

The Dry Spinning of Dibutylchitin Fibers

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SYNOPSIS

Dibutylchitin was prepared by treatment of krill chitin with butyric anhydride in the presence of perchloric acid as a catalyst of reaction carried out at 25 to 30°C. Dibutylchitin is easily soluble in several organic solvents, such as acetone, alcohols, methylene chloride, and dimethylformamide. Samples of polymers with molecular weights high enough to form fibers were obtained, and dibutylchitin fibers were made by a simple method of dry spinning its 20 to 22% solutions in acetone. Select properties of dibutylchitin fibers were investigated. It was found that dibutylchitin fibers had tensile properties similar to or better than those of chitin and some chitin derivatives described in the literature. An attempt to convert dibutylchitin fibers to chitin fibers was made. It was found that chitin fibers with good tensile properties could be obtained by alkaline hydrolysis of dibutylchitin fibers without destroying the fiber structure. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Chitin, a natural polysaccharide, is insoluble in common organic solvents due to extensive hydrogen bonding and its highly crystalline structure. These properties strongly restrict any practical applications of chitin. Attempts to prepare fibers from chitin and some chitin derivatives have been reported. Tokura and co-workers have described the preparation of chitin fibers¹ using formic acid as a solvent. Acylation of chitin to introduce bulky groups into the chitin chain has been found to give chitin derivatives^{2,3} with improved solubility behavior. Thus, acetylchitins with different degrees of substitution have been synthesized and converted to fiber form.^{4,5} Again, formic acid was used as a solvent.⁵ The limited solubility of acetylchitin necessitated the use of this unattractive and toxic solvent and led to a search for more soluble chitin derivatives. Butylchitin, with a larger substituent group in the chain, was synthesized using methanesulphonic acid as both catalyst and solvent and shown to be easily soluble in several organic solvents, such

as acetone, methanol, ethanol, dimethylformamide, and methylene chloride.³ A simpler method for the synthesis of highly substituted butylchitin using perchloric acid as a catalyst has been described recently.⁶ In this study the preparation of dibutylchitin fibers by dry spinning from acetone solution is described and some properties of the fibers are presented.

EXPERIMENTAL

Materials

Krill chitin, the product of the Sea Fisheries Institute, Gdynia, Poland, additionally purified from residual calcium carbonate, had a degree of acetylation 0.983 and intrinsic viscosity value 18.6 dL/g, determined at 25°C in 5% LiCl solution in *N*-methylpyrrolidone (NMP).

Reagents

Butyric anhydride, 98% (Aldrich); perchloric acid, 70 to 72% (Merck); diethyl ether; acetone; tetrahydrofuran (THF); NMP; LiCl; and NaOH of normal laboratory grade were used without further purification.

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Preparation of Dibutylchitin

Chitin powder (100 g) was added in portions to a freshly prepared mixture of butyric anhydride (1.9 L) and 70% perchloric acid (44 mL). The reaction was allowed to proceed at 25 to 30°C under heterogeneous conditions with stirring. The reaction was exothermic, and a cooling bath was applied to maintain a temperature constant. After 2 h, diethyl ether (1 L) was added and the esterification reaction was stopped. The solid product was recovered by filtration, washed three times with diethyl ether and five times with distilled water, and then suspended in water and neutralized to pH 7 with ammonium hydroxide solution and boiled for a few minutes to remove any traces of acid. The product was collected by filtration, washed successively with water and ether, and dried in a vacuum oven at 50°C. The product was placed in acetone (2.5 L) to allow the dibutylchitin to dissolve. The acetone solution of the polymer was separated from any insoluble material; most of the acetone was removed on a rotary evaporator, and the remainder was evaporated in a hot air stream. The yields were typically 90 to 95%.

Estimation of Intrinsic Viscosity Values

The intrinsic viscosity values of dibutylchitin samples were determined in acetone at 25°C using an initial concentration of polymer ca. 0.5 g/dL.

Infrared Investigation

Infrared spectra were recorded from film samples using a Perkin-Elmer 2000 Fourier transform infrared (FTIR) instrument. Chitin films were prepared from solution in 5% LiCl-NMP, and dibutylchitin films were cast from acetone.

Estimation of Degree of Esterification

The chemical composition of butylchitin was determined by elemental analysis.

Molecular Weight Measurements

Samples of dibutylchitin were analyzed using the normal procedure for gel permeation chromatography (GPC)/viscosity with THF as a solvent by RARA Technology Ltd., England. Columns with Polymer Laboratory (PL) gel 2 × mixed bed-B (30 cm, 10 μm) were used. Samples were run in duplicate.

Preparation of Dibutylchitin Fibers

The dibutylchitin fibers were prepared by dry spinning using 20 to 22% solutions of polymer in

acetone as a dope on a laboratory scale plant in the Department of Textile Industries, University of Leeds, England. The spinning apparatus consisted of an extrusion unit, drying chamber, and wind-up unit. The extrusion unit consisted of a dope reservoir of capacity 200 mL connected through filters with a metering pump of capacity 0.3 cm³/rev and a spinneret (8 holes, hole diameter 120 μm). The drying chamber, 6 m in length, was heated to a temperature of 80°C at the top and 45°C at the bottom of the chamber. The spinning solution was prepared by dissolving 100 g of polymer in 520 to 570 mL of acetone and storing the dope overnight at room temperature to allow dibutylchitin to dissolve; then the solution was stirred for 1 h to ensure homogeneity. The dope was introduced into the reservoir and stored overnight to allow air bubbles to come out. Fiber spinning was carried out with a volumetric flow rate of 5.85 cm³/min. Filaments were wound up at a rate of 70 m/min on a paper bobbin.

Fiber Properties Investigation

The density of the fibers was determined in a mixture of known volumes of toluene and carbon tetrachloride. The linear density (count of a single filament [dtex]) was determined according to the formula

$$\text{filament count (dtex)} = \frac{\pi d^2 \rho_f}{400}$$

where d is the fiber filament diameter (μm) and ρ_f is the fiber density (g/cm³). Actual measurements were also made by weighing known yarn lengths. The fiber dtex was calculated according to the equation

$$\begin{aligned} \text{filament count (dtex)} \\ = \frac{\text{weight of filament (g)}}{\text{length (m)}} \times 10^4 \end{aligned}$$

Fiber diameter was measured using a Projectina microscope. The tensile properties of the fibers were measured on an Instron textile tester, model 1026 H 3169, with a cross-head speed of 10 mm/min after conditioning at 20°C and 65% relative humidity. Data quoted are the mean of at least 10 test results. Examination of surface and cross sections of the fibers was made on a scanning electron microscope (Stereoscan, Cambridge Instruments Ltd.). X-ray fiber patterns were measured by the reflection method with nickel-filtered CuK α radiation on a

Rigaku X-ray diffractometer operated in the ω - 2θ scanning mode between 5 and 30°.

RESULTS AND DISCUSSION

Preparation of Dibutrylchitin

In an earlier study,⁶ the effect of catalyst concentration and reaction time on the molecular weight and yield of dibutrylchitin was examined. It was found that varying the concentration of perchloric acid in the range of 0.25 to 0.64 g per gram of chitin had no significant effect on the dibutrylchitin molecular weight but strongly influenced the yield of soluble polymers. The use of perchloric acid in amounts ca. 0.5 g/g of chitin gave a yield of ca. 90% of dibutrylchitin at 20°C. It was also found that a reaction time of 2 h was sufficient to obtain a product with a molecular weight high enough to form fibers. Three samples of acetone-soluble dibutrylchitin were then prepared using the established reaction conditions, and the results are shown in Table I. The sample with the highest value of the intrinsic viscosity (1.45 dL/g) was obtained at the lowest temperature used. Increasing the reaction temperature led to more significant chain degradation during the reaction.

Characterization of Dibutrylchitin

The elemental analysis of the dibutrylchitin sample with the highest intrinsic viscosity value (1.45 dL/g) gave C, 55.75%; H, 7.50%; and N, 4.14%. Theoretical values calculated for dibutrylchitin $C_8H_{11}NO_5(C_3H_7CO)_2$ are C, 55.98%; H, 7.29%; and N, 4.08%. The results obtained suggested that the degree of chitin butyrylation was very close to 2.

IR spectra of chitin and dibutrylchitin films are presented in Figure 1(a). In the spectrum of dibutrylchitin, there is a greatly reduced absorption at 3500 cm^{-1} due to the loss of the hydroxyl groups,

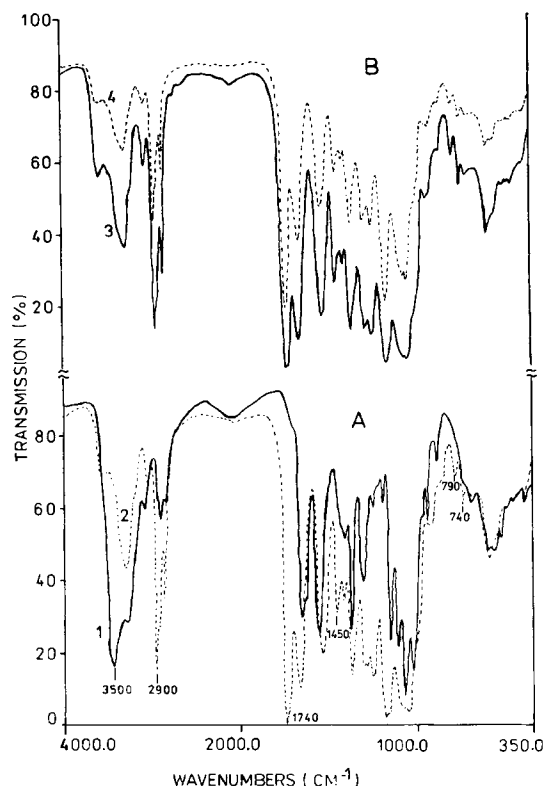


Figure 1 (a) IR spectra of films of krill chitin (1) with $[\eta] = 18.6$ dL/g (5% LiCl solution in NMP, 25°C) and dibutrylchitin (2) with $[\eta] = 1.28$ dL/g (acetone, 25°C). (b) IR spectra of films of dibutrylchitins with $[\eta] = 1.23$ dL/g (3) and with $[\eta] = 1.45$ dL/g (acetone, 25°C).

and new absorptions appear at 1740 cm^{-1} and around 1450 cm^{-1} , characteristic of the esters of fatty acids. Furthermore, absorptions appear at around 2900, 790, and 740 cm^{-1} , which correspond to aliphatic $—CH_2—$ and $—CH_3$ groups. The spectra of other dibutrylchitin samples were essentially the same [Fig. 1(b)].

Molecular weights and molecular weight distribution measurements by GPC made on the sample with an intrinsic viscosity 1.45 dL/g gave $\bar{M}_w = 160$

Table I Conditions and Results of Chitin Esterification

Sample Number	Chitin Mass (g)	BA* Chitin Ratio (g/g)	HClO ₄ Chitin Ratio (g/g)	Temp. (°C)	Reaction Time (h)	DBCH** Mass (g)	DBCH Yield (%)	DBCH Intrinsic Viscosity (dL/g)
1	100	18.9	0.53	30	2	153	94.1	1.23
2	100	18.9	0.53	28	2	150	92.3	1.28
3	100	18.9	0.53	25	2	148	91.0	1.45

* BA = butyric anhydride.

** DBCH = dibutrylchitin.

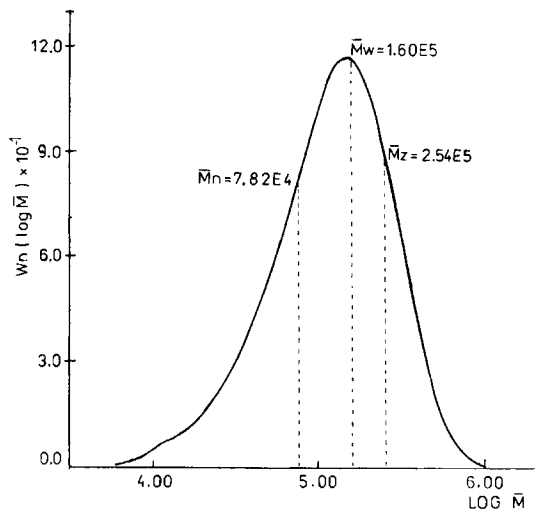


Figure 2 Molecular weight and molecular weight distribution of dibutylchitin sample with $[\eta] = 1.45$ dL/g (acetone, 25°C); $\bar{M}_w = 160 \times 10^3$; $\bar{M}_n = 78.2 \times 10^3$; $\bar{M}_w/\bar{M}_n = 2.0$.

$\times 10^3$ and $\bar{M}_n = 78.2 \times 10^3$ with a polydispersity value $\bar{M}_w/\bar{M}_n = 2$. The molecular weight distribution of this sample is shown in Figure 2.

Spinning and Properties of Dibutylchitin Fibers

Due to the good solubility of dibutylchitin in acetone, it was possible to prepare dopes containing 20 to 22% of polymer. Dibutylchitin dissolved completely, and there was no necessity to filter the dope before introducing it into the dope reservoir. In spite of the high dope viscosity, deaeration occurred easily on standing overnight. Fiber spinning was carried out without difficulty, and silklike fibers with smooth surfaces were obtained without any attempt to optimize conditions.

SEM micrographs of the fibers' surfaces prepared from the samples with intrinsic viscosity values 1.28 and 1.45 dL/g are shown in Figures 3 and 4. In cross section, the fibers had dumb-bell forms in the range from 40 to 120 μm in length and from 11 to 23 μm in width. SEM micrographs of fiber cross sections are presented in Figures 5 and 6. As can be seen, the fibers have a nonporous structure.

The properties of the dibutylchitin fibers are given in Table II along with those of chitin, alkylchitins, and acetylchitin fibers, taken from the literature.^{4,7} Although the tenacities of the dibutylchitin fibers are smaller than tenacity of chitin and

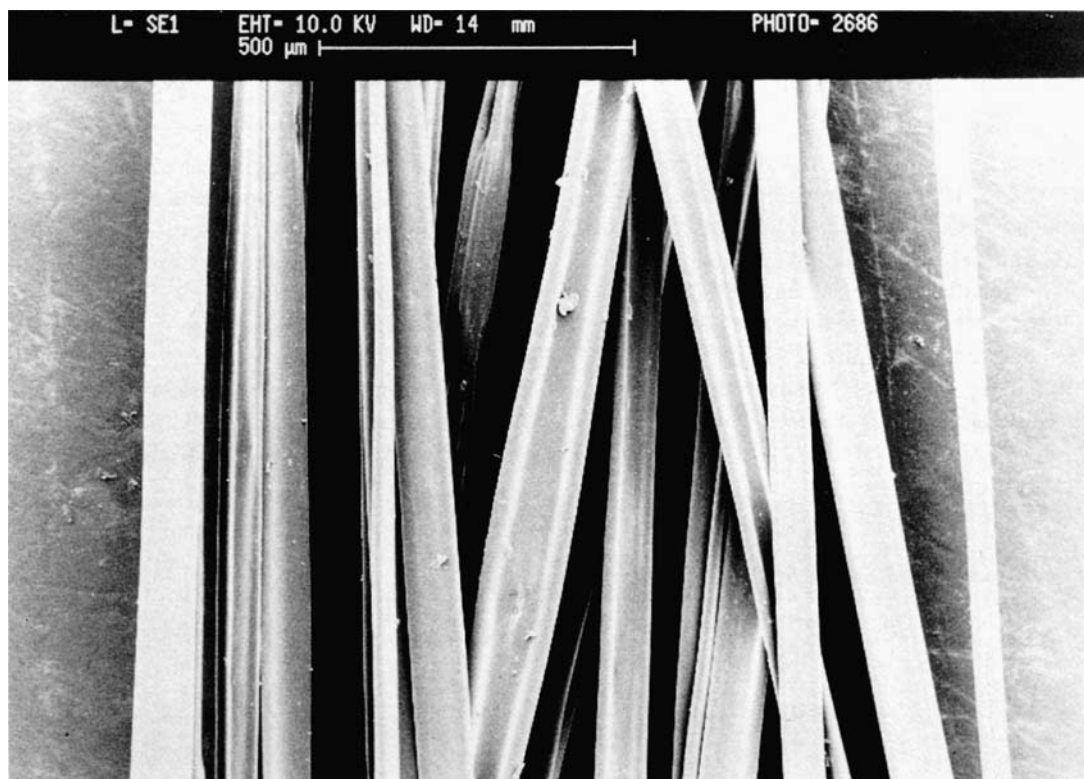


Figure 3 SEM micrograph of surfaces of dibutylchitin fibers prepared by dry spinning method [polymer with $[\eta] = 1.28$ dL/g].

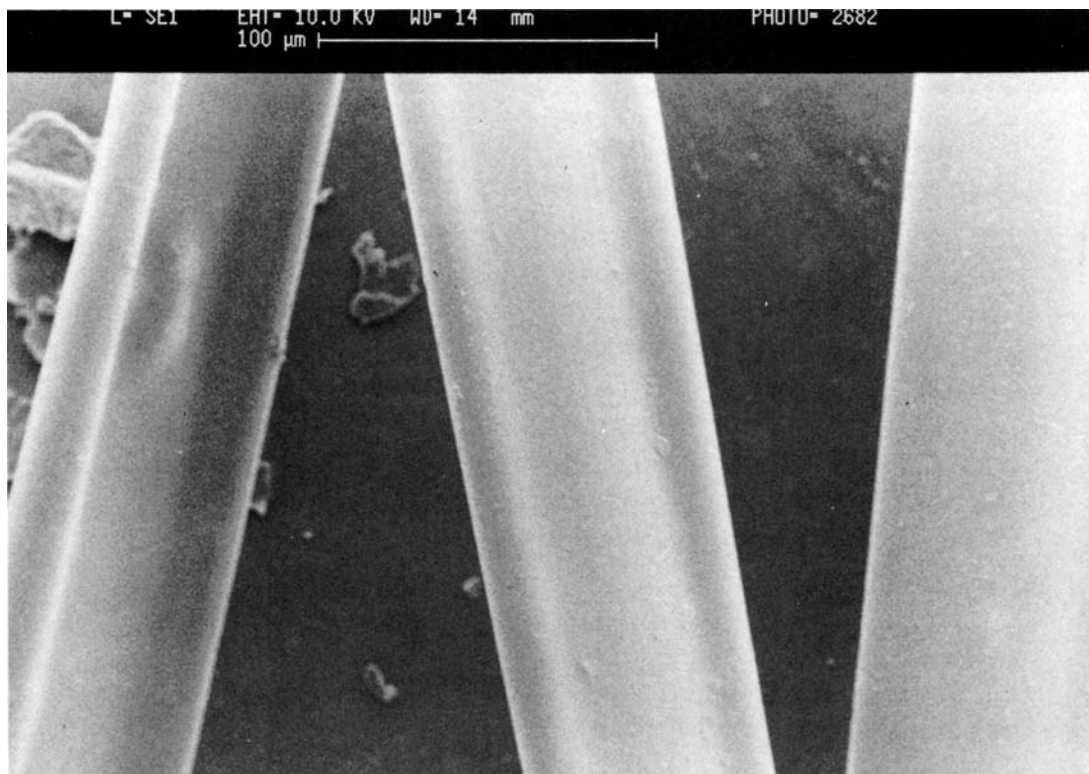


Figure 4 SEM micrograph of dibutyrilchitin fiber surfaces, $[\eta]$ of polymer 1.45 dL/g.



Figure 5 SEM micrograph of dibutyrilchitin fiber cross section, $[\eta]$ of polymer 1.45 dL/g.



Figure 6 SEM micrograph of dibutylchitin fiber cross section, $[\eta]$ of polymer 1.28 dL/g.

acetylchitin fibers, their extensibility is much higher, and the tensile factor, expressed as $T \times E^{1/2}$, has the highest value among the tensile factor values calculated for chitin and other chitin derivatives listed in Table II.

An attempt to convert dibutylchitin fibers to chitin fibers was also made. It was found that the heterogeneous alkaline hydrolysis of dibutylchitin fibers, carried out at 25 to 50°C, produced chitin fibers. Results of hydrolysis reactions carried out

Table II Properties of Dibutylchitin, Chitin, Alkylchitin, and Acetylchitin Fibers (20°C, 65% RH)

Sample	Degree of Substitution	Density (g/cm ³)	Linear Density (dtex)	Tenacity T (g/dtex)	Extensibility E (%)	Tensile Factor $T \times E^{1/2}$	Ref.
DBCH1.28*	2.0	1.21	15.21	0.79	39.0	4.93	
DBCH1.45*	2.0	1.21	15.21	0.83	36.9	5.04	
Butyl chitin	0.4	1.43	4.61	0.71	1.0	0.71	7
Amyl chitin	0.4	1.46	4.70	0.83	3.5	1.55	7
Acetyl chitin	2.0	1.31	13.89	1.33	7.0	3.52	4
Chitin	0	1.40	9.49	1.15	8.4	3.33	7
Chitin	0	1.40	4.62	1.25	3.6	2.37	7
Chitin from DBCH1.28*	0	1.35	4.24	2.50	35.41	14.88	
Chitin from DBCH1.45*	0	1.35	4.24	2.51	43.86	16.62	

* 1.28 and 1.45: Dibutylchitin intrinsic viscosity values.

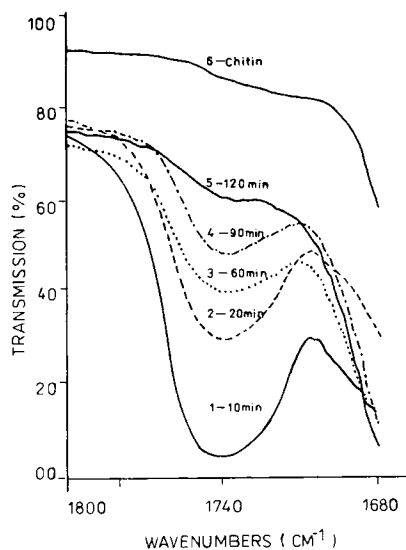


Figure 7 Deacylation of dibutrylchitin with $[\eta] = 1.45$ dL/g during alkaline hydrolysis in 5% NaOH at 50°C (1 ÷ 5-IR spectra of dibutrylchitin films treated by alkaline solution under heterogeneous conditions; 6 - IR spectrum of chitin film).

under heterogeneous conditions at 50°C in 5% NaOH, following by IR measurements, are shown in Figure 7, in which disappearance of absorption due to ester groups at 1740 cm^{-1} can be seen. Measurements were made using films of dibutrylchitin

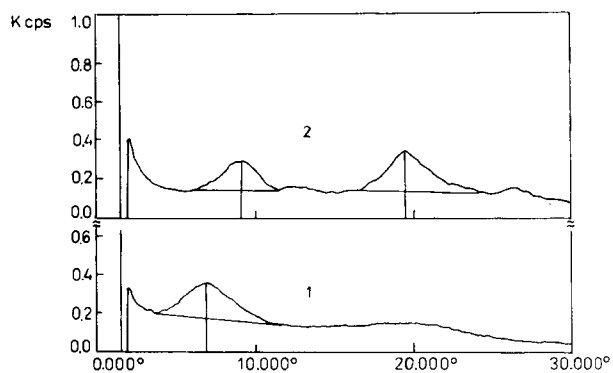


Figure 9 X-ray diffractograms of dibutrylchitin fiber (1) and chitin fiber (2) obtained from dibutrylchitin fiber.

with an intrinsic viscosity 1.45 dL/g, hydrolyzed at the aforementioned conditions. The hydrolysis kinetic is well described by the equation of the first-order reaction. Some properties of these chitin fibers are also presented in Table II. As can be seen, these chitin fibers, prepared from dibutrylchitin fibers, have good tenacities and a high extensibility. During the deacylation reaction, a twofold reduction of the fiber thickness occurs. A cross section of chitin fiber with a nonporous structure, obtained from butrylchitin fiber, is shown in Figure 8. According to the structural analysis by X-ray diffraction, it can be seen that the crystalline structure of chitin fiber differs significantly from initial dibutrylchitin fiber

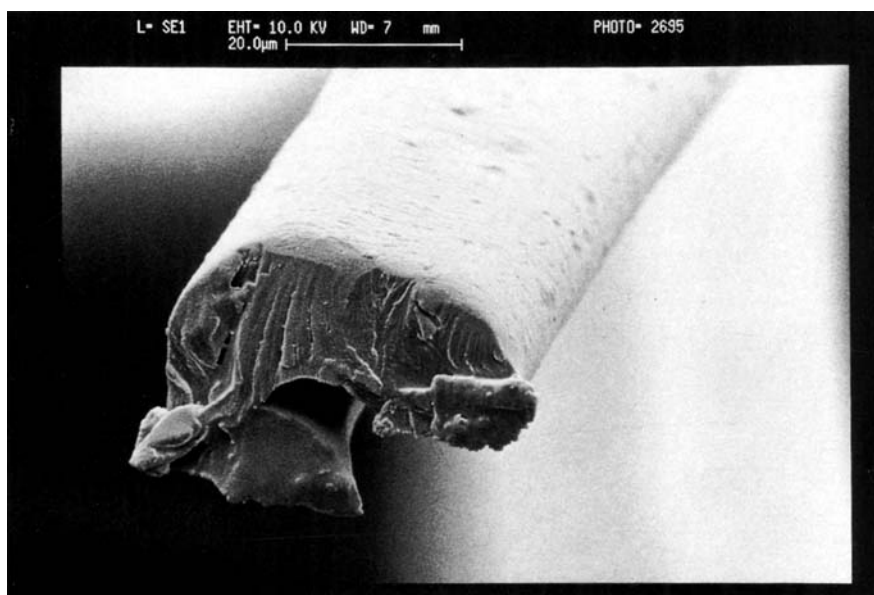


Figure 8 SEM micrograph of chitin fiber cross section (fibers were obtained after 2.5 h hydrolysis of dibutrylchitin fibers in 5% NaOH at 50°C).

after the debutyrylation process (Fig. 9). The full details of the butyrylchitin alkaline hydrolysis investigation and the preparation of chitin fibers will be presently shortly (in a future article).

CONCLUSIONS

Due to the easy solubility of dibutyrylchitin in acetone, it was possible to obtain solutions with high polymer concentrations and apply a simple method of dry spinning for fiber preparation. A preliminary study of the fiber spinning from acetone solution seems to indicate no great difficulties. When further investigations into the effects of varying parameters such as molecular weight and spinning and drying conditions have been completed, it may be possible to improve on the properties of the dibutyrylchitin fibers described in the present work. It was demonstrated that chitin fibres with good properties could be easily obtained by alkaline hydrolysis of the dibutyrylchitin fibers.

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