

Studies on Chitin. III.* Preparation of Chitin Fibers

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ABSTRACT: The chitin fiber was obtained from a chitin-formic acid solution which was found to be spinnable. This solution was prepared through repeated freezing process by the addition of dichloroacetic acid and isopropyl ether. Dichloroacetic acid and methanesulfonic acid were also found to be solvents for chitin, though the spinnability could not be observed owing to rapid reduction of viscosity even at low temperature. Chitin fibers were successfully prepared from formic acid solution, and better qualities were found for these than for the fibers prepared through the chitin viscose. X-ray diffraction analysis suggested that the regenerated chitin would have a similar structure to the natural chitin. The clear and flexible chitin film was prepared from formic acid-dichloroacetic acid or formic acid-urea solution by casting on a glass plate and solidifying in ethanol.

KEY WORDS Chitin / Chitin Fiber / Formic Acid / Dichloroacetic Acid /
Isopropyl Ether / Spinnability / Film Formability / X-Ray Diffraction /

Chitin, one of the unutilized natural polysaccharides, consists of *N*-acetylglucosamine residues which have an acetamino group on the C₂ position of the D-glucose unit. Utilization of chitin as a resource is extremely limited because of the poor solubility and poor reactivity, which are due to the strong micelle structure which was formed through hydrogen bonds between aminoacetyl groups. The spinnability and film forming ability would be expected from the linear chain structures, like those in cellulose, obtained when chitin dissolves at high concentrations without degradation of the molecule. The polyamide-type micelle should be broken up prior to solubilization of chitin into a solvent or prior to being subjected to chemical reactions. The preparation of chitin viscose was reported previously through the xanthation of alkali chitin by the application of a freezing procedure.¹ Chitin fiber was obtained from the chitin viscose under the spinning condition of rayon fiber at a low temperature, but it was not suitable for practical use because of the weakness of both its tenacity and its knot strength in the wet state. However, the freezing procedure would

seem to be useful to break up the micelle structure of a chitin molecule. On this basis, several solvents for polyamides were applied to dissolve the chitin; the formic acid-dichloroacetic acid system was found to be a suitable solvent for obtaining a viscous chitin solution, when the freezing procedure was repeated. In this paper, the preparation of chitin solution at a high concentration, of chitin fiber, and of chitin film are reported, along with preliminary studies on the properties of chitin fiber. The chitin fiber was analyzed by the X-ray diffraction method and the spacings of regenerated chitin fiber were found to be similar to those of natural chitin proposed by C. D. Carlstrom² and J. Blackwell *et al.*³

EXPERIMENTAL

Chitin powder (30—45 mesh) from Alaska King Crab Shell was supplied kindly by Kyowa Yushi Co. Ltd..

Preparation of Chitin Solution

Five to seven grams of chitin powder was suspended in 100 cm³ of 99% formic acid at room temperature and swollen chitin was then frozen at -20°C for a day. The frozen chitin suspension was melted at

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room temperature. The turbid gel was turned gradually to a clear gel by repeating this procedure several times. The obtained clear chitin gel was dispersed by the addition of a small amount of dichloroacetic acid (DCA). As the dispersed chitin solution showed poor spinnability at higher chitin concentrations, isopropyl ether was added to reduce the viscosity of chitin solution to *ca.* 100 poise immediately before spinning, and the solution was filtered through flannel under pressure. Thus obtained chitin solution was spun into the first coagulation bath through a platinum nozzle at a pressure of 1.0–1.2 kg cm⁻². The detailed conditions for the spinning are summarized in Table I. The chitin fiber wound on a cassette was boiled in the water to remove any trace of formic acid or DCA for 1 h and air-dried after washing in running water overnight.

Chitin film was prepared by casting the chitin-formic acid solution [3% of DCA (v/v) or 2 equivalent moles of urea/*N*-acetylglucosamine residue] on the glass plate and solidifying it by ethanol. The chitin film was dried at room temperature by pressing it between filter papers after several washings with ethanol.

Measurements on the Properties of Chitin Fibers

Denier. Denier of the chitin fiber was measured using an Asahi Seiko Denieroscope. The average denier was estimated from the measurements of 40 single fibers of 40 mm length for each sample.

Tenacity, Elongation, and Knot Strength. A Toyo-Baldwin Tencilon UTM-II was applied for the measurements of the tenacity, elongation, and knot strength of the chitin fiber of 20 mm length. The average values were obtained from 10 measurements for each sample. Wet strength was measured after the immersion of fiber into water at 20°C or 90°C for 3 min. The rate of stretching was 20 mm/min (100%/min). Elongation elasticity was measured at the stretching rate of 4 mm/min (20%/min) and 2.000 mg ($d \times l/25$ g) of initial load.

Moisture Recovery. The moisture recovery was estimated by measuring the weight at different humidities.

$$\text{Moisture recovery} = (W_1 - W_0)/W_0 \times 100 (\%)$$

W_0 , dry weight (110°C × 3 h)

W_1 , wet weight (20°C, 65% RH × 3 h)

Table I. Spinning conditions for the chitin fibers^b

Sample number		31	56	79	80	61	62
Spinning condition	Solvent ^a	FA-DCA (92:8)		FA-DCA-iPE (83:11:5)		FA-DCA-iPE (92:5:3)	
	Concn/%, w/v	3.0	4.0	3.8	3.8	4.6	4.6
Spinning pressure				1.0–1.3 (kg cm ⁻²)			
Nozzle				Pt, 0.09 mm ϕ —50 holes			
Coagulation bath	1st	EtOAc	iPE	Ace	Ace-iPE	EtOAc	EtOAc-iPE
	2nd	EtOH	50% AcOH:EtOH (2:5)			Cold Water	
Stretching bath				Water (60°C)			
1st roller/m min ⁻¹		5.6	5.2	6.5	6.5	6.2	6.2
2nd roller/m min ⁻¹		7.3	5.8	7.8	8.8	8.0	8.4
Elongation ratio		1.32	1.10	1.20	1.35	1.29	1.35

^a Solvent compositions are expressed as a volume ratio.

^b Abbreviations: FA, formic acid; DCA, dichloroacetic acid; iPE, isopropyl ether; EtOAc, ethyl acetate; Ace, acetone; AcOH, acetic acid; Cold water, 12–14°C.

Scanning Micrograph. Microscopic scans were taken by a JEOL Scanning Microscope JSM-T20 after the spattering of Au-Pd (80:20) on the fiber surface *in vacuo*.

X-Ray Diffraction Pattern. The fibre pattern of chitin fiber was recorded with Cu-K_α radiation from a Toshiba X-ray Generator ADX-401. The spacings were calculated from the fibre pattern using silicon powder as a standard.

RESULTS AND DISCUSSION

Dissolution of Chitin

Dichloroacetic acid or urea was found to be useful to disperse the chitin into formic acid; otherwise some micro-gel particles were included even below 1% (w/v) of chitin. The minimum concentration to disperse the chitin gel was found to be 8% (v/v) of DCA or 2 equivalent moles of urea to *N*-acetylglucosamine residue at 4% of chitin concentration. It is very interesting that urea also reduces the viscosity of chitin viscose remarkably at the 1 equivalent mole to *N*-acetylglucosamine residue in the case of spinning of chitin fiber, as reported previously.¹ The spinnability was found only for fibers from the formic acid-dichloroacetic acid system at 3–4.8% of chitin concentration, with the addition of isopropyl ether at the concentration

of 3–5% (v/v). Chitin solution became clear and of lower viscosity by the addition of the solvent.

Although chitin is easily dissolved in dichloroacetic acid or methanesulfonic acid at a high concentration even at low temperature, the spinnability could not be observed, because the viscosity of the solution tended to decrease noticeably, with a corresponding fall in molecular weight, within a short period. Also, sulfuric acid was found not to be a suitable solvent, owing to the fast carbonization even at low temperature.

The chitin film was prepared from formic acid-DCA or formic acid-urea solution by casting the chitin solution simply onto a glass plate and solidifying by ethanol at room temperature. The properties of chitin film are now under investigation.

Properties of Chitin Fibers

The general properties of chitin fibers prepared under different spinning conditions are listed in Table II. The stress-strain curves for these fibers are shown in Figure 1. Also the relationships between yield stress (g/d) and yield strain (%) of the values at the breaking points of chitin fibers are shown in Figure 2. It was suggested from Figures 1 and 2 that the fiber prepared by an ethyl acetate (1st coagulation bath)-water (2nd coagulation bath) system seems to have the best quality, followed by the fiber

Table II. Properties of chitin fibers

Sample number	31	56	79	80	61	62	
Tenacity/g d ⁻¹	Dry (20°C, 65%RH)	1.32	0.68	1.26	1.59	1.33	1.02
	Wet (20°C, 100%RH)	0.18	0.23	0.16	0.23	0.27	0.14
	Wet (90°C, 100%RH)	0.18	0.23	0.27	0.37	0.50	0.40
Elongation/%	Dry (20°C, 65%RH)	2.7	2.9	3.4	2.7	4.3	2.8
	Wet (20°C, 100%RH)	7.8	10.8	4.6	3.6	8.6	4.6
	Wet (90°C, 100%RH)	7.1	13.0	6.8	7.5	10.1	8.8
Knot strength/g d ⁻¹	0.45	0.45	0.12	0.08	0.24	0.11	
Density/g cm ⁻³	1.382	1.347	1.395	1.397	1.385	1.384	
Moisture recovery/%	12.9	13.0	12.9	14.0	14.1	14.7	
Denier/d	25.5	3.2	2.0	3.0	2.1	2.0	

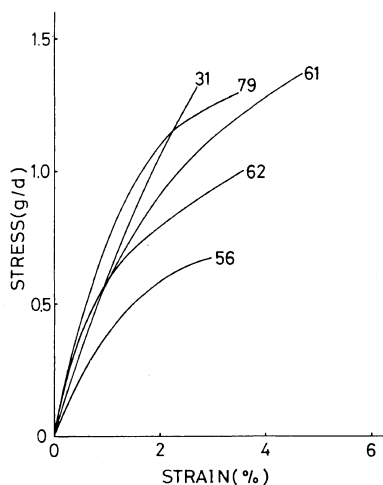


Figure 1. Strain-Stress curves of chitin fiber at 20°C, 65% RH.

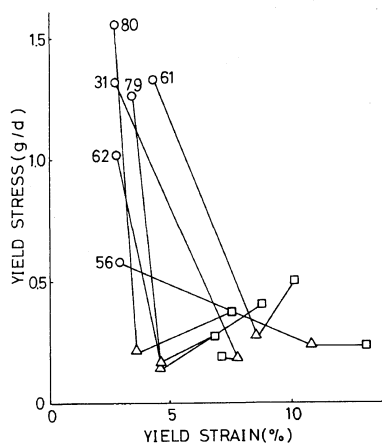


Figure 2. Relationship between yield strain and yield stress. ○, 20°C, 65%RH; △, 20°C, 100%RH; □, 90°C, 100%RH.

prepared with an ethyl acetate (1st)-ethanol (2nd) system. On the other hand, an acetone (1st)-ethanol-acetic acid (2nd) system gave the highest value of Young's modulus and the lowest knot strength of the fiber. It was found from the X-ray diffraction pattern that the fiber prepared by ethyl acetate-water combination gave the best molecular orientation among the fibers, as shown in Figure 4. This well oriented structure seems to be reflected in the higher values of the wet strength (20°C, 100% RH and 90°C, 100% RH), as shown in Figure 2.

However, the chemical structure and the degree of orientation seem to be independent of the moisture recovery, as the values lie between 12.9–14.7%, which are similar to those of rayon fibers. The density of the chitin fiber was similar to those of polyester fibers and smaller than those of rayon fibers. As the density of polyamide fibers is comparatively low, the acetyl amino side group of the chitin molecule might affect the density of chitin fibers.

The fibers obtained by the formic acid method have better properties than those prepared through chitin viscose. Wet strengths (20°C, 100% RH and 90°C, 100% RH) and knot strength were especially improved, in contrast to the reduction of elongation ratio. In general, wet strengths of chitin fibers were higher at 90°C, 100% RH than at 20°C, 100% RH, although this is not the case for acetylated chitin fibers.⁴ The role of OH groups in maintaining the crystal structure of chitin molecule, corresponding to the moisture recovery of chitin and chitin derivatives, is under investigation.

The microscopic photographs of the fiber surface are shown in Figure 3. Only the fiber obtained by using isopropyl ether as the first coagulation bath showed a dull surface and many cracks along the fiber axis. But the fibers prepared under other conditions have a lustrous and smooth surface.

X-ray Diffraction Analysis

An obtained diffraction pattern is shown in Figure 4 as an example. Reflections having the spacings of 2.5, 3.4, 5.1, and 10.1 Å on the meridian (fiber axis) and 4.6 and 11.2 Å on the equator were observed for the fiber prepared by ethyl acetate system (#61). Fiber diffraction patterns were almost the same for other samples irrespective of the different degree of orientation. The spacing of 10.1 Å along the fiber axis is similar to the value proposed for the disaccharide repeating unit in the natural chitin by C. D. Carlstrom² and J. Blackwell *et al.*³ Further investigation on the X-ray diffraction analysis is now proceeding.

Chitin was almost regenerated by spinning chitin-formic acid solution into an organic solvent. However, the properties of chitin fiber should be improved further in order to put the fiber to practical use. A survey should be done to find out better spinning conditions, because the chitin fiber has some promising properties against chemicals and a promising future as a biodegradable material.

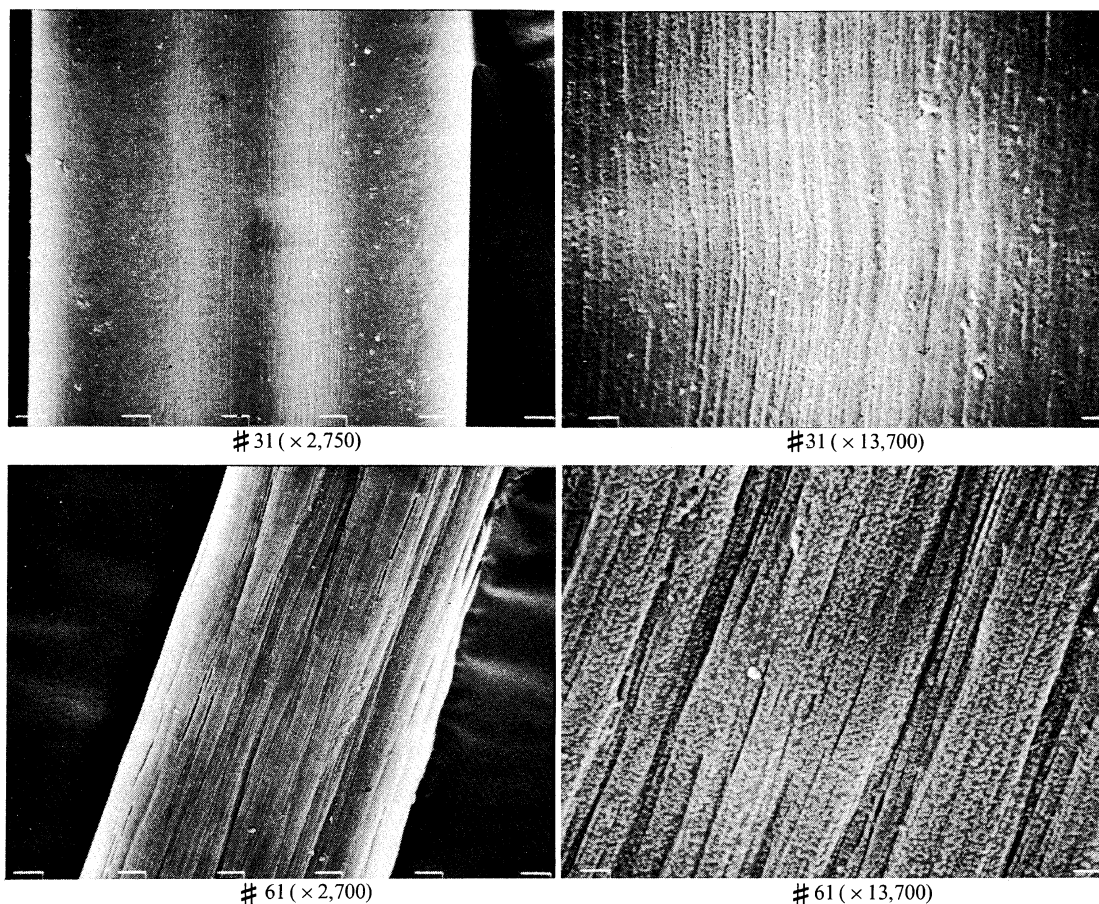


Figure 3. Scanning microscopic pictures of chitin fibers. Au-Pd (80:20) spattering.

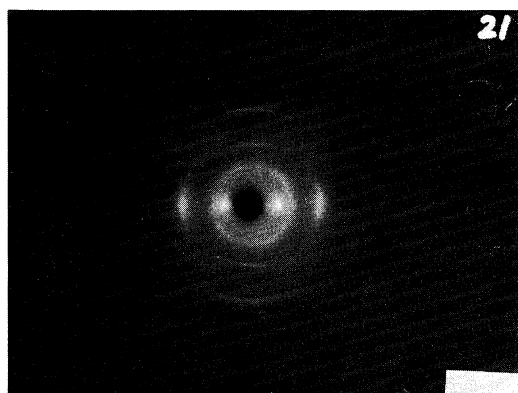


Figure 4. X-ray diffraction pattern of chitin fiber prepared with ethyl acetate(1st)-water(2nd) system as a coagulation bath (#61); Cu-K α radiation (35 kV, 20 mA), 0.25 mm slit for 50 h on Fuji X-ray film (1 \times 150). Fiber axis is vertical. A 40 mm flat camera was used.

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