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Preparation of chitosan filament applying new coagulation system

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Abstract

A new coagulation system for chitosan, aqueous alcohol solution of calcium chloride or acetate, was found and successfully applied for spinning of chitosan filament. FT-IR and atomic absorption spectrophotometric experiments indicated that chitosan coagulation was induced through calcium chelation with amino group of chitosan molecule. The original spun filament was soluble in water because chitosan exists as an acetic acid salt form. Among several treatments, diluted sodium hydroxide aqueous solution eliminated acetate as well as calcium ion. Obtained filament showed excellent properties. The present coagulation system, essentially a mild and safe has an advantage over the conventional hazardous system which were based on the copper ammonium or xanthate systems.

Keywords: Chitosan; Filament; Spinning; Tensile strength

1. Introduction

The preparation of chitosan filament has been studied only under drastic conditions such as concentrated alcolart or copper ammonium solution (Tokura et al., 1987). However, these coagulation systems were too drastic and harmful to apply for biomedical purpose due to toxicity regulations together with environmental aspects. Thus, much milder coagulation system has been requested to clear the biomedical safety regulation and environmental pollution.

On the process to prepare chitin solution applying calcium chloride dihydrate saturated methanol solution, the solubility of chitin has been found to be suppressed remarkably by the increment of degree of deacetylation of chitin molecule (Shirai, Takahashi, Rujiravant, Nishi, & Tokura, 1995). Since calcium chloride dihydrate saturated methanol is cosolvent for nylon 6 or nylon 6.6, solubility of chitin against the solvent is assumed to depend on the calcium ion chelation toward amide bonds to cleave hydrogen bond network between molecules. A predominant interaction of calcium ion toward amino groups on chitosan molecule was found to reduce the solubility of chitin with lower degree of acetylation. The result suggests that calcium ion is a quite excellent component of coagulation system for chitosan. We have already reported about wet spinning using calcium chloride as a coagulation system, such as phosphoryl-chitin-alginate mixed filament (Tokura & Tamura, 2001) and chitosan coated alginate filament (Tamura & Tokura, 2002).

Thus, calcium chloride or calcium acetate saturated water–methanol (1:1 v/v) was first found in this study to be a better coagulation solvent to prepare chitosan filament than former coagulation systems as a much milder coagulation system. Ethanol was also applied successfully to coagulate chitosan filament instead of methanol owing to biomedical safety aspect. Chelated calcium ion was eliminated in dilute sodium hydroxide aqueous solution without reduction of tensile strength.

2. Experimental

2.1. Materials and reagents

Chitosan was prepared from Queen Crab shells according to slightly modified method reported by Hackman (1958). The degree of acetylation (DA) was 6.5%, which

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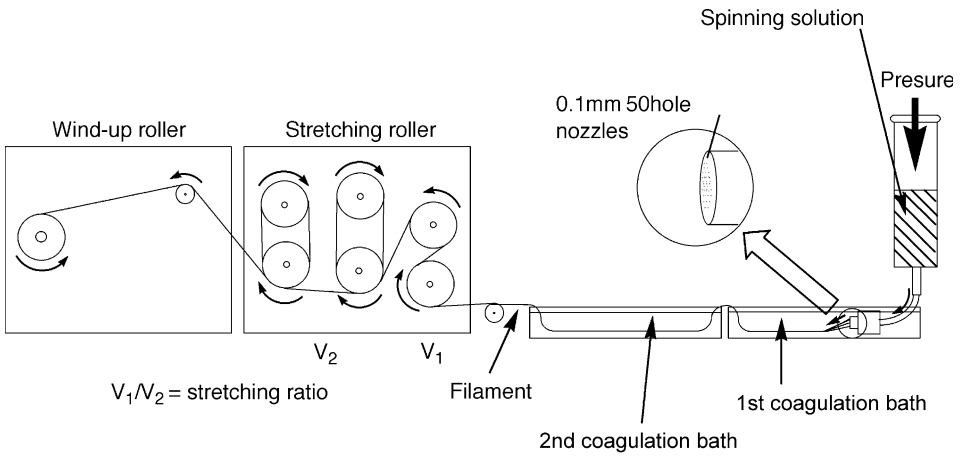

Fig. 1. Spinning apparatus for chitosan filament.

was estimated from infrared absorption spectrum method reported by Sannnan, Kurita, Ogura, and Iwakura (1978). Chemicals were purchased from Wako Pure Chemical Co. Ltd and used without further purification.

2.2. Dope and coagulation solution

Chitosan dope solution was prepared by dissolving 10 g of chitosan powder in 100 ml of 10% aqueous acetic acid solution under vigorous agitation followed by filtration through flannel. The viscous solution was stand for overnight to debubble.

A 100 g of calcium chloride or calcium acetate was suspended in water–methanol (or ethanol) = 1:1(v/v) mixture and refluxed for 1 h to prepare calcium chloride saturated aqueous methanol (or ethanol) followed by cooling down of viscous solution to room temperature as first coagulation bath. Second coagulation bath was composed of 50% aqueous methanol or ethanol depending on the composition of first coagulation bath.

2.3. Spinning of filament

Spinning of chitosan filament was achieved at room temperature using the spinning system shown in Fig. 1. The rate of first windup roller was 6.3 m/min under the pressure of 0.6–0.8 kg/cm^2 applying stainless steel nozzle (3 cm of diameter) with 0.1 mm$\phi \times 50$ holes. The stretching was performed under wet state at the ratio of 1.0–1.2. Chitosan filament on cassette was treated immediately with various conditions as listed in Table 1. After the treatment, chitosan filament on cassette was washed with distilled water and finally dried in air.

2.4. Tensile strength

The stress–strain diagram of the filament was measured by the JIS (Japanese Industrial Standard) 1013-7.5 and 7.6 methods using Tensilon RTA-250 apparatus. This method is equivalent to ISO 2062. The initial sample length was 20.0 mm and stretching rate was 20.0 mm/min. The force at the breaking point was measured as tensile stress, which was transferred to tensile strength.

2.5. Measurements

Calcium content in chitosan filament was estimated by Hitachi Z-500 atomic absorption spectrophotometer. JEOL JSM-6100 scanning electron microscope was applied to check filament surface. FT-IR spectra were measured with Perkin Elmer 1600 series using KBr method. X-ray diffraction spectra were measured Rigaku R-Axis series. The X-rays were generated at 40 kV and 60 mA using nickel-filtered Cu Kα radiation.

3. Results and discussion

3.1. Coagulation of chitosan filament

The spinning of chitosan filament was proceeded smoothly in calcium salt saturated 50% aqueous alcohol solution, although stacking of chitosan gel to nozzle became serious by the reduction of water content under the same calcium concentration. The use of calcium acetate for

Table 1
Treatment condition of chitosan filaments

Treatments	Solvent (H_2O:MeOH)	Treatment time (h)	Water solubility[a]
No			+
5w/v% EDTA	1:1	5	−
3w/V% Na_2HPO_4	1:1	5	−
0.8w/v% NaOH	1:9[b]	5	±
0.8w/v% NaOH	1:9[b]	48	−

[a] +, soluble; ±, swelling; −, insoluble.
[b] H_2O:MeOH or H_2O:EtOH.

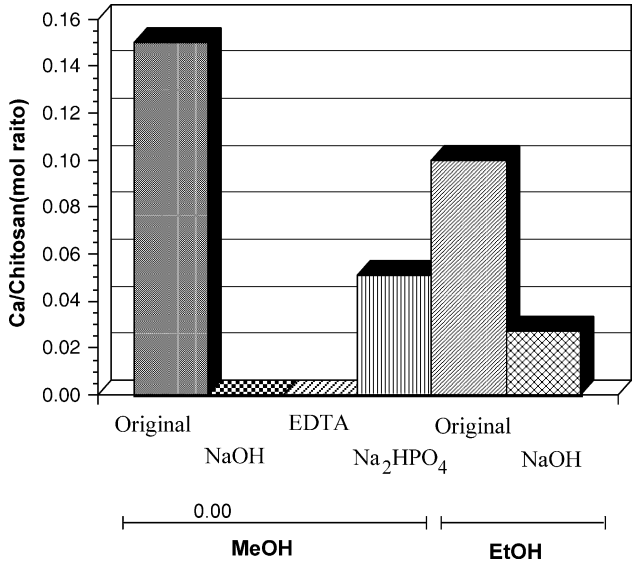

Fig. 2. Calcium ion content of original and treated chitosan filaments.

coagulation system is preferable to avoid chloride effect. Calcium chloride saturated 50% aqueous ethanol system was also applied successfully for the coagulation of chitosan. This system would have an advantage to apply for biomedical purpose due to non-harmful condition throughout the spinning. Chitosan concentration of 10 w/v% for dope solution and calcium chloride saturated 50% aqueous alcohol solution for coagulation system are highly recommended for the perfect coagulation and stable spinning of filament using the present chitosan ($MW = 4 \times 10^4$, $DA = 6.5\%$). In the calcium chloride dihydrate saturated methanol system, obtained filament was light-yellow, water soluble and rather low tenacity (13–15 dTex).

3.2. Treatment of filament

The filament right after the spinning (original filament) was water soluble and very weak. Since atomic absorption spectrophotometric analysis indicated the existing of calcium ion in the filaments probably due to the chelation with amino group of chitosan, several aqueous alcohol solutions were applied to remove calcium ion (Table 1). Although filament became insoluble under 5-h treatment with EDTA·4Na (Tetra-sodium ethylene diamine tetra-acetic acid) and sodium hydrogen phosphate (Na_2HPO_4), much longer treatment (48 h) was necessary using diluted sodium hydroxide (NaOH) solution. Fig. 2 shows the calcium ion content in the original and variously treated filaments. The original

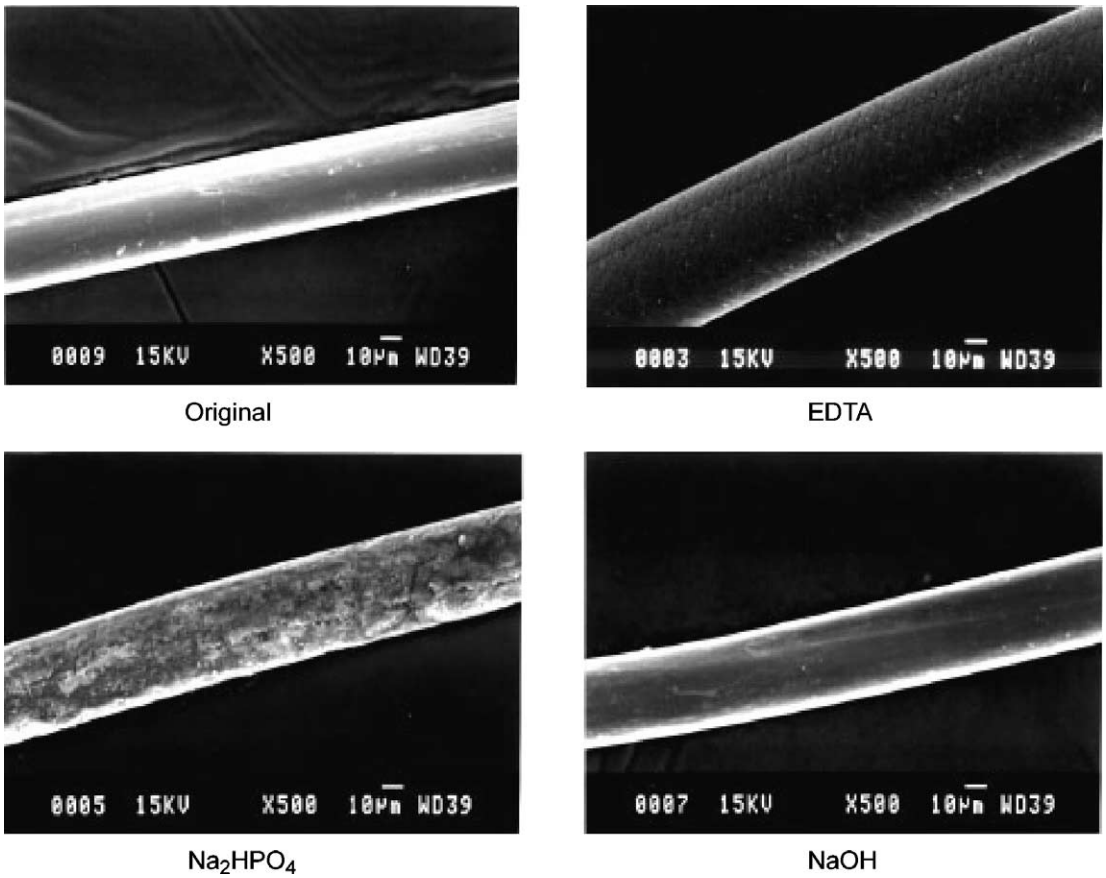

Fig. 3. SEM images of original and treated chitosan filaments.

filament contains a calcium ion against seven units of glucosamine residues. Although calcium ion was completely eliminated by the NaOH and EDTA treatments, one third of the calcium ion remained in the Na_2HPO_4 treated filament. In this case, fine crystal particles were formed on the surface of the filament observed by SEM analysis (Fig. 3). The identification of the material is now under way. The calcium content in the original filament spun in the calcium chloride saturated 50% aqueous ethanol system was two third of the methanol system. However, complete elimination of calcium ion was unsuccessful even after NaOH treatment.

Raw material chitosan and filaments treated under several conditions were further analyzed by the FT-IR spectroscopy (Fig. 4). Strong absorption peaks (1520 and 1620 cm^{-1}) for the original filament were identified as calcium salt and acetic acid salt form of chitosan, respectively. When original chitosan filament was heated in isopropanol according to Toffey and Glasser (2001),

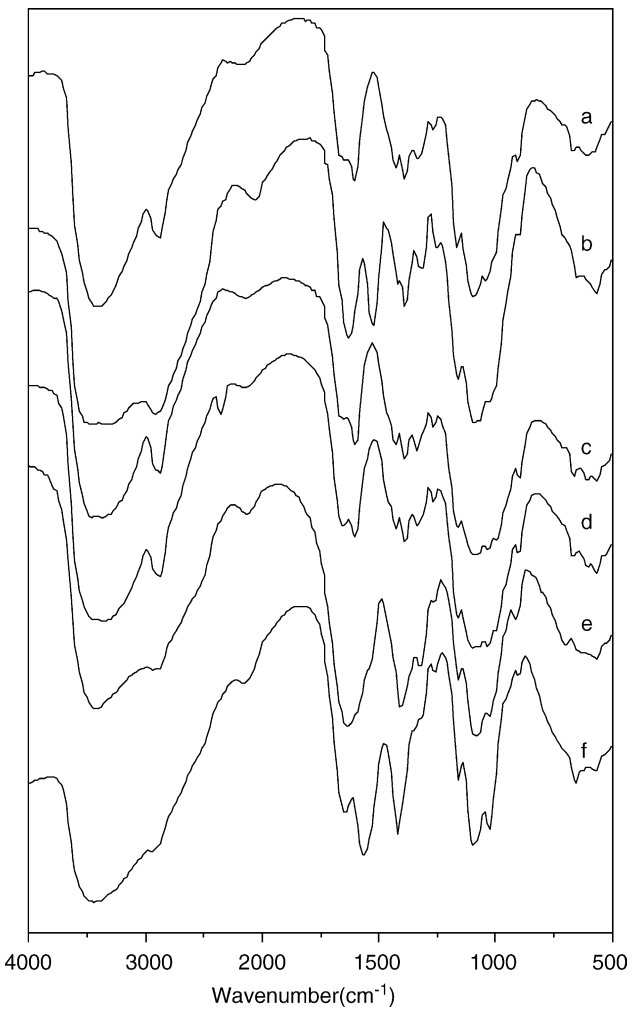

Fig. 4. FT-IR spectra of chitosan filaments. (a) chitosan powder; (b) original chitosan filament; (c) chitosan filament treated with NaOH; (d) chitosan filament treated with Na_2HPO_4; (e) chitosan filament treated with EDTA; and (f) acetic acid form of chitosan.

degree of *N*-acetylation was increased from 6.5 to 25%. The result strongly supports that acetic acid salt form of amino group might contribute to the acetylation reaction. Most effective elimination of acetic acid was found by the treatment with NaOH, because the spectrum pattern was completely the same as that of original filament (Fig. 4(a) and (c)). EDTA treated filament showed strong absorption peaks (1620 and 1436 cm^{-1}) similar to the acetic acid form of chitosan (Fig. 4f) and original chitosan filament. These peaks might be attributed to the EDTA salt or acetic acid/EDTA mixed salt form, since calcium was completely eliminated by the EDTA treatment. Such elimination and replacement reactions may bring the characteristic SEM features of EDTA treated filament (thick diameter and the rough surface).

X-ray fiber images are shown in Fig. 5. The images of NaOH and Na_2HPO_4 treated filaments were characteristic for anhydrous type chitosan crystalline structure ($2\theta = 14.8°$ (110) and $2\theta = 20.8°$ (200)) (Yui, Imada, Okuyama, Obata, Suzuki, & Ogawa, 1994). Although SEM observation revealed fine crystal particle formation on the surface of the filament treated with Na_2HPO_4 (Fig. 3), there was no peak attribute to the hydroxy apatite or calcium phosphate because of the small amount of the product surrounding the filament. XRD image of chitosan filament treated with NaOH showed extremely high orientation of chitosan molecules compared with other treated filaments, probably due to the complete elimination of acetate and calcium ion.

3.3. Strengths of chitosan filament

Tensile and knot strengths of the filament were measured using Tensilon RTA-250 apparatus both in dry and wet states. The results are shown in Tables 2 and 3. As shown in Table 2, the chitosan filament prepared under milder condition showed almost similar properties with those prepared by previous method (Tokura et al., 1987). Tensile strengths of filaments treated with NaOH and Na_2HPO_4 in dry state were 1.18 and 0.72 cN/dTex, respectively, which were improved in two to three times compared with the original chitosan filament (0.39 cN/dTex). The improvement of the filament properties may be caused by the tight interaction of chitosan molecules by the elimination of chelated calcium ion as well as acetate from the original filament. Contrary, tensile strength of filament treated with EDTA was declined to 0.31cN/dTex, in which the filament was thick with several holes on the surface. All of the tensile strengths of filaments in wet state were declined compared to those in dry state. The original filament was unable to measure the strength since this filament dissolved in water. Amino group of original chitosan filament was *N*-reacetylated (DA = 25%) in isopropanol medium. Only a slight increase of *N*-acetyl group caused a drastic improvement of tensile strength probably due to the stronger hydrogen bond between *N*-acetyl group.

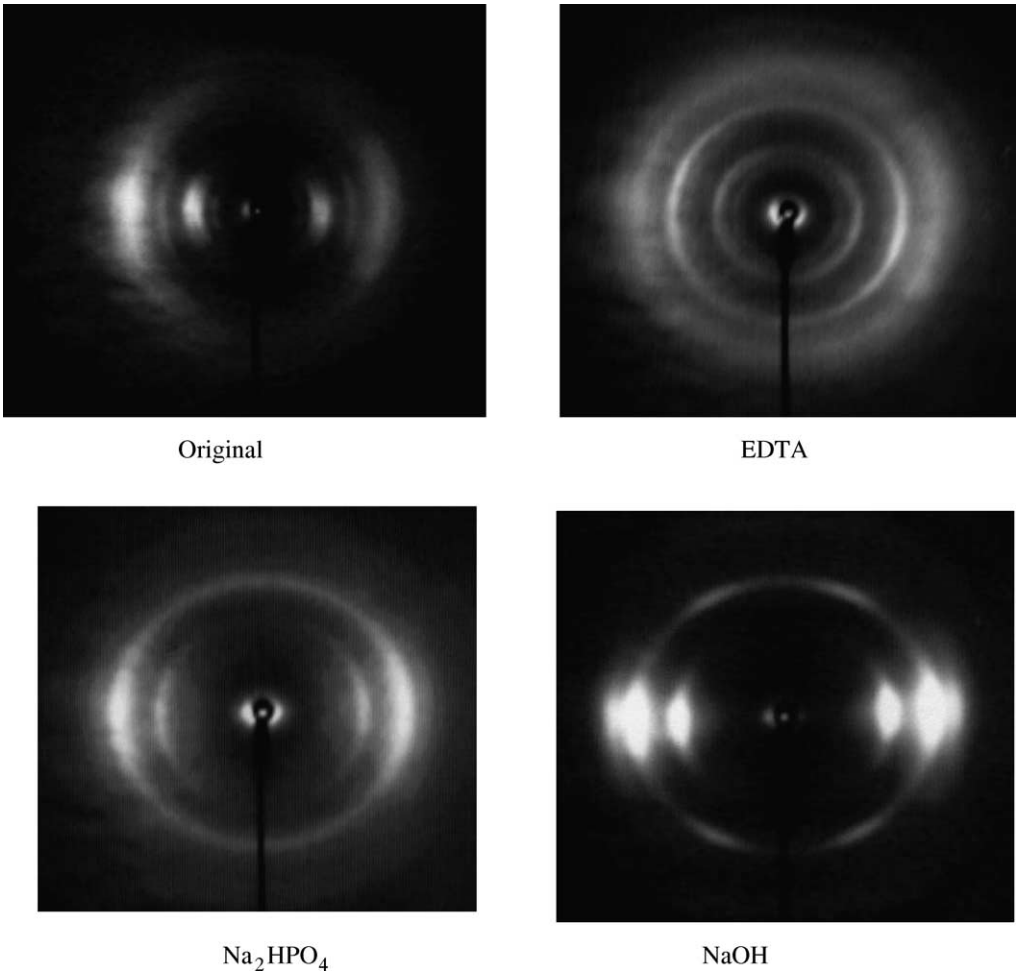

Fig. 5. X-ray fiber images of original and treated chitosan filaments.

Knot strength is an important characteristic factor for filament because this character reflects practical purpose such as stretching, compressing, bending and torsion. In the present study, knot strength of the filaments in dry state decreased compared with that of the original filament except the Na_2HPO_4 treated filament. In the wet state, Na_2HPO_4 treated filament showed highest strength and NaOH treated one also showed higher strength than that in dry state. The result is very interesting since the strength of conventional filament in wet state is weaker than that in dry state. The tendency is also interesting for the biomedical usage where the material is always used in wet state. These properties are summarized as a wet/dry ratio as shown in Fig. 6. The ratios in the knot strength were larger than that in the tensile strength. Especially, the strength of NaOH treated filament in wet state was about two times stronger than that in dry state. The progress of wet-dry ratio in knot strength might suggest the high orientation of chitosan molecules. Although tensile strength was improved in the reacetylated original chitosan filament in the dry state, no improvement was observed on knot strength in dry state. However, comparing the wet-dry ratio as a measure of strengths between dry and wet state, knot strength exceeded than tensile strength. The results suggest that the present chitosan and reacetylated filaments are preferable in the practical purpose in wet state.

Table 2
Tensile strength of chitosan filaments

Sample	Tenacity (dTex)	Dry		Wet	
		Strength (cN/dTex)	Elongation (%)	Strength (cN/dTex)	Elongation (%)
Original	12.04	0.39	11.34	–	–
NaOH	3.86	1.18	6.65	0.55	4.28
EDTA	22.08	0.31	7.66	0.01	–
Na_2HPO_4	14.22	0.72	16.02	0.28	13.93
Acetylated[a]	6.03	0.92	9.61	0.32	3.36
Previous[b]	7.10	1.80	29.6	0.88	33.1

[a] Original filament was refluxed in isopropanol for 5 h. DA = 25%.
[b] Tokura et al., 1987.

Table 3
Knot strength of chitosan filaments

Sample	Tenacity (dTex)	Dry		Wet	
		Strength (cN/dTex)	Elongation (%)	Strength (cN/dTex)	Elongation (%)
Original	12.04	0.18	17.89	–	–
NaOH	3.86	0.08	9.56	0.16	11.63
EDTA	22.08	0.15	26.18	0.02	–
Na_2HPO_4	14.22	0.29	13.55	0.28	23.12
Acetylated[a]	6.03	0.08	16.91	0.1	12.48
Previous[b]	7.10	1.53	–	5.53	–

[a] Original filament was refluxed in isopropanol for 5 h. DA = 25%.
[b] Tokura et al., 1987.

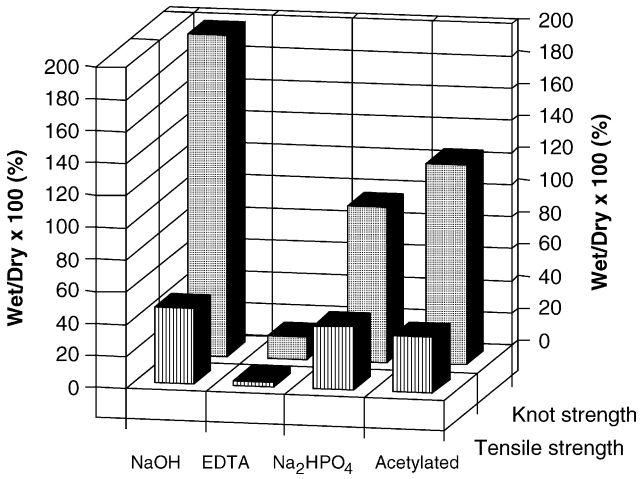

Fig. 6. Wet-dry ratio of original and treated chitosan filaments.

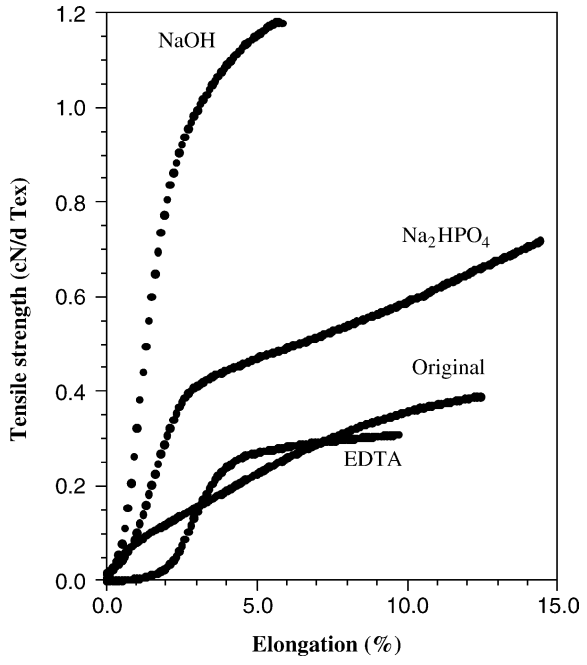

Fig. 7. Stress–strain curves of original and treated chitosan filaments.

Stress–strain curves of filaments are shown in Fig. 7. In the case of Na_2HPO_4 treatment, elongation and tensile strength of the filament were improved than the original filament. The deposition of hydroxyapatite like material on the surface of the filament may contribute this phenomenon. Remarkable improvement of Young's modulus was found for the NaOH treated filament in which calcium and acetate were eliminated completely from the filament. The value (50.1cN/dTex, 1.39 GPa) was improved over three times compared to the original filament (15.6cN/dTex, 0.43 GPa). The present results strongly suggest that elimination of calcium from the filament is essential to improve fiber property.

4. Conclusion

A predominant interaction of calcium ion to amino groups on chitin molecule was found to reduce the solubility of chitin against calcium chloride dihydrate saturated methanol. Thus, calcium chloride or calcium acetate saturated water–methanol (1:1 v/v) was first found to be better coagulation solvent to prepare chitosan filament than former coagulation systems. Then ethanol was applied successfully to coagulate chitosan filament instead of methanol owing to biomedical safety aspect. The treatment with diluted sodium hydroxide aqueous solution improved the filament properties due to the tight interaction of chitosan molecules by the elimination of chelated calcium ion as well as acetate from the original filament.

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