline treatment were carried out with a JSM 5500 LV scanning electron microscope made by JEOL, equipped with a wolfram cathode. The observations were performed at a voltage of 10 kV. The photographs of the sample were magnified 1000 – 10,000 times.

NMR spectroscopy measurements

The ¹³C NMR spectra were obtained with a DSX 300 MHz Bruker spectrometer. The samples were placed in a 4-mm rotor made of zirconium oxide (ZrO₂), and the CP-MAS (Cross-Polarisation Magic Angle Spinning) modified experiment was applied; this procedure enables the transfer of magnetisation from highly sensitive ¹H spins to the spins ¹³C diluted with isotopes. The RAMP

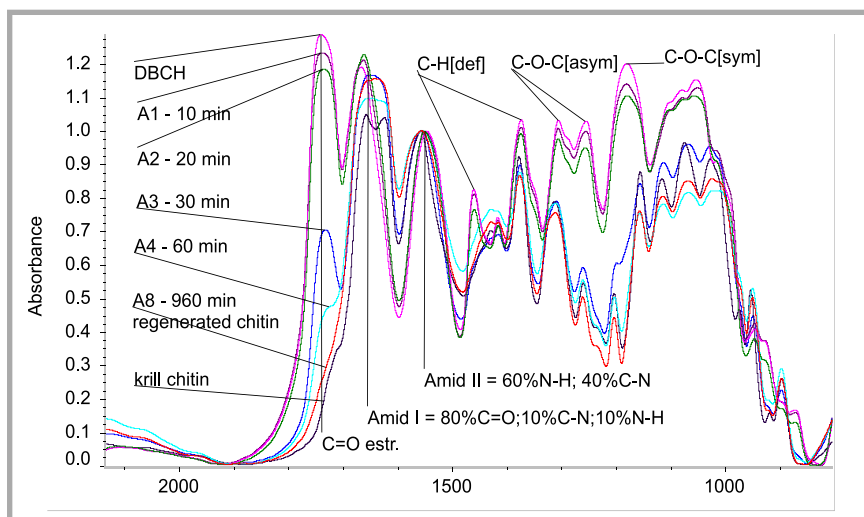


Figure 5. FTIR spectra ranging from 2150 to 850 cm⁻¹ for DBCH fibres, initial chitin and products of alkaline hydrolysis of DBCH at 20°C (A1 – 10 min, A2 – 20 min, A3 – 30 min, A4 – 60 min, A5 – 120 min, A6 – 240 min, A7 – 480 min, A8 – 960 min).

sequence modification was applied, which made the magnetisation transfer independent of the rotation speed.

The following measuring parameters were used: the number of accumulated points – 2048, the number of accumulations (scans) – 1024, replication period, i.e. the break between accumulations – 6 s, mixing time – the transfer time for polarisation – 2.5 ms, transfer period – 6 dB.

Results and discussion

The alkaline treatment of DBCH fibres with 5% aqueous solution of KOH causes their gradual transformation into regenerated chitin fibres. In this study, the above statement was confirmed for the fibres under investigation with the help of FTIR spectroscopy and WAXS diffraction.

Medium-IR 2150 - 850cm⁻¹ (Figure 5) spectra were compared for the fibres pressed in NaCl, which were obtained during the de-esterification of DBCH fibres in 5% KOH at 20 °C and 90 °C. The spectrum of DBCH fibres contains an intense vibration band of strong absorption at 1740 cm⁻¹ and another at around 1450 cm⁻¹; such bands are characteristic of the esters of fatty acids. Furthermore, bands of stronger absorption appear at around 2900 cm⁻¹, 790 cm⁻¹ and 740 cm⁻¹, corresponding to the aliphatic groups –CH₂– and –CH₃, whose content in DBCH is much higher than in chitin.

The DBCH fibres spectrum contains the band from the C=O oscillator of ester

group. This band is the chief parameter for determining the degree of chitin esterification. A successive decrease in the number of butyryl groups is also observed (Figure 5).

In the spectra of fibres, the maximum of the band drifts towards lower wave numbers, i.e. from 1741 cm⁻¹ for DBCH, 1738 cm⁻¹ for A1, 1736 cm⁻¹ for A2 and 1733 cm⁻¹ for A3. This drift reveals [increasing action on the C=O bond energy]. The amide I band is sensitive to the chemical structure of the macromolecule. The separation of macromolecules by means of aliphatic chains of butyric acid causes the breakage of the hydrogen bonds formed by the C=O oscillator of the amide group. The C=O oscillator absorbs IR radiation for DBCH at about 1668 cm⁻¹. During the alkaline treatment of DBCH, the loss of butyric substituents takes place, which causes a lowering of the distance between chains of macromolecules. Due to this phenomenon, the C=O oscillator approaches the area of hydrogen bonds. The maximum of absorption of the Amide I band drifts towards lower energy, e.g. for the sample A2 (in which a still significant number of butyric substituents exists), to 1662 cm⁻¹. Next, a successive formation of hydrogen bonds takes place between the C=O and O-H oscillators of neighbouring macromolecules. As a result of this process, the defects of crystalline network affecting the supermolecular structure are fixed in the material of the fibre.

The duration of the process before total hydrolysis is reached mainly depends on

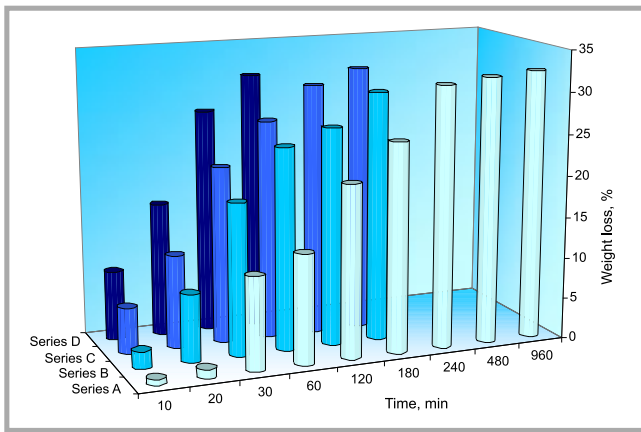


Figure 6. Weight loss of the fibres after the deacetylation was determined.

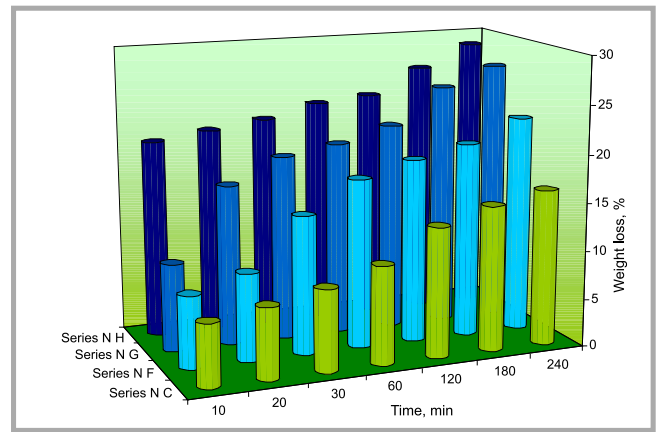


Figure 7. Weight loss of the fibres after the N-deacetylation treatment was determined.

the fibre diameters and the temperature (as some tens of minutes at 90 °C up to a few hours at 20 °C) In the first stage of the hydrolysis process, only the surface layer of a fibre is affected. After several seconds of hydrolysis it is already possible to obtain DBCH fibres covered with a thin layer of the regenerated chitin. Leaving the material in the solution for a longer time brings about a deeper KOH penetration and successive hydrolysis throughout the whole volume of a fibre. The regeneration into chitin proceeds gradually depending on the temperature of the bath. It was found out that the de-esterification of DBCH fibres in all the cases examined (series A, B, C and D) causes a mass loss of fibres in the amounts of about 30 wt.%. (Figure 6).

The alkaline treatment of DBCH fibres to obtain fibres from the regenerated chitin and next chitosan fibres (with different *DD* values) causes a gradual mass loss of the fibres. At the first stage of the process, i.e. deacetylation, a mass loss of about wt. 30% is observed. This is caused by the drop of the number of butyric groups. The higher the temperature, the bigger the mass loss is. The experimental values of the mass loss are well correlated with the stoichiometric calculations.

The examination of WAXS diffraction showed that thanks to the applied method of DBCH hydrolysis (using aqueous KOH), it was possible to rebuild the supermolecular structure of the fibres in such a way that it became very similar to the structure of native krill chitin. The comparison of the relevant diffractograms is shown in Figure 8.

The calculated values of the degree of crystallinity for all four series (77% in A,

74% in B, 76% in C, 76% in D) are very close to the value for native krill chitin, which is equal to 78%).

In the next stage of the experiments, both the initial DBCH micropore fibres as well as the fibres obtained from the regenerated chitin were treated with saturated KOH solutions at a higher temperature in order to deacetylate the polymer as it was described before. As a result of deacetylation, a 15 - 28% mass loss of the examined fibres was observed, which rose as the temperature of the treatment was increased. The weight loss of the fibres and their linear density values after the alkaline treatment were determined (Figure 7).

The resulting chitosan fibres show various degrees of deacetylation which depend on the concentration of KOH solution, time and the temperature of the treatment. The experimental values of the mass loss are well correlated with the stoichiometric calculations.

The observations of the surface topography and the cross-section of the obtained fibres were carried out using scanning electron microscopy (SEM). The analysis of the SEM microphotographs allows estimation of the effect of a spinning technique on the morphology of the micropore fibres during the chemical treatment that leads to obtaining regenerated chitin and chitosan.

The SEM photos of DBCH fibres show that at first the outer layer of the fibres solidifies and a fibre skin is formed. Then a slower solvent evaporation from the fibre interior takes place, and the core formation is observed. As a result of the further solvent evaporation, the core becomes concave and the cross-section of the fibre resembles the shape of a bean (Figure 1).

During the dry-wet spinning method, the significant effect of the aqueous medium on the stream of a spinning solution being solidified is especially interesting. It

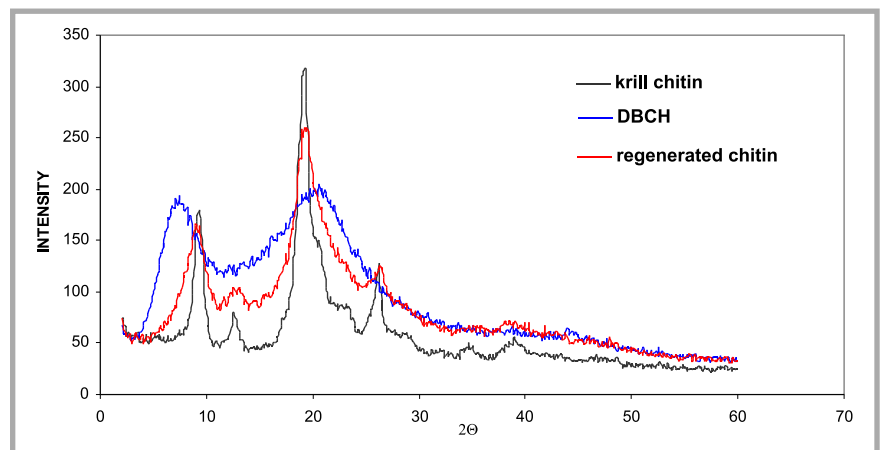


Figure 8. Comparison of WAXS diffraction patterns for krill chitin, DBCH and regenerated chitin obtained using KOH.

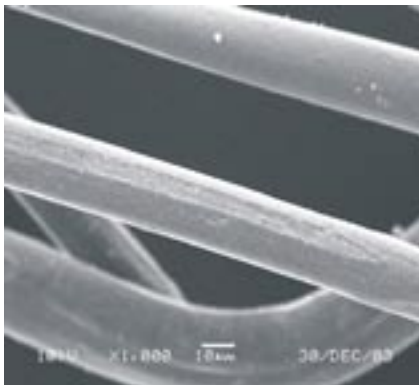


Figure 9. SEM micrograph of surface of regenerated chitin fibres, magnification 1000 \times .

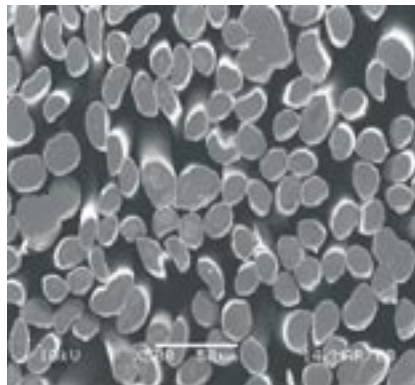


Figure 10. Cross-section of regenerated chitin fibres, SEM micrograph, magnification 500 \times .



Figure 11. SEM micrograph of the surface chitosan fibres at temperature 70 °C (sample N C13), magnification 1000 \times .



Figure 12. SEM micrograph of the surface chitosan fibres at temperature 70 °C (sample N C13), magnification 3000 \times .

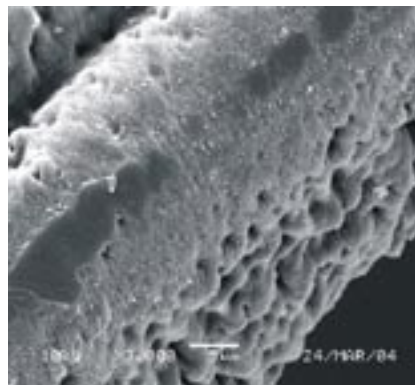


Figure 13. SEM micrograph of the surface chitosan fibres at temperature 120 °C (sample N G7), magnification 3000 \times .

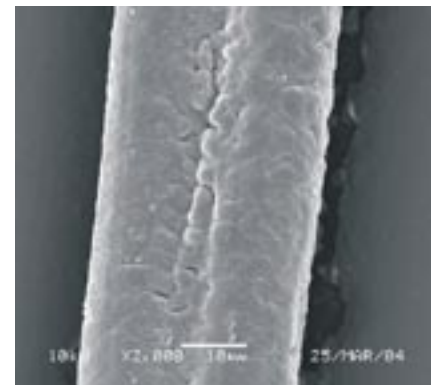


Figure 14. SEM micrograph of the surface chitosan fibres at temperature 140 °C (sample N H7), magnification 2000 \times .

can be supposed that DBCH fibres partly solidified in air with a still elastic skin swell in a water bath in which water diffuses into the fibre interior, and DBCH is quickly precipitated. At this stage of solidification, a 'sponge-like' structure is formed in the fibre core, which can be seen in the cross-sections of the fibres obtained this way (Figure 2). Such a loose structure formed in a fibre core is characterised by the presence of empty spaces (voids).

DBCH fibres treated with a 5% aq. KOH solution at room temperature reveal a change in the cross-section shape after several tens of minutes. The elongated shape of the cross-section (of the fibres shown in Figure 9) changes and becomes circular (Figure 10). It can be assumed that the swelling of the sponge core is accompanied by the phenomena of equalisation and stress relaxation.

Longitudinal views of the untreated DBCH fibres (Figure 1) show a uniform and smooth surface. After deacetylation at room temperature, characteristic foldings resulting from the core concavity

are observed on the surface of the fibres. These are the effect of N-deacetylation of the fibres made of regenerated chitin (Figures 11 - 14). Spheric blisters of 5 μ m diameter appear on the surface of the fibres. At the final stage of N-deacetylation (after 4 hours), the blisters become a basic element of the fibre topography.

The duration of chitin regeneration from DBCH at 20 °C, 50 °C, 70 °C and 90 °C (series A, B, C and D respectively) by means of 5% KOH solutions depends on the temperature of the alkaline treatment. The process carried out at room temperature is almost completed after 120 min, while the same process at 90 °C takes only 10 min.

When chitin is deacetylated to chitosan at 70 °C (series N C), the deacetylation degree grows gradually with the duration of the process; for example, after 120 min of deacetylation it equals 55%, while after 240 min it reaches the value of 70%. When chitin fibres are treated by saturated KOH at 140 °C (series N H) the process of deacetylation proceeds rapidly. After 10 min a DD value of 78%

is obtained. Further treatment causes a slow increase in the DD value up to 93% after 240 min. The results of DD determinations are presented in Tables 1 and 2. The course of N-deacetylation of chitin at the applied conditions of the temperature, KOH concentrations and duration of the treatment is additionally shown in Figures 15 and 16 (see page 18).

As seen from Table 3, the results of DD obtained by means of ^{13}C NMR method remain in good correlation with the results obtained using the FTNIR method presented in Tables 1 and 2. Thus, the FTNIR measurements can serve as a tool to obtain reliable results for deacetylation degrees.

The FTNIR method of determining the DD values for chitin or chitosan fibres is easy and quick. Besides, it requires no special preparation of the samples.

Additionally, we stated that the FT NIR method of determining the deacetylation degree values for chitosan fibres is the most sensitive method available.

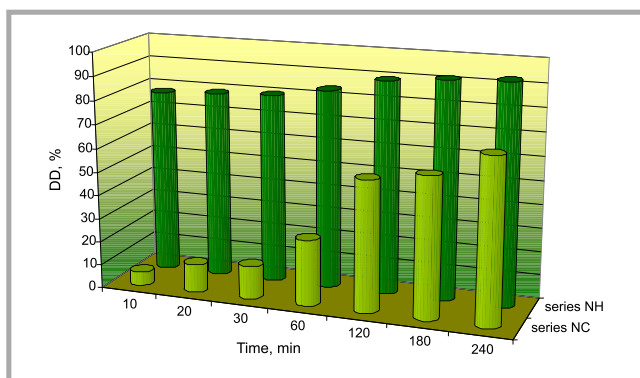


Figure 15. Chitosan fibres' DD values determined from spectral coefficients for samples from series NC and NH (N-deacetylation of chitin fibres at 70 °C and 140 °C in saturated KOH solution).

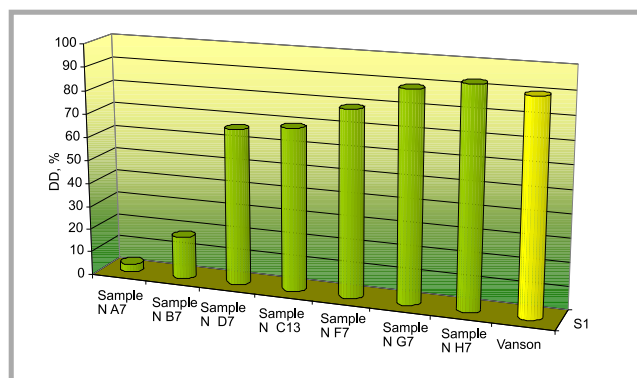


Figure 16. Chitosan fibres' DD values determined from spectral coefficients related to Vanson chitosan. Samples treated for 240 min at different temperatures using various KOH concentration.

Conclusions

- As a result of the alkaline treatment of DBCH fibres by means of diluted KOH solutions, microporous fibres with regenerated chitin were obtained. They were characterised by a supermolecular structure very close to that of the initial krill chitin.
- Further hydrolysis with saturated KOH solutions at higher temperatures leads to chitin deacetylation and the obtention of microporous chitosan fibres with differentiated degrees of deacetylation depending on the temperature and duration of the deacetylation process.
- A new method of calculating the deacetylation degree based on the analysis of FTNIR spectra and the adequate software was elaborated.
- It can be assumed that the obtained fibres possess very advantageous practical properties due to their microporous structure.

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