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Fiber preparation of *N*-acylchitosan and its cellulose blend by spinning their aqueous xanthate solutions

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Abstract

This study aims to develop a method of preparing novel fibers of *N*-acylchitosan and *N*-acylchitosan–cellulose by spinning an aqueous alkaline solution of their sodium xanthates. A solution of sodium *N*-acylchitosan salt in aqueous 14% NaOH was treated with carbon disulfide to afford an aqueous solution of sodium *N*-acylchitosan xanthate. The solution of sodium *N*-acylchitosan xanthate, and its solution mixed with sodium cellulose xanthate, were spun at 45–50°C through a viscose-type spinneret into a coagulation bath containing aqueous 10% H_2SO_4, 32% Na_2SO_4 and 1.3% $ZnSO_4$. A total of eight fibers of *N*-acetylchitosan, *N*-propionylchitosan, *N*-acetylchitosan–cellulose (6 : 4, 4 : 5 and 3 :7 w/w) and *N*-propionylchitosan–cellulose (4 : 6, 5 : 5 and 3 :7 w/w) were prepared. All these fibers were white and had good mechanical properties. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: N-acylchitosan–cellulose blends; Fiber; *N*-propionylchitosan; *N*-acetylchitosan; Cellulose xanthate

1. Introduction

Alkaline cellulose (sodium cellulose salt) and cellulose xanthate [*O*-(sodium thio)thiocarbonyl cellulose] are well known in the rayon industry (Muller and Purves, 1965). In literatures, alkaline chitin (sodium chitin salt) had been prepared by treatment of chitin with aqueous concentrated NaOH (Thor and Henderson, 1940a), and sodium chitin xanthate [*O*-(sodium thio)thiocarbonyl chitin] (Thor and Henderson, 1940b) had also been prepared by treatment of the alkaline chitin with carbon disulfide. An attempt has been made to prepare chitin–cellulose fiber by spinning an aqueous alkaline solution of sodium chitin xanthate with sodium cellulose xanthates into a coagulation bath containing aq. 10% H_2SO_4, 25% Na_2SO_4 and 1% $ZnSO_4$ (Noguchi et al., 1973). A more precise study has been needed for producing the fiber commercially. No report has dealt with the preparation of *N*-propionylchitosan fiber and *N*-propionylchitosan–cellulose fiber.

We now report a method for preparing an *N*-acetylchitosan fiber, an *N*-propionylchitosan fiber, three *N*-acetylchitosan–cellulose fibers and three *N*-propionylchitosan–cellulose fibers by spinning their aqueous sodium xanthate solutions.

2. Experimental

2.1. Materials

A 9% solution of sodium cellulose xanthate in aq. 5% NaOH (viscose) was prepared by the conventional method (Muller and Purves, 1965) via sodium cellulose salt (alkaline cellulose) from a commercial product of wood pulp (95–96% cellulose, 0.04–0.2% lignin and 0.06–0.07% ash). *N*-acetylchitosan and *N*-propionylchitosan (d.s. 1.0 for *N*-acyl) were prepared by *N*-acylation of crab shell chitosan (MW about 50 000, Katakura Chikkarin, Tokyo) (Hirano et al., 1976).

2.2. Methods

FTIR spectra (KBr) were recorded on a Jasco FTIR 5300 spectrometer (Jasco, Tokyo). Elemental analyses were performed at the Micro-analytical Center of Kyoto

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University, Kyoto. D.s. values for *N*-acyl groups were calculated from the elemental analysis data. The filament fineness, expressed in denier (one denier being the weight (g) of a filament 9 km in length) was measured on a Vibroscop Micro (Lenzing Technic Instrument, Austria), and the filament strength and elongation were measured on a Vibrodyn 400 (Lenzing Technic Instrument, Austria).

2.3. Spinning solutions

2.3.1. Aqueous solution of sodium N-acetylchitosan xanthate

A powdered sample (2.0 g, > 80 mesh) of *N*-acetylchitosan (Hirano et al., 1976) was swollen by stirring in aq. 46% NaOH (7.6 ml) at room temperature for 3 h. The solution was adjusted to 25 ml volume by adding pieces of crushed ice to make a viscous 8% solution of sodium *N*-acetylchitosan salt in aq. 14% NaOH. To the solution was added carbon disulfide (1 ml, 1.3 mol/GlcNAc), and the mixture was allowed to remain at room temperature for one day (Hirano et al., 1994). A small amount of insoluble precipitate was filtered off through a flannel sheet. A clear orange–red solution of 8% sodium *N*-acetylchitosan xanthate was obtained and used in the present study as a spinning solution for *N*-acetylchitosan fiber (**1**).

2.3.2. Aqueous solution of sodium N-propionylchitosan xanthate

A powdered sample (2.0 g, > 80 mesh) of *N*-propionylchitosan (Hirano et al., 1976) was swollen by stirring in aq. 46% NaOH (10.0 ml) at room temperature for 10 h. The solution was adjusted to 40 ml volume by adding pieces of crushed ice to make a viscous ~5% solution of sodium *N*-propionylchitosan salt in aq. 14% NaOH. To the solution was added carbon disulfide (4 ml, 5.0 mol/GlcN–propionyl). The mixture was allowed to remain at room temperature for one day. An insoluble precipitate was filtered off through a flannel sheet. A clear orange–red viscous solution of ~5% sodium *N*-propionylchitosan xanthate in aq. 14% NaOH was obtained, and used as a spinning solution in the present study for *N*-propionylchitosan fiber (**2**).

2.3.3. Solution of sodium N-acetylchitosan xanthate mixed with sodium cellulose xanthate

An 8% solution of sodium *N*-acetylchitosan xanthate in aq. 14% NaOH, obtained as above, was mixed at room temperature with a 9% solution of sodium cellulose xanthate in aq. 5% NaOH in ratios of 2 : 1 (v/v) for fiber **3-1**, 1 : 1 (v/v) for fiber **3-2** and 1 : 2 (v/v) for fiber **3-3**. Each of the homogeneous solutions was used as a spinning solution for *N*-acetylchitosan–cellulose fibers.

2.3.4. Solution of N-propionylchitosan xanthate mixed with sodium cellulose xanthate

A 5% solution of sodium *N*-propionylchitosan xanthate in aq. 14% NaOH, obtained as above, was mixed at room temperature with a 9% solution of sodium cellulose xanthate in aq. 5% NaOH in ratios of 3 :1 (v/v) for fiber **4-1**, 2 :1 (v/v) for fiber **4-2** and 1 : 20 (v/v) for fiber **4-3**. Each of the homogeneous clear solutions was used as a spinning solution for *N*-propionyl–cellulose fibers.

2.4. Spinning

The spinning solution (20–25 ml) obtained as above was degassed under diminished pressure for a few minutes and put into an L-shaped glass tube, one end of which was 20 cm in length × 3 cm in diameter while the other end was 9 cm in length × 0.8 cm in diameter). To the 0.8 cm diameter end, an viscose-type gold–platinum (6 :4 w/w) spinneret (12.5 × 18.0 × 0.3 mm in size, Japan Nozzle, Kobe) was connected by inserting a sheet of flannel filter. The nozzle diameter was 12.5 mm and had 300 holes, each hole being 0.25 mm in diameter for entrance, 0.10 mm for exit and 0.03 mm for pass length. At the other end of the glass tube an air stream at 0.4 kg/cm^2 pressure was caused to flow by an air pump to extrude the spinning solution at 0.5–10 ml min^{-1}. The spinning solution was spun into a coagulating bath (40 cm in path length) containing aq. 10% H_2SO_4, 32% Na_2SO_4 and 1.3% $ZnSO_4$, and the coagulating solution was circulated at 45–50°C with a water pump from a storage bottle (1500 ml) to the coagulating bath and back to the storage bottle. Filaments from the spinneret were passed through the coagulating solution and collected on a roller (10 cm in diameter) connected to a motor to produce fiber. The wet fiber obtained was treated in boiling water for 10–20 min and in aq. 0.5% NaOH at 60–70°C for a few minutes, washed thoroughly with deionized water and pressed for dehydration. The fiber was suspended in MeOH (100 ml/g fiber) and the corresponding carboxylic anhydride (1 ml/g fiber) was added. The mixture was allowed to remain at room temperature for 5 h. The fiber was taken out, washed thoroughly with deionized water, pressed for dehydration and air-dried to form the corresponding white *N*-acylchitosan fiber having d.s. 1.0 for the *N*-acyl group.

2.5. Data

2.5.1. N-acetylchitosan fiber (1)

ν_{max} (KBr): 1657 and 1554 cm^{-1} (C=O and NH of NAc). Anal. calc. for $[C_8H_{13}NO_5 \cdot 0.79H_2O]_n$: C, 44.19; H, 6.71; N, 6.45. Found: C, 43.91; H, 6.90; N, 6.40.

2.5.2. N-propionylchitosan fiber (2)

ν_{max} (KBr): 1657 and 1554 cm^{-1} (C=O and NH of *N*-propionyl). Anal. calc. for $[C_9H_{15}NO_5 \cdot 0.61H_2O]_n$: C, 47.37; H, 7.11; N, 6.14. Found: C, 47.10; H, 7.23; N, 6.09.

2.5.3. N-acetylchitosan–cellulose composite fibers (3)

ν_{max} (KBr): 1650 and 1550 cm^{-1} (C=O and NH of NAc). Anal. N (%): 4.28 for fiber **3-1**, 2.97 for fiber **3-2** and 1.93 for fiber **3-3**.

Table 1
Component analysis and some mechanical properties of filaments of *N*-acylchitosan and *N*-acylchitosan–cellulose in the dry state

Filament[a]	N (%)	*N*-acylchitosan (%)[b]	Fineness as denier (g/9000 m)	Strength (g/denier)	Elongation (%)
1	6.40	93	3.43	0.83	29.8
2	6.09	94	3.60	0.47	23.9
3-1	4.28	62	5.31	0.18	4.8
3-2	2.97	43	6.96	0.26	4.5
3-3	1.93	28	3.62	0.53	19.1
4-1	3.93	61	2.03	0.67	21.0
4-2	3.16	49	0.79	0.91	22.6
4-3	0.19	3	3.66	0.53	15.9
Cellulose[c]			4.51	0.99	54.7

[a] *N*-acetylchitosan filament (**1**), *N*-propionylchitosan filament (**2**), *N*-acetylchitosan–cellulose filaments (**3-1**, **3-2** and **3-3**) and *N*-propionylchitosan–cellulose filaments (**4-1**, **4-2** and **4-3**).

[b] Calculated from N content. The theoretical values for 100% *N*-acylchitosan are 6.90% for *N*-acetylchitosan filament and 6.45% for *N*-propionylchitosan filament.

[c] Cellulose filament was prepared by spinning a 9% solution of sodium cellulose xanthate in aq. 5% NaOH by the same procedure, and was used as a control.

2.5.4. N-propionylchitosan–cellulose composite fibers (4)

$\nu_{\max}$ (KBr): 2650 and 1550 cm^{-1} (C=O and NH of *N*-propionyl). Anal. N (%): 3.93 for fiber **4-1**, 3.16 for fiber **4-2** and 0.19 for fiber **4-3**.

3. Results and discussion

Eight novel white fibers of *N*-acylchitosan and *N*-acylchitosan–cellulose were prepared. The fibers showed C=O and NH absorptions of the *N*-acyl group at 1650 and 1550 cm^{-1} in the FTIR spectra. Partial *N*-deacetylation occurred during the alkaline chitin preparation, as evidenced by the C/N ratios of the elemental analyses. The fiber was treated with the corresponding carboxylic anhydride (1 ml/g of fiber) in MeOH (Hirano et al., 1976). The elemental analyses of the treated fibers **1** and **2** revealed their d.s. 1.0 for *N*-acyl groups.

As shown in Table 1, the tenacity and elongation values of *N*-acylchitosan filaments were 0.8 and 0.5 times those of cellulose filaments, respectively. These values for *N*-propionylchitosan filaments were slightly lower than those of *N*-acetylchitosan filaments. In the *N*-acylchitosan–cellulose filaments, both the denier and elongation values increased with an increase in their cellulose content. However, the molecular conformation and interaction of *N*-acylchitosan and cellulose chains in the filaments are unknown.

The chitin–cellulose fiber has just been commercialized in a Japanese textile industry as a natural functional fiber for fabrics including socks and underwear (Yoshikawa et al., 1996, Hirano, 1996).

References

Hirano, S. (1996). Biotechnol. Ann. Rev., *2*, 237–258.

Hirano, S., Ohe, Y., & Ono, H. (1976). Carbohydr. Res., *47*, 315–320.

Hirano, S., Usutani, A., & Zhang, M. (1994). Carbohydr. Res., *256*, 331.

Muller, T.E., & Purves, C.B. (1965). Methods Carbohydr. Chem., *3*, 238–251.

Noguchi, J., Wada, O., Seo, H., Tokura, S., & Nishi, N. (1973). Kobunshi Kagaku, *30*, 320–326.

Thor, C.I.B., & Henderson, W.F. (1940). Am. Dyestuff Rep., *29*, 461–464.

Thor, C.I.B., & Henderson, W.F. (1940). Am. Dyestuff Rep., *29*, 465–469.

Yoshikawa, M., Midorikawa, T., Otsuki, T., & Terashi, T. (1996). *Jpn. Kokai, Tokkyo Koho*. JP 08–92820 [96–92820].