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Novel fibers of *N*-acylchitosan and its cellulose composite prepared by spinning their aqueous xanthate solutions

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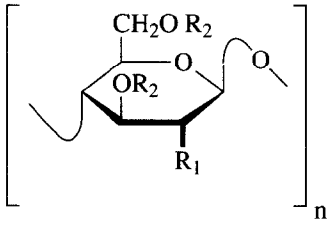
Novel fibers of *N*-acylchitosan and *N*-acylchitosan-cellulose composite were prepared. An aq. 14% NaOH solution of sodium *N*-acylchitosan xanthate [*O*-(sodium thio) thiocarbonyl *N*-acylchitosan] and of its mixture with sodium cellulose xanthate [*O*-(sodium thio) thiocarbonyl cellulose) was spun at 45–50°C through a viscose-type spinneret into a coagulating bath containing aq. 10% H_2SO_4, 32% Na_2SO_4 and 1.3% $ZnSO_4$. All the fibers obtained were white. *N*-Propionylchitosan-cellulose composite filament had better mechanical properties than did *N*-acetylchitosan-cellulose composite filament. These fibers were digested by chitinase and lysozyme, in which the hydrolysis rate was controlled by the *N*-acyl structure of chitosan. © 1997 Elsevier Science Ltd

INTRODUCTION

Chitin and cellulose have a structural backbone of a (1→4)-linked β-D-glucan with no branching. Alkaline cellulose (sodium cellulose salt) and cellulose xanthate [*O*-(sodium thio)-thiocarbonyl cellulose] are well known in the rayon industry. In the literature, alkaline chitin (sodium chitin salt) was prepared by treatment of chitin with aq. conc. NaOH (Thor and Henderson, 1940a), and sodium chitin xanthate [*O*-(sodium thio) thiocarbonyl chitin] (Thor and Henderson, 1940b) was also prepared by treatment of the alkaline chitin with carbon disulfide. A chitin–cellulose composite fiber has been attempted by spinning a mixed aq. alkaline solution of sodium chitin and cellulose xanthates into an aq. coagulating bath containing 10% H_2SO_4, 25% Na_2SO_4 and 1% $ZnSO_4$ (Noguchi *et al.*, 1973).

Natural chitin has strong intramolecular and intermolecular hydrogen bonds. However, the *N*-acetylchitosan (a regenerated chitin), which is prepared by chemical *N*-acetylation of chitosan with acetic anhydride (Hirano *et al.*, 1976), has weak molecular hydrogen bonds and d.s. 1.0 for *N*-acyl. In fact, sodium *N*-acetylchitosan salt (alkaline chitin) is more easily prepared from the regenerated *N*-acetylchitosan than is that from natural chitin (Hirano *et al.*, 1991), and this results in the straighforward preparation and structural analysis of sodium *N*-acetylchitosan xanthate (Hirano *et al.*, 1994). No report has dealt with the preparation of fiber by spinning an aq. solution of sodium *N*-propionylchitosan xanthate [*O*-(sodium thio)thiocarbonyl *N*-propionylchitosan] (Scheme 1).



Scheme 1. R_1 = —NHC(=O)CH_2CH_3; R_2, R_3 = —C(=S)SNa.

In this paper, we report the preparation of novel fibers of *N*-acetylchitosan, *N*-propionylchitosan and their cellulose composites by spinning each of their aq. sodium xanthate solutions.

EXPERIMENTAL

Materials

An aq. 2% acetic acid solution of a crab shell chitosan (MW about 50 000, Katakura Chikkarin Co., Tokyo)

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was filtered through a grass filter, and was neutralized with aq. NaOH to afford a purified precipitate of chitosan, degree of substitution (d.s.) 0.1 for NAc; $[\alpha]_D^{23}$ – 7° (*c* 1.0, aq. 2% acetic acid). An aq. 5% NaOH solution of 9% sodium cellulose xanthate (viscose) was prepared by the conventional method (Noguchi *et al.*, 1973) 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), and the solution was supplied from the manufacturing plant of viscose rayon at Omikenshi Co., Kakogawa. *N*-Acetylchitosan and *N*-propionylchitosan (d.s. 1.0 for *N*-acyl) were prepared by *N*-acylation of chitosan (Hirano *et al.*, 1976).

METHODS

FTIR spectra (KBr) were recorded on Jasco FTIR 5300 spectrometer (Jasco Co., Tokyo), and specific rotations on a Jasco Dip-181 polarimeter (Jasco Co., Tokyo). Elemental analyses were performed at the Micro-analytical Center of Kyoto University. d.s. values for *N*-acyl groups were calculated from the elemental analysis data. In addition to the filament fineness, which is expressed by the weight (g) of a filament of 9000 m in length as one denier, both the strength and elongation of the filaments were analyzed at the analytical room of the Omikenshi Co.

SPINNING SOLUTIONS

An aq. solution of sodium *N*-acetylchitosan xanthate

A powder of *N*-acetylchitosan (2.0 g, >80 mesh) was swollen by stirring in aq. 46% NaOH (7.6 ml) at room temperature for 3 h; the solution was adjusted to 25 ml by addition of pieces of crushed ice. A viscous aq. 14% NaOH solution of 8% alkaline *N*-acetylchitosan was obtained. 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. A small insoluble precipitate was filtered off through a sheet of cloth. A clear orange-red solution of 8% sodium *N*-acetylchitosan xanthate [*O*-(sodium thio)thiocarbonyl *N*-acetylchitosan] was obtained and used as a spinning solution for *N*-acetylchitosan fiber (1).

An aq. solution of sodium *N*-propionylchitosan xanthate

A powder of *N*-propionylchitosan (2.0 g, >80 mesh) was swollen by stirring in aq. 46% NaOH (10.0 ml) at room temperature for 10 h, and the solution was adjusted to 40 ml by addition of pieces of crushed ice. A viscous aq. 14% NaOH solution of 5% alkaline *N*-propionylchitosan was obtained. 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 cloth sheet. A clear orange-red viscous solution of about 5% sodium *N*-propionylchitosan xanthate [*O*-(sodium thio) thiocarbonyl *N*-propionylchitosan] was obtained and used as a spinning solution for *N*-propionylchitosan fiber (2).

A solution of sodium *N*-acetylchitosan xanthate mixed with sodium cellulose xanthate

An aq. 14% NaOH solution of 8% sodium *N*-acetylchitosan xanthate obtained above was mixed at room temperature with an aq. 5% NaOH solution of 9% sodium cellulose xanthate in the 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 homogenous solutions was used as a spinning solution for *N*-acetylchitosan-cellulose fibers.

A solution of *N*-propionylchitosan xanthate mixed with sodium cellulose xanthate

An aq. 14% NaOH solution of 5% sodium *N*-propionylchitosan xanthate obtained above was mixed at room temperature with an aq. 5% NaOH solution of 9% sodium cellulose xanthate in the 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 homogenous solutions was used as a spinning solution for *N*-propionylchitosan-cellulose composite fibers.

Spinning

The viscous spinning solution (20–25 ml) obtained above was degassed under diminished pressure for a few minutes, and put into an L-shaped glass tube (20 and 9 cm in length, 3 and 0.8 cm in diameter) connected with a viscose-type spinneret (12.5 × 18 × 0.3 mm, 300 holes and 0.1 mm in hole diameter, Japan Nozzle Co., Kobe) at the 0.8 mm diameter end. From the other end of the glass tube, a stream of air flowed at a low pressure with an air pump. 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 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. 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 to dehydrate it and air dried to obtain the corresponding white *N*-acylchitosan fiber having d.s. 1.0 for the *N*-acyl group.

N-Acetylchitosan fiber (1)
ν_{max}(KBr): 1657 and 1554 (C=O and NH of NAc) cm^{-1}. 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.

N-Propionylchitosan fiber (2)
ν_{max}(KBr): 1657 and 1554 (C=O and NH of *N*-propionyl) cm^{-1}. 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.

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

N-Propionylchitosan-cellulose composite fibers (4)
ν_{max}(KBr): 2650 and 1550 (C=O and NH of *N*-propionyl) cm^{-1}. Anal. N (%): 3.93 for fiber 4-1, 3.16 for fiber 4-2, and 0.19 for fiber 4-3, respectively.

HYDROLYSIS OF FIBERS BY CHITINASE

The filament was cut into pieces (shorter than 0.5 mm in length), and a portion (20 mg) of the filament pieces was suspended in 2 ml of 0.05M McIlvaine buffer solution (pH 6.8). 1 mg of chitinase from *Streptomyces griseus* (3 U/mg, Sigma) was added, and the mixture incubated at 37°C by mechanical shaking for 2 h. The reaction was stopped by heating in a boiling water bath for 5 min. The mixture was centrifuged at 1000 *g* for 10 min, and aliquots were withdrawn from the supernatant solution. The increase of the reducing-sugar value was analyzed by a modified Schales and Schales method (Imoto and Yagishita, 1971), and expressed as μmol of *N*-acetyl-D-glucosamine.

RESULTS AND DISCUSSION

Novel fibers of *N*-acylchitosan and their cellulose composite fibers were obtained, and all these fibers were white. The fibers showed C=O and NH absorptions of *N*-acyl group at 1650 and 1550 cm^{-1} in the FTIR spectra. A partial *N*-deacylation was found in the fibers as examined by the C/N ratio 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 fibers 1 and 2 revealed their d.s. to be 1.0 for *N*-acyl groups. Natural chitin is partially *N*-deacetylated, and partial *N*-deacetylation also occurs during the alkaline chitin preparation. The *N*-deacetylated portion present in the chitin fibers forms metal chelates and ionic salt complexes, resulting in weaker and colored textile fabrics. The *N*-acylchitosan and cellulose chains exist probably in a homogeneous state in the filament, because the mixed spinning solution was clear without any precipitate.

In *N*-acylchitosan-cellulose composite filament (Table 1), the denier value increased with an increase of *N*-acetylchitosan content but decreased with an increase of *N*-propionylchitosan content. In addition, the denier value was effected significantly at around 50% of *N*-acylchitosan content. The filament of fiber 3-2 (43% of *N*-acetylchitosan) showed denier value 1.5 times higher than that of cellulose filament, but filament 4-2 (49% of *N*-propionylchitosan) showed a lower denier value (about 1/6) than that of cellulose. The filament strength decreased with an increase of *N*-acetylchitosan content and decreased slightly with an increase of *N*-propionylchitosan content. The filament elongation also decreased with an increase of *N*-acetylchitosan, and decreased a little with an increase of *N*-propionylchitosan content. As shown in Table 2, fibers 1 and 2 were digested by chitinase. The hydrolysis rate of fibers 1 and 2 was similar to those of *N*-acetylchitosan and *N*-propionylchitosan powders. This indicates that the molecular interaction in *N*-acylchitosan filament is weaker than that in natural chitin and similar to that in the *N*-acylchitosan powder. *N*-Propionylchitosan fiber was about 11 times less hydrolyzable than *N*-acetylchitosan fiber because of enzyme substrate specificity

Table 1. Some properties of *N*-acylchitosan filament and its cellulose composite filament

Filament[a]	N (%)	*N*-Acyl-chitosan (%)[b]	Fineness as denier (g/9 m)	Dry	
				Strength (g/d)	Elongation (%)
1	6.40	93	nd	nd	nd
2	6.09	94	nd	nd	nd
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	3.18	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 filament (3-1, 3-2 and 3-3), and *N*-propionylchitosan-cellulose filament (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 fiber and 6.45% for *N*-propionylchitosan fiber.
[c]Cellulose fiber was prepared by spinning an aq. 5% NaOH solution of 9% sodium cellulose xanthate by the same procedure, and was used as a control.

Table 2. Hydrolysis of *N*-acylchitosan fibers by chitinase

Fiber[a]	Increase of reducing sugar value (μmol/2 h)
1	2.12
2	0.19
Crab shell chitin	0.20
N-Acetylchitosan	2.03
N-Propionylchitosan	0.20

[a] *N*-Acetylchitosan fiber (1) and *N*-propionylchitosan fiber (2).

(Hirano and Yagi, 1980). These novel fibers may be usable as novel natural functional fibers for fabrics including socks and underwear, because extracellular lysozyme activity is enhanced in contact with *N*-acylchitosan at cellular level and prevents pathogenic infections (Hirano, 1996).

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