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Carbohydrate Polymers 38 (1999) 293–298

Carbohydrate Polymers

Chitosan staple fibers and their chemical modification with some aldehydes

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Received 19 May 1998; received in revised form 9 September 1998; accepted 14 September 1998

Abstract

Nine wet-spinning conditions were examined for the preparation of chitosan staple fibers, and novel five *N*-alkylidene and *N*-arylidene-chitosan staple fibers were obtained by the post-treatment of the chitosan fibers with aldehydes including vanillin. The tenacity and elongation values of the chitosan filaments were almost unchanged by their post-treatment with monoaldehydes except that with formaldehyde and glyoxal. However, these values decreased significantly in the partially *N*-modified filaments, which were obtained by the pre-treatment with vanillin. The chitosan filaments (31–79 μm in diameter) had a scaly structure on the filament surface as examined by SEM observation. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Chitosan fibres; Glyoxal; Vanillin; *N*-alkylidene-chitosan fibres; *N*-arylidene-chitosan fibres

1. Introduction

Chitosan is a (1 → 4)-linked 2-amino-2-deoxy-β-D-glucan and generally prepared from chitin by chemical *N*-deacetylation. Cellulose has been used in the viscose rayon industry, but chitosan and chitin have not been much used in the textile industry. Chitosan fibers have been prepared by several investigators (Agboh and Qin, 1996) with use of aq. acetic acid and aq. acetic acid–polyethylene glycol as the spinning solvents, and aq. NaOH (Struszczyk et al., 1992, Struszczyk et al., 1994, and Nousianien, 1995; East et al., 1989, East et al., 1993; Wei and Hudson, 1994; Lipp-Symonowicz and Kowalska, 1994; Knaul and Creber, 1997), aq. $CuSO_4$-conc. ammonia (Tokura et al., 1987) and aq. NaOH–40% methanol (Urbanczyk, 1997) as the coagulating solvents. The development of new spinning and coagulating solvents as well as new technique is still important for the preparation of high quality chitosan fibers and their derived fibers.

The present work reports nine spinning conditions for the preparation of chitosan staple fibers, and some properties of novel *N*-arylidene- and *N*-alkylidene-chitosan fibers (Scheme 1) derived from the chitosan staple fibers.

2. Experimental

2.1. Materials

Crab shell chitosan (Katakura Chikkarin Co., Ltd., Tokyo) was purified in our laboratory and used in the present study: 1000 cps (MW 24 × 10^4) and $[\alpha]_D^{23}$ $-7°$ (*c* 0.5, aq. 2% acetic acid). Anal. Calc. for $[C_6H_{11}NO_4 \cdot 0.70H_2O]_n$: C, 41.47; H, 7.14; N, 8.06. Found: C, 41.76; H, 7.00; N, 7.78. Other three chitosan samples (D.S.$<$0.1 for *N*-acetyl) from Youngdeok Chitosan Co., Korea were also used, and their viscosity at 0.07 ~ 0.1 g/100 ml of aq. 2% acetic acid were 200–250 cps (MW ca. 14 × 10^4), 420 cps (MW ca. 18 × 10^4), and 520 cps (MW ca. 19 × 10^4), respectively. The molecular weights shown in the parentheses were estimated on the basis of the data on a viscosity-molecular weight relations reported by Hiroi et al. (1981) and Tokura (1995).

2.2. Methods

FT-IR spectra were recorded on a Jasco FTIR 5300 spectrometer (Jasco Co., Ltd., Tokyo), and specific rotations on a Jasco Dip-181 polarimeter (Jasco Co., Ltd., Tokyo). The filament titer (dtex) values at a dry condition were analyzed on a Vibroscop Micro (Lenzing Technic Instrument Co.

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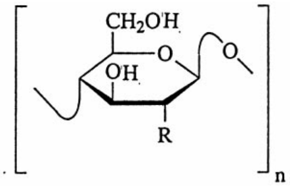
PII: S0144-8617(98)00126-X



Scheme 1. $R = -N{=}CHCH_2CH_3$ [1]; $-N{=}CH(CH_2)_2CH_3$ [2]; $-N{=}CHC_6H_5$ [3]; $-N{=}CHC_6H_4(OH)$ [4]; $-N{=}CHC_6H_3(OCH_3)(OH)$ [5].

Ltd., Austria), and the tenacity (g/dtex) and elongation (%) values on a Vibrodyn 400 (Lenzing Technic Instrument Co. Ltd., Austria). Elemental analyses were performed at the Micro-analytical Center of Kyoto University, Kyoto. DS values for *N*-substituents were based on the elemental analysis data. Scanning Electron Microscopic (SEM) analyses were performed on a scanning electron microscope (JSM-6301F), Jeol. Ltd., Tokyo.

2.3. Preparation of N-(4′-hydroxy-3′-methoxybenzylidene) chitosan

Chitosan (0.8 g) was dissolved in 90 ml of aq. 2% acetic acid–methanol (1:2, v/v). To the solution was added vanillin (2.75 g, 3.6 moles/GlcN), which had been previously dissolved in methanol (10 ml). The mixture was kept at room temperature overnight to afford a yellow hydrogel. The gel was homogenized mechanically, and the homogenate was collected by filtration, washed with water and methanol several times, and air-dried to afford a dark yellow product in yield 1.28 g (87%); $\nu_{\max}^{\mathrm{KBr}}$ 1640(C=N), ∽1050 (C–O), 750 (vicinal trisubst. phenyl) cm^{-1}. Anal. Calc. for $[C_6H_9NO_4(C_8H_8O_2)_{0.87}(H)_{0.13}\cdot 0.44H_2O]_n$: C, 54.47; H, 5.99; N, 4.90. Found: C, 54.41; H, 6.20; N, 4.91.

2.4. Spinning of chitosan staple fibers

Chitosan (0.5 g) was dissolved in aq. 2% acetic acid (5 ml) by occasional stirring at room temperature overnight. The viscous solution was diluted with methanol (10 ml) for the tests of the spinning conditions A, C, E and G, and with aq. 2% acetic acid (10 ml) for the tests for the spinning conditions B, D, F and H (Table 1). Air bubbles in the solution were removed by mechanical stirring at a reduced pressure, and the solutions were allowed to remain at room temperature overnight for aging. Each of the clear chitosan solutions (ca. 3% concentration) was used as a dope for the present fiber spinning.

The dope was spun as previously described (Hirano et al., 1997; Hirano and Midorikawa, 1998) through a viscose-type spinneret (hole number 300, hole diameter 0.15 mm, Japan Nozzle Company, Kobe) into a coagulation bath at 30°C–40°C containing each of the two coagulating solvents (Table 1). The produced filaments were stretched to 1.2–1.4-fold in aq. 2% NaOH–ethyleneglycol at room temperature, and cut into about 25 cm-length. The staple fibers were kept in aq. 10% NaOH–30% sodium acetate solution for one day, washed several times with deionized water, and dried by the two methods: A portion of the filaments was suspended in 100% methanol at room temperature overnight, mechanically pressed, and air-dried to afford opaque cotton-like chitosan staple fibers (the drying treatment A). The other portion of the filaments was suspended in aq. 30% methanol and then in aq. 50% methanol overnight, respectively, and air-dried on stretching to afford transparent chitosan staple fibers (the drying treatment B). Table 1 shows some mechanical properties of the chitosan filaments, which were prepared under these nine spinning conditions.

2.5. Chemical N-modification of the chitosan filaments with aldehydes

The chitosan fibers, which were obtained under the spinning conditions C by the drying treatment B (Table 1), were used throughout the present study. The dry chitosan filaments (0.3 g) were suspended in methanol (20 ml), and air-bubbles present on the filament surface were removed by stirring under a reduced pressure for a few seconds. Each 10 moles/GlcN of formaldehyde, glyoxal, propionaldehyde, *n*-butrylaldehyde, benzaldehyde, 2-hydroxybenzaldehyde, and vanillin was added. After string at room temperature for a few minutes, the mixture was allowed to remain at room temperature overnight. The filaments thus treated were washed several times with methanol, air-dried, and used for the elemental and FT-IR analyses. The *N*-modified

Table 1
Spinning conditions and some-mechanical properties of the chitosan filaments obtained by the drying treatment A

	Solvents		Stretching	Filaments		
	Spinning	Coagulating		Titer (dtex)	Tenacity (g/dtex)	Elongation (%)
A	aq. 2%AcOH–MeOH	aq. 10%NaOH–30%AcONa	no	10.0	1.27	13.0
B	aq. 2%AcOH	aq. 10%NaOH–30%AcONa	no	14.9	0.68	12.6
C	aq. 2%AcOH–MeOH	aq. 10%NaOH–30%AcONa	yes	4.16	1.43	17.3
D	aq. 2%AcOH	aq. 10%NaOH–30%AcONa	yes	8.43	0.87	23.0
E	aq. 2%AcOH–MeOH	aq. 10%NaOH–30%Na_2SO_4	no	8.98	0.73	13.6
F	aq. 2%AcOH	aq. 10%NaOH–30%Na_2SO_4	no	8.84	0.98	21.4
G	aq. 2%AcOH–MeOH	aq. 10%NaOH–30%Na_2SO_4	yes	7.07	1.38	16.5
H	aq. 2%AcOH	aq. 10%NaOH–30%Na_2SO_4	yes	10.2	1.17	28.1
I	aq. 2% oxalic acid	aq. 10%NaOH–30%AcONa	no	6.21	0.85	15.1

Table 2
Effect of the molecular weight of chitosan on its filament mechanical properties

Molecular weight(x10^4)	Chitosan filament[a]		
	Titer (dtex)	Tenacity (g/dtex)	Elongations (%)
14	3.91	0.79	11.7
18	5.44	0.84	10.4
19	4.44	0.98	9.4
24	5.00	1.10	11.2

[a] Prepared under the spinning A conditions by the drying treatment B.

chitosan fibers were also obtained from the chitosan staple fibers, which were obtained by the drying treatment A (the data are not shown).

1. *N*-Propylidenechitosan fibers (1) $\nu_{\max}^{\mathrm{KBr}}2889(\mathrm{C-H})$, 1640 (C=N for the Schiff base), and ∽ 1050 (C–O) cm^{-1}. Anal. Calc. for $[C_6H_9NO_4(C_3H_6)_{1.00}\cdot\ 0.84H_2O]_n$: C, 49.97; H, 7.72; N, 6.48. Found: C, 50.07; H, 7.83; N, 6.48.
2. *N*-n-Butyridenechitosan fibers (2) $\nu_{\max}^{\mathrm{KBr}}2890(\mathrm{C-H})$, 1640 (C=N for the Schiff base), and ∽ 1050 (C–O) cm^{-1}. Anal. Calc. for $[C_6H_9NO_4\ (C_4H_8)_{0.97}\ (H)_{0.03}\ \cdot 0.48H_2O]_n$: C, 53.41; H, 8.00; N, 6.31. Found: C, 53.37; H, 8.13; N, 6.22.
3. *N*-Benzylidenechitosan fibers (3) $\nu_{\max}^{\mathrm{KBr}}2889(\mathrm{C-H})$,1640 (C=N for the Schiff base), 750 and 700 (mono subst. Phenyl), and ∽ 1050 (C–O) cm^{-1}. Anal. Calc. for $[C_6H_9NO_4\ (C_7H_6)_{0.92}\ (H_2)_{0.08}\ \cdot 0.81\ H_2O]_n$: C, 58.19; H, 6.35; N, 5.46. Found: C, 58.37; H, 6.13; N, 5.42.
4. *N*-2-Hydroxybenzylidenechitosan fibers (4) $\nu_{\max}^{\mathrm{KBr}}2889(\mathrm{C-H})$,1640 (C = N for the Schiff base), 755 (ortho subst. Phenyl), and ∽ 1050 (C–O) cm^{-1}. Anal. Calc. for $[C_6H_9NO_4\ (C_7H_6O)_{\cdot 0.81}\ (H_2)_{0.19}\ \cdot 0.59\ H_2O]_n$: C, 54.73; H, 6.03; N, 5.47. Found: C, 54.73; H, 6.03; N, 5.42.
5. *N*-(4′-Hydroxy-3′-methoxybenzylidene)chitosan fibers (5) $\nu_{\max}^{\mathrm{KBr}}$ 1640 (C=N for the Schiff base), 750 (vicinal subst. Phenyl), and ∽ 1050 (C–O) cm^{-1}. Anal. Calc. for $[C_6H_9NO_4\ (C_8H_8O_2)_{0.79}\ (H_2)_{0.21}\ \cdot 0.20\ H_2O]_n$: C, 54.66; H, 5.97; N, 5.18. Found: C, 54.56; H, 6.10; N, 5.12.

2.6. Spinning of partially N-modified fibers after the pre-treatment of chitosan with vanillin

To a solution of chitosan (0.8 g) in 24 ml of aq. 2% acetic acid–methanol (1:2, v/v was added a sample [0.16 g (0.2 mole/GlcN for 6 and 0.32 g (0.4 moles/GlcN) for 7] of vanillin, which had been previously dissolved in methanol (1 ml). After stirring for a few minutes, the mixed solution was allowed to remain at room temperature overnight to afford a yellow solution, and the solution was spun as described above. No hydrogel appeared even after standing at room temperature for one day under the present low molar ratios of vanillin per GlcN.

1. *N*-(4′-Hydroxy-3′–methoxybenzylidene) chitosan fibers (6) $\nu_{\max}^{\mathrm{KBr}}1640$ (C=N for the Schiff base), 755 (vicinal subst. Phenyl), and ∽ 1050 (C–O) cm^{-1}. Anal. Calc. for $[C_6H_9NO_4(C_8H_8O_2)_{0.18}\ (H_2)_{0.84}\ \cdot 0.36H_2O]_n$: C, 46. 24; H, 6.71; N, 7.41. Found: C, 46.36; H, 6.70; N, 7.37.
2. *N*-(4′–Hydroxy–3′–methoxybenzylidene) chitosan fibers (7) $\nu_{\max}^{\mathrm{KBr}}1640$ (C=N for the Schiff base), 750 (vicinal subst. Phenyl), and ∽ 1050 (C–O) cm $- {}^{1}$. Anal. Calc. for $[C_8H_9NO_4(C_8H_8O_2)_{0.38}\ (H_2)_{0.64}\ 0.45H_2O]_n$ C, 49.03; H, 6.47; N, 6.44. Found: C, 49.06; H, 6.50; N, 6.42.

3. Results and discussion

3.1. Spinning solvents

Chitosan solution in aq. Acetic acid was very viscous and miscible with methanol without any precipitates (Hirano et al., 1976). The dilution of the viscous chitosan solution with methanol remarkably reduced the viscosity and gave a chitosan solution in a homogenous molecular distribution at a proper viscosity fro spinning ($>$ 3% chitosan). The chitosan solution in aq. 2% acetic acid–methanol (1:1, v/v) is considered to be one of the excellent spinning solvents for the preparation of chitosan filaments.

3.2. Properties of chitosan fibers

Chitosan staple fibers, which were prepared under nine spinning conditions A–I (Table 1) and obtained by the drying treatment B, had the following mechanical properties:

- the chitosan filaments, which were prepared from the chitosan solution in aq. 2% acetic acid–methanol, had slightly higher tenacity values and slightly lower elongation values than those prepared from the chitosan solution in aq. 2% acetic acid only,
- the elongation and tenacity values of the chitosan filaments were little influenced with the coagulating solvents of aq. 10% NaOH–aq. 30% Na_2SO_3 and aq. 10% NaOH–aq. 50% sodium acetate,
- both the tenacity and elongation values increased slightly by the stretching treatment in an aq. 2% NaOH–ethyleneglycol solution, and

Table 3
Degree of *N*-substitution and some mechanical properties of *N*-arylidene and *N*-alkylidene-chitosan filaments[a]

Filaments	D.s. for *N*-subst.	Titer(dtex)	Tenacity(g/dtex)	Elongation(%)
Chitosan[b]	0	4.16	1.43	17.3
1	1.0	5.49	1.25	12.9
2	1.0	4.90	1.10	14.5
3	0.9	5.91	1.18	17.2
4	0.8	6.30	1.25	15.6
5	0.8	4.36	1.60	13.7
6	0.2	4.18	0.46	1.8
7	0.4	6.88	0.22	1.5

[a] Obtained by the drying treatment B.
[b] Obtained by the spinning condition C.

- the chitosan filaments, which were prepared from a solution in aq. 2% oxalic acid (the spinning condition 1) as the spinning solvent, had an essentially similar mechanical properties to those prepared from aq. acetic acid solution (Hirano et al., 1990).

All the present chitosan fibers were white and stable in water and aq. alkaline solutions, but unstable and soluble in aq. acidic solutions. The drying treatment A gave the cotton-like chitosan staple fibers, which were shrunk to about 1/3 over the original filaments in length. The drying treatment B gave the chitosan staple filaments, which were kept almost the original length with little shrinkage. The chitosan filaments as obtained by the drying treatment A had the tenacity (0.58–0.88 d/dtex) and elongation (4.9%–8.0%) values, and those as obtained by the drying treatment B had the tenacity (0.68–1.43 g.dtex) and elongation (12.6%–28.1%). In general, the filaments obtained by the

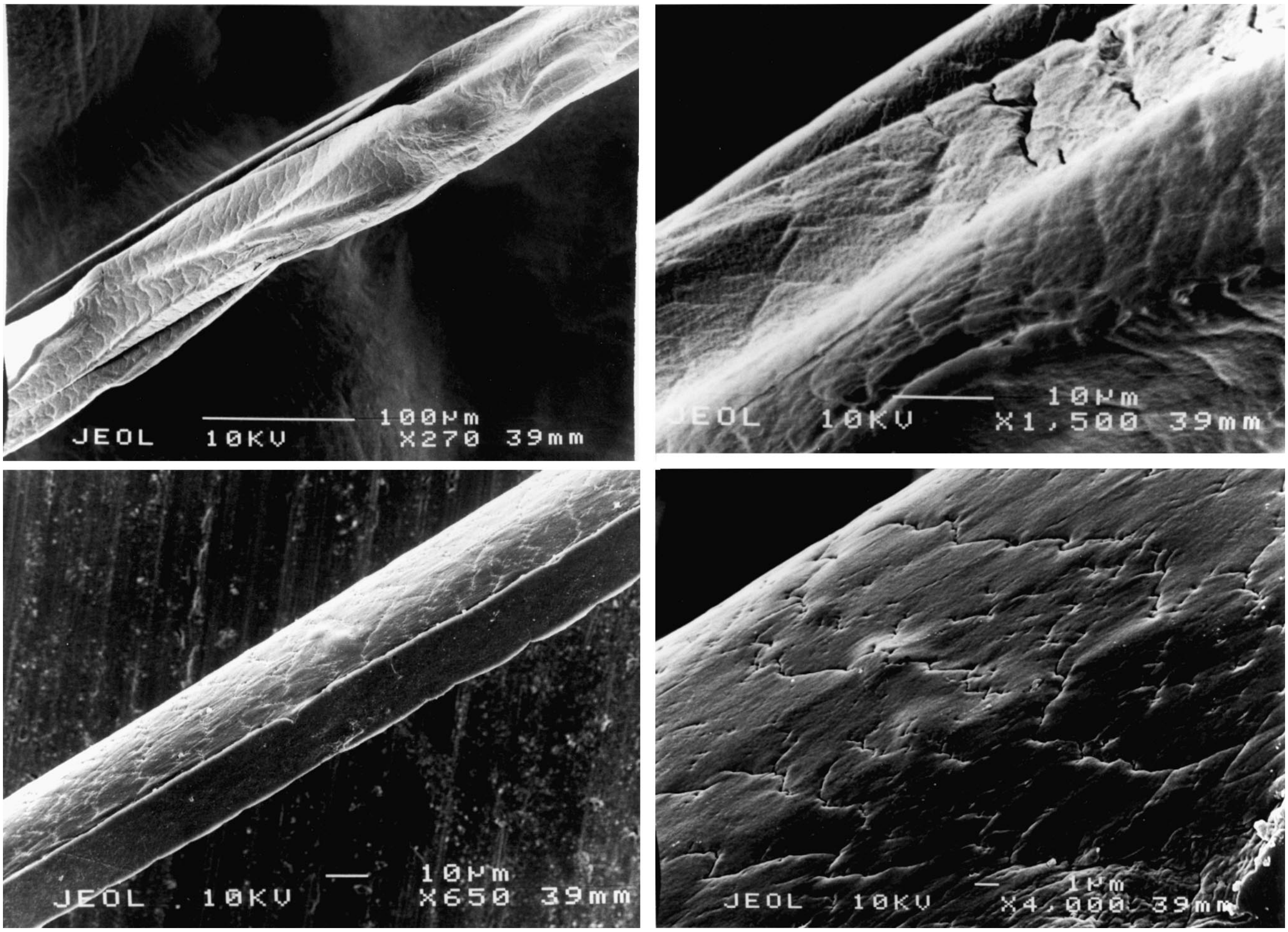


Fig. 1. SEM photographs of chitosan filaments. A chitosan filament (79 μm in diameter) obtained by the drying treatment A (up) and a chitosan filament (31 μm in diameter) obtained by the drying treatment B (down)

drying treatment B gave better mechanical properties than those obtained by the drying treatment A.

The tenacity values of the chitosan filaments increased slightly with increase of the molecular weight of chitosan, but the elongation values were little influenced (Table 2).

3.3. Properties of N-arylidene-and N-alkylidene-chitosan fibers

In the *N*-modified chitosan filaments as obtained by the post-treatment of chitosan filaments with each of propion-, n-butyl-, benz-, 2-hydroxybenz- and 4-hydroxy- 3-methoxybenz-aldehydes (see 2.5), the d. s. values for the Schiff's base in the fibers were 0.8–1.0 as analyzed by the elemental analyses. Fibers 1–4 were white, and 5 was yellow. FT-IR spectra of these fibers were identical with those prepared from chitosan by treatment with the corresponding mono-aldehydes in aq. acetic acid–methanol (Hirano, 1997). These data indicate that amino groups not only on the filament surface but also within the filament are modified under the present conditions. The chitosan filaments seem to have a porous structure inside, in which aldehyde and methanol molecules pass through. Both the tenacity and elongation values of the filaments (1–5) were little effected by the post-treatment of the chitosan filaments with aldehydes examined, but were drastically weakened by the post-treatment of the chitosan filaments with each of formaldehyde and glyoxal (Table 3). In the reaction of the chitosan filaments with these aldehydes, new cross-linked structures are produced as–NH–CH_2–NH– for formaldehyde and as–N = CH–HC=N– for glyoxal (Hirano and Takeuji, 1983) in the filaments, and the original molecular arrangement is probably hindered, resulting in the breakable filaments. The *N*- (4′-hydroxy-3′-methoxy benzylidene) chitosan filaments obtained by the pre-treatment of chitosan with vanillin were yellow for 6 (d. s. 0.2 for the Schiff base) and dark yellow for 7 (d. s. 0.4 for the Schiff base). The color seems to enhance with an increase of the d. s. value of 4-hydroxy-3-methoxybenzylidene group. However, both the tenacity and elongation values were very weak (Table 3). The *N*-(4′-hydroxy-3′-methoxy-benzylidene) chitosan as well as its fibers (5–7) were giving off vanilla aroma for more then 6 months in the open air at room temperature. Vanillin is known as a flavoring agent in confectionery, beverages, food and perfumery. The resultant fibers obtained were stable in water and aq. alkaline solutions, but unstable and soluble in aq. acid solutions.

3.4. A SEM observation of the surface structure of the chitosan filaments

A scaly and slightly rough structure appeared on the surface of both the chitosan filaments (78–79 μm in diameter) obtained by the drying treatment A, and the stretched filament (31–33 μm n diameter) obtained by the drying treatment B (Fig. 1). However, the scaly structure was slightly smooth on the stretched filament surface. The scaly structure on the surface of the filament is considered to be formed during the dehydration and neutralization processes of the filaments.

4. Conclusion

Relatively good mechanical chitosan staple fibers were obtained from a chitosan (MW 24 × 10^4) solution at > 3% concentration in aq. 2% acetic acid–methanol by spinning into a coagulating solution of aq. 10% NaOH–aq. 30% sodium acetate or aq. 10% NaOH–aq. 30% Na_2SO_4, followed by stretching in aq. 2% NaOH–ethyleneglycol with the drying treatment B. Amino groups not only on the chitosan filament surface but also in their inside were *N*-modified by treatment with mono-aldehydes to afford the novel *N*-arylidene- and *N*-alkylidene-chitosan fibers (d. s. 0.8–1.0 for the Schiff's base). The tenacity and elongation values of filaments were little effected by the post-treatment of the chitosan fibers with aldehydes examined except for formaldehyde and glyoxal, but was drastically weakened by the pre-treatment. The post-treatment method of chitosan fibers with aldehydes is widely usable for the preparation of novel functional *N*-modified chitosan fibers, which are difficult to prepare by their direct spinning because the original mechanical properties of the chitosan filaments were kept even after the *N*-modification.

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