

Crystalline Structure and Mechanical Properties of Wet-Spun Dibutyrylchitin Fibers and Products of Their Alkaline Treatment

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ABSTRACT: Dibutyrylchitin was obtained during krill chitin esterification with butyric anhydride in the presence of perchloric acid. The wet spinning of a 14.5% solution in dimethylformamide created dibutyrylchitin filaments, which were treated with an alkali solution for chitin regeneration. Fiber samples with different degrees of chitin restoration were obtained, and their fine structure and mechanical properties were investigated. The restoration of the chitin structure resulted in a gradual increase in the degree

of crystallinity, the density of the structured area, the tensile strength, and the average elongation at rupture and in a decrease in the diameter of the fibers. The crystallinity degree of fully regenerated chitin, the final product of alkaline hydrolysis, reached a value close to that of native chitin. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1861–1868, 2004

Key words: FT-IR; morphology; structure; WAXS

INTRODUCTION

Chitin, a homopolymer of 2-acetamido-deoxy-D-glucopyranose, is the second most abundant natural polymer next to cellulose, being present in marine invertebrates, insects, and fungi and yeast.¹ Chitin is an effective material for wound dressings and absorbable sutures because of its biodegradability, biocompatibility, and promotion of wound-healing acceleration.^{2–6} Unfortunately, the poor solubility of chitin strongly restricts any practical application of this valuable polymer. The chemical modification of chitin often leads to improved solubility in chitin derivatives, and one of them readily soluble in common organic solvents is dibutyrylchitin (DBCH). The preparation of DBCH and several of its chemical and physical properties have been described in our previous publications.^{7–13} The solubility of DBCH in organic solvents allows fibers,^{9,10} fleece, nonwovens,¹⁴ and knitting materials to be made in forms useful for industrial applications. Moreover, an alkaline treatment applied to the final materials made from DBCH lead to chitin materials without the destruction of their macrostructure.^{12,13} Biological investigations of DBCH and regen-

erated chitin fibers carried out according to European standards have shown that both kinds of fibers fulfill the basic requirements of medical devices according to ISO 10993 (“Biological Evaluation of Medical Devices”).^{15–17} The pathomorphological findings indicate very good biocompatibility for DBCH and regenerated chitin fibers and an ability to accelerate the wound-healing process. Thus, the formation of useful fabrics from soluble DBCH and the subsequent preparation from them of different kinds of regenerated chitin materials seem to be constitute a good method of production of a wide assortment of valuable materials for novel bioactive and biodegradable wound dressings and sutures.

The fine structure and mechanical properties of DBCH filaments obtained with a dry method of spinning⁹ and chitin filaments prepared from those DBCH fibers are described in refs. 18 and 19. Dry-spun DBCH fibers and chitin fibers made from them have very irregular shapes, and a contour line of their cross sections is caused by the method of DBCH fiber spinning. In this work, the results of investigations of the crystalline structure and mechanical properties of wet-spun DBCH fibers are presented. DBCH fibers were treated with an alkaline solution, and regenerated chitin fibers and fibers with different degrees of esterification were obtained. The fine structures and properties of the products of DBCH hydrolysis were studied as well, and the results of that investigation are also presented.

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EXPERIMENTAL

Materials

Krill chitin, a product of the Sea Fisheries Institute (Gdynia, Poland), was purified of residual calcium carbonate and other mineral residues. The purification was carried with a chitin treatment with 2M HCl. The chitin used for further experiments had a degree of acetylation of 0.98 and an intrinsic viscosity value (IVV) of 17.0 dL/g, as determined in a solution of dimethylacetamide containing 5% LiCl (5% LiCl/DMAc) at 25°C.

Reagents

Butyric anhydride (98%; Aldrich, USA), perchloric acid (70–72%; Merck, Germany), diethyl ether, acetone, dimethylacetamide (DMAc), LiCl, dimethylformamide (DMF), and NaOH of a normal laboratory grade were used without further purification.

DBCH synthesis

DBCH was obtained from the reaction of chitin with butyric anhydride according to the procedure described in ref. 9. The reagents were used in the following concentrations: 1M chitin, 20M butyric anhydride, and 0.6M HClO₄. The reaction was carried out at 25°C for 4 h. The final product, acetone-soluble DBCH, was collected in a yield of 93%. IVV of the polymer was determined in 5% LiCl/DMAc solutions at 25°C.

Wet-spinning procedure of DBCH fibers

DBCH fibers were obtained with a laboratory-scale spinning apparatus usually used for the spinning of rayon fibers. DMF was used as a solvent of DBCH. The preparation of DBCH dope for the spinning procedure and the rheological characteristics of the semiconcentrated solutions were described in ref. 10. Fibers were spun from the dope containing 100 g of DBCH in 700 mL of DMF with a spinneret with 300 holes (hole diameter = 80 μm) into the water coagulation bath. The formed fibers were washed with water in the second bath, immersed three times in the next bath with hot water, and washed with cold water again. Then, the fibers were wound up on the rollers at a rate of 40 m/min and were air-dried. Silklike fibers with smooth surfaces and a filament diameter of approximately 20 μm were obtained.

Alkaline treatment of the DBCH fibers

The DBCH hydrolysis and kinetics of the reaction carried out under heterogeneous conditions are described in ref. 12. Dry samples of wet-spun DBCH fibers were weighed and immersed in an excess

amount of a 5% (1.25M) NaOH water solution and were hydrolyzed at 50°C for definite periods. Then, the samples were taken out, washed several times with water to remove any traces of alkali, and dried. Dry products of the alkaline treatment were weighed and then treated with acetone to extract all nonreacted DBCH. The fibers that remained after the acetone treatment were dried and weighed again. The IVVs of the obtained samples of the fibers insoluble in acetone were determined in 5% LiCl/DMAc solutions at 25°C.

Testing procedures

Estimation of IVVs

IVVs of initial chitin and the products of DBCH alkaline hydrolysis (samples of partially acylated chitin) were determined at 25°C in 5% LiCl/DMAc solutions. The initial concentrations of the polymers were approximately 0.1 g/dL. IVV of DBCH was determined in 5% LiCl/DMAc solutions with an initial polymer concentration of approximately 0.5 g/dL.

Infrared (IR) investigations

IR spectra of chitin, partially acylated chitin samples, and DBCH were recorded with a PerkinElmer 2000 FTIR instrument (USA). All the samples were applied in the form of films. Chitin and partially acylated chitin films were prepared from 5% LiCl/DMAc solutions; DBCH films were cast from acetone solutions.

Investigation of the mechanical properties of the fibers

Tensile strength tests of the fibers were carried out on an Instron model 3110 tensile testing machine (Great Britain). The 10-mm-long fibers were tensed at a speed of 100 mm/min.

Microphotography of the fibers

Microphotographs were made with a JSM-15 scanning microscope (JEOL, Japan) equipped with a traditional tungsten source of electrons. Observations were made at a voltage of 15 kV. Monofilaments of the fibers were taken to obtain the cross section. They were stuck with a conductive adhesive to prepare supporting stands and were placed in a JEOL thin-film sprinkler and sprinkled with carbon and gold in a high vacuum of 3×10^{-5} Torr. The photographs of the samples were magnified 1000 times.

Wide-angle X-ray scattering (WAXS)

A WAXS investigation was performed on an HZG-4 diffractometer (Germany) with Cu K α radiation. The

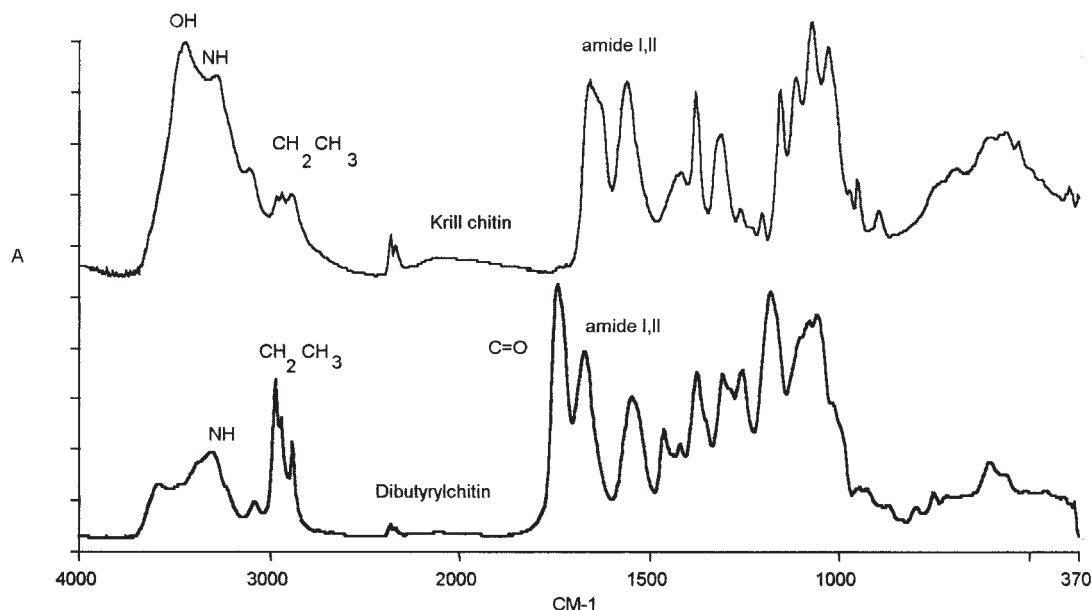


Figure 1 IR spectra of krill chitin and DBCH obtained from krill chitin.

accelerating voltage was 30 kV, and the plate current intensity was 20 mA. The beam monochromatization was achieved with Roos double filters and a pulse analyzer. A scintillation counter served as a detector. X-ray scattering patterns were registered for diffraction angles ranging from 5 to 50° with a step-by-step method with steps of 0.1° and a pulse summation period of 10 s.

RESULTS AND DISCUSSION

Characterization of DBCH

The synthesis of DBCH, carried out under the aforementioned conditions, yielded a product with an IVV of 1.80 dL/g. According to the elemental analysis, the product contained 55.84% C, 7.51% H, and 4.10% N (the calculated values were 55.98% C, 7.29% H, and 4.08% N), and this suggested that the degree of chitin esterification was very close to 2.

To confirm the chemical structure of the obtained product, we conducted studies with IR spectroscopy.

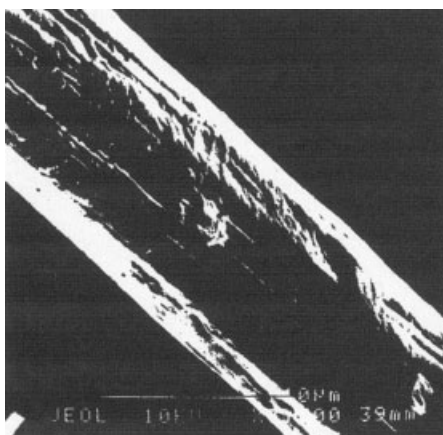
IR spectra of chitin and DBCH are shown in Figure 1. In the IR spectrum of DBCH, there is no band of absorption at approximately 3500 cm^{-1} due to hydroxyl groups, but there are new bands of strong absorption at 1740 cm^{-1} and around 1450 cm^{-1} , which are characteristic of the esters of fatty acids. Furthermore, bands of stronger absorption appear around 2900, 790, and 740 cm^{-1} , corresponding to aliphatic groups ($-\text{CH}_2-$ and $-\text{CH}_3$), the content of which was much higher in DBCH than in chitin.

Characterization of the DBCH fibers and the products of their alkaline treatment

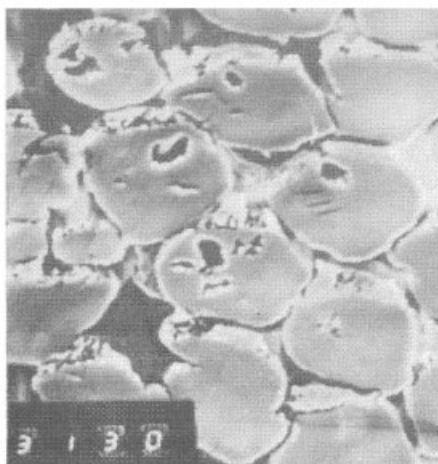
In contrast to DBCH fibers spun with a dry method of spinning,⁹ the wet method of spinning performed in a DMF solution resulted in fibers with regular, near-circular cross sections with a diameter of approximately 20 μm . Scanning electron microscopy (SEM) photographs of the surface of wet-spun DBCH fibers and cross sections of the fibers are shown in Figure 2.

The hydrolysis of DBCH fibers was carried out under heterogeneous conditions at 50°C in an excess of 1.25M water solutions of NaOH. The reaction, which was started on the surfaces of the fibers, was accompanied by the weight loss of the samples due to the loss of the bulky butyric groups. Any traces of nonreacted DBCH were removed from the samples with acetone, and the obtained samples of the fiber, insoluble in acetone, were polymers with different degrees of esterification. The degree of esterification decreased with an increase in the time of alkaline treatment, and the final product of hydrolysis was pure regenerated chitin.

IR spectra of the initial DBCH fibers (sample F0), the products of the alkaline hydrolysis of DBCH fibers having different degrees of esterification (samples F15, F25, and F40), and the IR spectrum of fully regenerated chitin (sample F150) are shown in Figure 3. Depending on the time of the alkaline treatment, absorptivity decreased because of the carbonyl band ($\text{C}=\text{O}$) in the ester group at approximately 1740 cm^{-1} and increased because of the hydroxyl groups at approximately 3500 cm^{-1} . In addition, a systematic change can be seen in the spectral image of the amide bands.



A



B

Figure 2 Microphotographs of wet-spun DBCH fibers: (A) the surface and (B) the cross section.

Both amide bands changed their position. The amide I band moved toward lower wave numbers with the conversion of DBCH into chitin; the amide II band moved in the opposite direction, that is, toward higher wave numbers. The amide I band, appearing as a singlet in the spectrum of DBCH at 1676 cm^{-1} , was split into two bands with maxima at 1655 and 1630 cm^{-1} in the spectra of the products of alkaline hydrolysis. The additional band at 1630 cm^{-1} may be attributed to the carbonyl vibration in the amide group engaged in the formation of intermolecular hydrogen bonds. This split of the amide I band is characteristic of IR spectra of chitin and can be observed in Figure 1. The emergence of this band reflected the restitution of intermolecular hydrogen bonds at the time of the DBCH hydrolysis. It confirmed the gradual conversion of DBCH into chitin. The IR spectrum of the regenerated chitin, the final product of the DBCH

hydrolysis, was the same as the IR spectrum of the initial chitin. On the basis of the spectra, the absorptivity ratio of the carbonyl band to that of the amide II band ($A_{\text{C=O,ester}}/A_{\text{amideII}}$) was calculated. The values of this ratio, related to the hydrolysis duration, are presented in Table I. From this ratio, the concentration of butyric groups in the product of the DBCH hydrolysis was determined. The calculated values are also given in Table I, which contains all the results for the alkaline treatment of the DBCH fibers.

After 20 min, more than 97% of the initial DBCH had undergone hydrolysis, and afterward, products with a high degree of chitin restoration were obtained. The products of the hydrolysis were characterized by growing IVVs determined in a 5% LiCl/DMAc solution, a solvent thermodynamically better for chitin than for DBCH (the IVV of the initial chitin was 17.0 dL/g , and the IVV of DBCH prepared from the chitin was 1.80 dL/g). The final product of the DBCH hydrolysis, fully regenerated chitin (sample F150), had a lower IVV than the native krill chitin because of the degradation process, which took place during DBCH synthesis carried out under a strong acid condition.⁸

Crystalline structures and crystallite sizes of DBCH and the products of DBCH hydrolysis

WAXS allowed us to determine the following characteristics of the polymer: the degree of crystallinity, the dimensions of the crystallites, and the interplanar distances for the crystallites (Table II). The diffraction patterns were analyzed with the Hindeleh–Johnson method.²⁰ The principle behind the method is the construction of a theoretical curve from a summation of the peak values representing diffraction in the crystalline and amorphous zones and a background curve. The diffraction patterns were processed on a computer. The program²¹ used Rosenbrock and Storey's method²² in minimization. The crystalline zone sizes were estimated from the half-width of the diffraction peaks. The method was based on Scherrer's formula.²³

For our investigation, we chose the following samples:

- Initial krill chitin in the form of a powder.
- DBCH obtained during the esterification of krill chitin and precipitated with water in the form of flakes.
- DBCH fibers obtained during the wet spinning of DBCH (sample F0).
- DBCH fibers additionally washed with hot water and dried (sample F0-2).
- Products of the alkaline hydrolysis of DBCH fibers with different degrees of acylation (samples F20, F30, and F90).
- Fully regenerated chitin fibers obtained from DBCH fibers (sample F150).

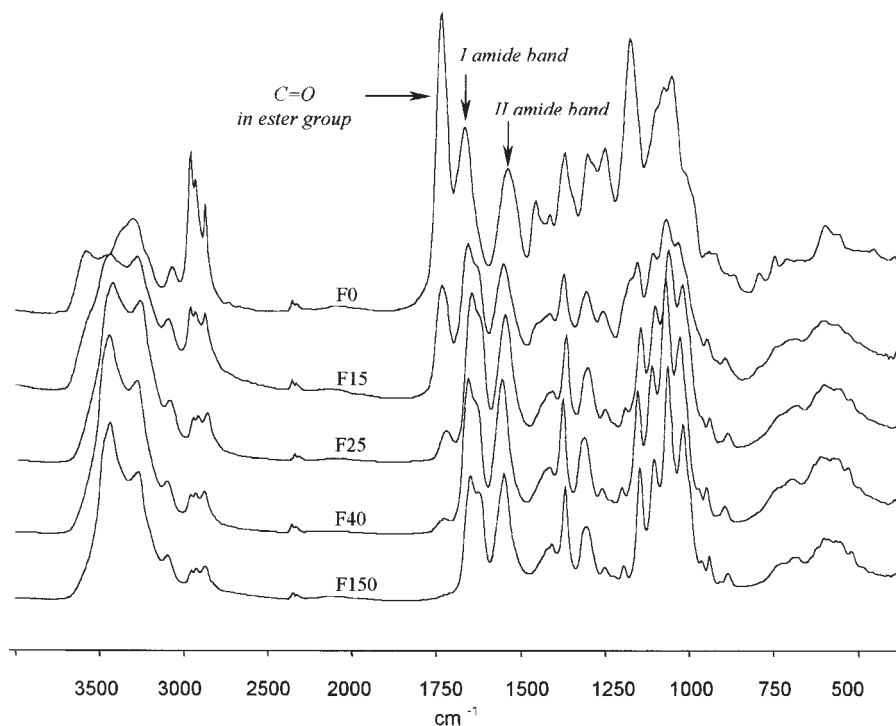


Figure 3 IR spectra of DBCH fibers (F0) and the products of the alkaline hydrolysis of DBCH fibers carried out under heterogeneous conditions (F15, F25, F40, and F150).

The WAXS diffraction patterns for the initial krill chitin, the DBCH fibers, and the products of the alkaline hydrolysis of the DBCH fibers are shown in Figure 4, and the peak deconvolution of the WAXS profile of a krill chitin sample is shown in Figure 5.

The WAXS examination showed that the product of chitin esterification, DBCH, had a crystallinity value significantly reduced in comparing with the crystallinity value of native chitin. DBCH fibers (sample F0), spun from a 12.5% DMF solution of DBCH and elongated

three times in hot water during the spinning process, were oriented along the axis and were characterized by a higher degree of crystallinity than that of the initial polymer (DBCH) precipitated with water in the form of flakes from an acetone solution. The same fibers, rinsed in hot water (sample F0-2), showed a slight decrease in the degree of crystallinity, an increase in the crystallite dimensions in the directions $D_{(010)}$ and $D_{(100)}$, and a slight increase in the interplanar spacing $d_{(010)}$. The recrystallization of the fiber material was caused by the

TABLE I
Characteristics of DBCH Fibers and Products of Their Alkaline Treatment Carried Out in a 1.25M Water Solution of NaOH at 50°C

Sample	Time of alkaline treatment (min)	Weight loss of the sample after alkaline treatment (%)	Content of nonreacted DBCH extracted with acetone (%)	IVV of the hydrolysis product insoluble in acetone, determined in a DMAc/5% LiCl solution (dL/g)	IR analysis of the alkaline hydrolysis products insoluble in acetone	
					$A_{C=O,ester}/A_{amideII}$	Degree of butyrylation (%)
F0	0 ^a	0 ^a	100.0 ^a	1.80 ^a	2.175 ^a	100 ^a
F10	10	15.73	60.1	3.30	1.015	46.67
F15	15	19.18	54.5	3.63	0.865	39.77
F20	20	33.09	2.7	4.52	0.112	6.01
F25	25	35.86	2.1	4.66	0.108	5.48
F30	30	36.90	2.0	4.70	0.101	4.65
F40	40	38.83	0.9	4.83	0.084	3.83
F90	90	39.01	0.3	5.30	0.078	2.57
F150	150	40.00	0	5.60	0	0

^a Data describing the initial DBCH fibers, which were not exposed to alkaline treatment.

TABLE II
Results of the WAXS Examination for Chitin, DBCH, and Products of DBCH Alkaline Hydrolysis

Sample	Treatment time (min)	Degree of crystallinity (%)	Crystallite dimensions				Interplanar distance			
			D_{010} (Å)	D_{220} (Å)	D_{100} (Å)	D_{110} (Å)	d_{010} (Å)	d_{220} (Å)	d_{100} (Å)	d_{110} (Å)
Initial chitin	0	65.3	100.1	99.8	66.1	83.3	9.58	7.01	4.63	3.39
DBCH	0	47.2	20.9	—	13.2	—	11.40	—	4.27	—
F0	0	54.7	29.8	—	11.8	—	12.36	—	4.31	—
F0-2	0	53.6	41.7	—	12.2	—	12.40	—	4.20	—
F20	20	59.1	27.7	68.3	44.6	33.3	10.53	6.97	4.64	3.29
F30	30	59.3	34.4	68.3	42.9	33.3	10.06	6.82	4.64	3.29
F90	90	62.8	42.7	68.3	42.9	31.0	9.87	6.87	4.60	3.25
F150	150	64.1	51.7	68.3	42.9	31.0	9.76	6.72	4.60	3.25

relaxation of tension in the DBCH chains as a result of intermolecular bond dissociation after slight swelling in the aqueous environment.

An increase in the time of the alkaline treatment of the DBCH fibers resulted in a decrease in the degree of esterification of the polymers and an increase in the concentration of hydroxyl groups. That caused the re-creation of hydrogen bonds and an increase in the degree of crystallinity of the hydrolysis products (samples F20, F30, and F90).

The final hydrolysis product was fully regenerated chitin fiber (sample F150) with an esterification degree of 0. The crystallinity degree of sample F150 was very close to the value determined for the native krill chitin sample used for DBCH synthesis.

DBCH, obtained during the esterification process, was characterized by crystallites smaller than those of the output krill chitin. Those sizes in the directions

$D_{(010)}$ and $D_{(100)}$ increased during the transformation of DBCH into regenerated chitin, but they did not match the sizes achieved for native chitin. This was due to the reduced value of the molecular weight of the regenerated chitin in comparison with the molecular weight of the initial chitin. A reduction of the polymerization degree of chitin occurred during the synthesis of DBCH during chitin acylation, which was carried out under a strong acid condition.

Tensile strength of the fibers

The tensile strength of the fibers was determined as the average proper tensile strength of a bunch of fibers, and the average elongation was determined as the relative elongation of a bunch of fibers. The fiber weight was determined on a torsion balance. Table III presents the results.

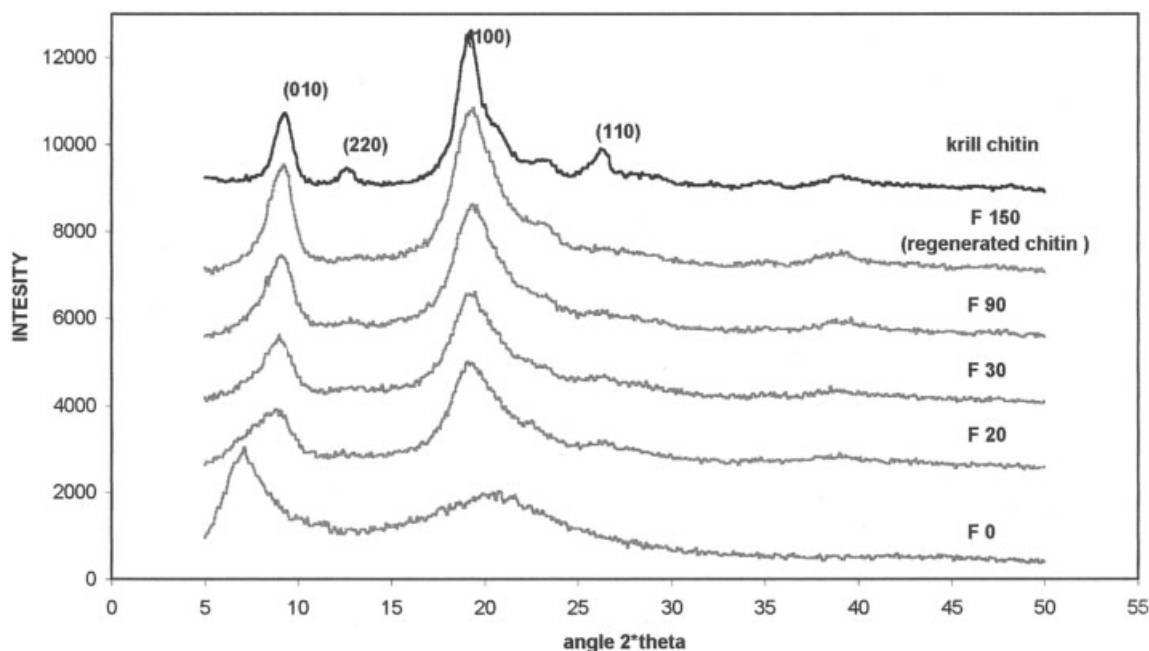


Figure 4 WAXS diffraction patterns for krill chitin, DBCH fibers (F0), and products of the alkaline hydrolysis of DBCH fibers (F20, F30, F90, and F150).

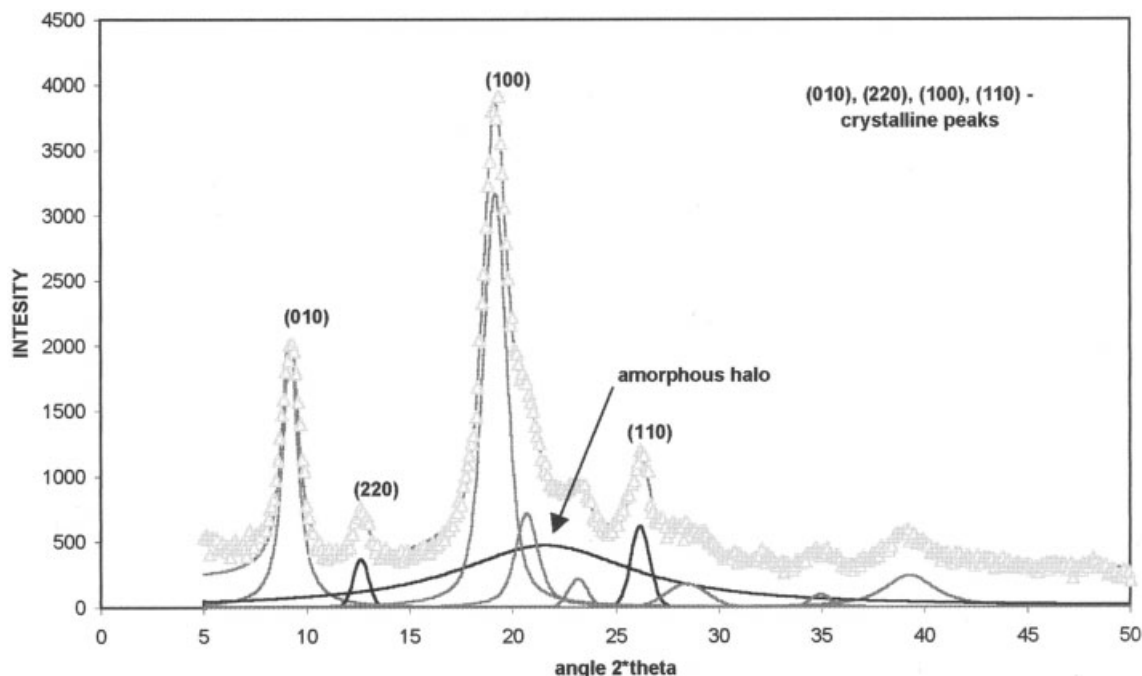


Figure 5 Peak deconvolution of the WAXS profile for krill chitin.

The results showed that an increase in the crystallinity degree was accompanied by an increase in the tensile strength and degree of elongation of the fibers. Sample F150, fully regenerated chitin, was characterized by the highest values of the tensile strength and elongation. The reasons for the increase in the mechanical properties of the fiber were the restoration of hydrogen bonds in the polymer chain and the higher degree of its crystallinity.

For sample F0-2, DBCH fibers were wet-spun and washed in hot water; a lower tensile strength was observed despite the size enlargement of the crystallites. A possible reason may be the loosening of the structure of the amorphous zones due to hot water action.

During the hydrolysis, the diameter of the fibers decreased because of the loss of bulky butyric groups, and fully regenerated chitin fiber (sample F150) had a diameter two times smaller than the diameter of the

DBCH fibers used as precursor of the chitin fibers. The SEM photographs of the surface of the final product of the alkaline hydrolysis of DBCH fibers (regenerated chitin) and cross sections of the regenerated chitin fibers are shown in Figure 6.

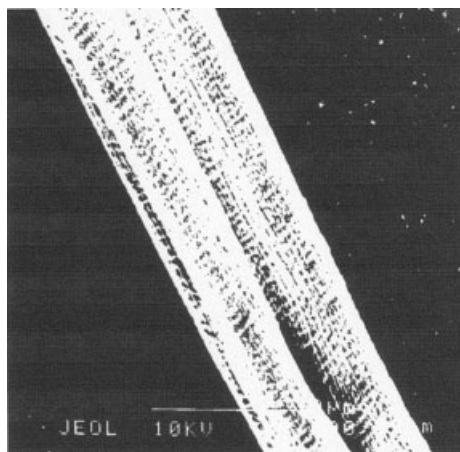
CONCLUSIONS

An investigation of the structures of krill chitin and dibutyrilchitin obtained during chitin esterification showed a significant reduction of the crystallinity degree and crystallite sizes of DBCH in comparison with native chitin because of the loss of hydrogen bonds and the reduction of the polymerization degree that occurred during the reaction carried out under a strong acid condition.

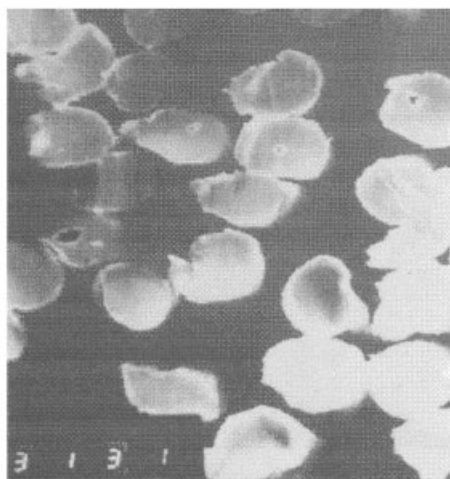
During wet spinning, DBCH fibers were obtained. The degree of crystallinity of the DBCH fibers was higher than the degree of crystallinity of the synthe-

TABLE III
Tensile Strength Results for the DBCH Fibers and Fibers Subjected to Hydrolysis

Sample	Degree of esterification (%)	Degree of crystallinity (%)	Average tensile strength of a bunch of fibers (cN/tex)	Elongation of an average bunch of fibers (%)	Monofilament diameter (μm)
F0	100	57.4	11.2	9.4	22.2
F0-2	100	53.6	9.0	11.3	21.0
F20	6.01	59.1	16.3	11.5	14.7
F30	4.65	59.3	17.1	11.5	12.2
F90	2.57	62.8	17.9	12.0	11.7
F150	0	64.1	18.1	16.8	10.3



A



B

Figure 6 Microphotographs of regenerated chitin fibers obtained from wet-spun DBCH fibers: (A) the surface and (B) the cross section.

sis product because of the orientation of the polymer chains along the axis of the fiber during the spinning.

The alkaline treatment of the DBCH fibers carried out under heterogeneous conditions in a 1.25M NaOH water solution yielded fibers with different degrees of esterification. The final product of the alkaline hydrolysis was pure regenerated chitin fiber.

The alkaline treatment applied to DBCH fibers resulted in a gradual increase in the density of the structured area and a decrease in the diameter of the

fibers. The crystallinity degrees of the fibers, the products of alkaline hydrolysis, increased because of the restoration of the chitin structure. The crystallinity degree of the fully regenerated chitin, the final product of hydrolysis, reached a value close to that of the native chitin.

The tensile strength and average elongation at rupture of the polymers increased as the acylation degree decreased because of the restoration of the chitin structure during hydrolysis. The mechanical properties of the fully regenerated chitin were highest.

References

1. Proceedings of the 1st International Conferences on Chitin/Chitosan; Muzzarelli, R. A. A.; Pariser, E. R., Eds.; MIT Press: Cambridge, MA, 1978; Program 78-7.
2. Hirano, S.; Tokura, S., Eds.; Chitin and Chitosan; Japanese Society of Chitin and Chitosan: Tottori, Japan, 1982.
3. Chitin, Chitosan and Related Enzymes; Zikakis, J. P., Ed.; Academic: New York, 1984.
4. Chitin in Nature and Technology; Muzzarelli, R. A. A.; Jeuniaux, C.; Gooday, G. W., Eds.; Plenum: New York, 1986.
5. Chitin and Chitosan: Sources, Chemistry, Biochemistry, Physical Properties and Applications; Skjak-Braek, G.; Sanford, P., Eds.; Elsevier: Amsterdam, 1989.
6. Chitin Derivatives in Life Science; Tokura, S.; Azuma, I., Eds.; Japanese Society of Chitin and Chitosan: Sapporo, Tokyo, 1992.
7. Szosland, L. In Chitin Handbook; Muzzarelli, R. A. A.; Peter, M. G., Eds.; 1997; p 53.
8. Szosland, L. *J Bioact Compat Polym* 1996, 11, 61.
9. Szosland, L.; East, G. C. *J Appl Polym Sci* 1995, 58, 2459.
10. Szosland, L.; Stepiewski, W. In *Advances in Chitin Science*; Domard, A.; Roberts, G. A. F.; Varum, K. M., Eds.; Jacques Andre: Lyon, France, 1998; Vol. 2, p 531.
11. Szosland, L. In *Advances in Chitin Science*; Domard, A.; Jeuniaux, C.; Muzzarelli, R. A. A.; Roberts, G., Eds.; Jacques Andre: Lyon, France, 1996; Vol. 1, p 297.
12. Szosland, L. *Fibres Text East Eur* 1996, 4, 76.
13. Szosland, L.; Szocik, H. In *Advances in Chitin Science*; Peter, M. G.; Domard, A.; Muzzarelli, R. A. A., Eds.; Universitat Potsdam: Potsdam, Germany, 2000; Vol. 4, p 375.
14. Szosland, L.; Krucińska, I.; Cisło, R.; Paluch, D.; Staniszevska-Kuś, J.; Solski, L.; Szymonowicz, M. *Fibres Text East Eur* 2001, 9, 54.
15. Paluch, D.; Szosland, L.; Kołodziej, J.; Staniszevska-Kuś, J.; Szymonowicz, M.; Solski, L.; Zywiecka, B. *Eng Biomater* 1999, 2, 52.
16. Paluch, D.; Pielka, S.; Szosland, L.; Kołodziej, J.; Staniszevska-Kuś, J.; Szymonowicz, M.; Solski, L. *Eng Biomater* 2000, 3, 17.
17. Paluch, D.; Szosland, L.; Staniszevska-Kuś, J.; Solski, L.; Szymonowicz, M.; Gebarowska, M. *Polym Med* 2000, 30, 3.
18. Urbanczyk, G.; Lipp-Symonowicz, B.; Szosland, L.; Jeziorny, A.; Urbaniak-Domagala, W.; Dorau, K.; Wrzosek, H.; Stajnowski, S.; Kowalska, S.; Sztajnert, E. *J Appl Polym Sci* 1997, 65, 807.
19. Urbańczyk, G. *Fibres Text East Eur* 1996, 4, 14.
20. Hindeleh, A. M.; Johnson, D. J. *J Phys D: Appl Phys* 1971, 4, 259.
21. Rabiej, S. *Eur Polym J* 1991, 27, 947.
22. Rosenbrock, H. H.; Storey, C. *Computational Techniques for Chemical Engineers*; Pergamon: Elmsford, NY, 1966.
23. Alexander, L. E. *X-Ray Diffraction Methods in Polymer Science*; Wiley: New York, 1969.