

CHAPTER IV RESULTS AND DISCUSSION

4.1 Characterization of Chitosan

4.1.1 Degree of Deacetylation

The degree of deacetylation of chitosan was confirmed by infrared spectroscopic measurement according to the method of Sannan *et al.* (1978). The value obtained was 94.41%, which was close to the value reported by the manufacturer (95%).

4.1.2 Molecular Weight

The molecular weight of chitosan was determined by using the intrinsic viscosity method. Figure 4.1 shows the plot between the concentrations of the sample solution and the values of both reduced and inherent viscosities.

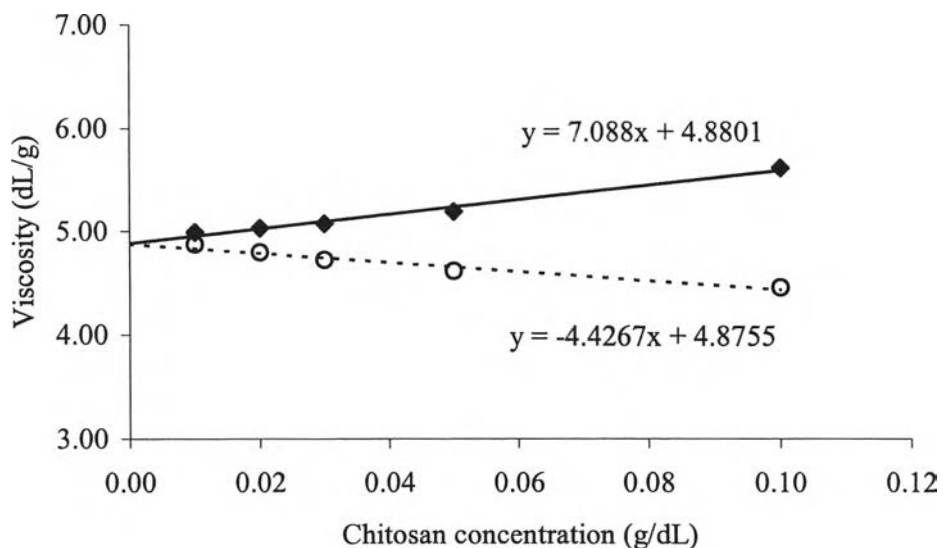


Figure 4.1 Values of reduced viscosity (◆) and inherent viscosity (○) of chitosan plotted against concentrations.

The value of intrinsic viscosity obtained from the intercept of the plot was 4.88 dL/g. The molecular weight of chitosan was calculated to be 4.25×10^5 , whereas the value reported by the manufacturer was about 1×10^5 . The difference in the values might be due to the different methods of determination.

4.2 Solution Viscosity Measurement

To determine the appropriate chitosan concentration for the spinning solution, viscosities of six chitosan solutions with the concentrations varied between 5–10% (w/v) in 4% (v/v) aqueous acetic acid were measured after aging overnight at room temperature by using a digital rheometer, and the results are shown in Figure 4.2.

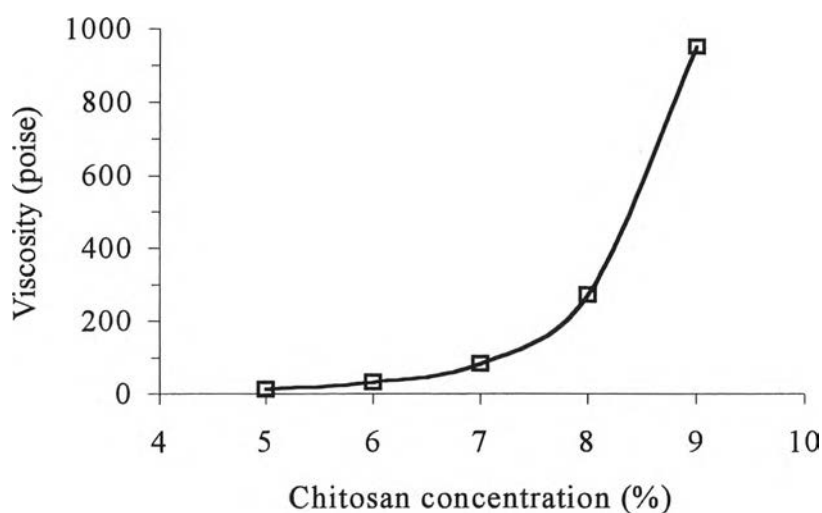


Figure 4.2 Plot of chitosan concentrations and the solution viscosity at room temperature of chitosan solutions in 4% (v/v) aqueous acetic acid.

The solution viscosity was very low at chitosan content of 5%. The solution viscosity increased rapidly at concentrations higher than 7%. A 9% chitosan solution showed a viscosity of more than 900 poises, and the solution of 10% chitosan could not be measured because it became a gel after aging.

A chitosan solution of 7% chitosan content exhibited a solution viscosity nearest to 100 poises, which is a typical value for a wet spinning solution as suggested by East and Qin (1993). Therefore, it was chosen as the spinning solution.

4.3 Effects of Spinning Conditions on Properties of Chitosan Fiber

Seven spinning conditions were performed in order to prepare chitosan fiber as shown in Table 4.1. Two types of coagulants for the first coagulation bath were studied: aqueous or alcoholic NaOH solutions, which were normally used, and calcium chloride (CaCl_2) saturated 50% aqueous methanol, which was recently proposed by Tokura and Tamura (2002) to be a milder condition for the preparation of chitosan fiber. In addition, the effects of the solution in the second bath and filament drawing applied in the spinning process were also investigated.

All fibers obtained from coagulating systems based on CaCl_2 were yellowish for both the as-spun and dried fibers. In contrast, the as-spun fibers from those based on NaOH were quite transparent, gradually became whitish, and then yellowish after drying.

Table 4.1 exhibits some test results of the fiber properties. It could be obviously seen that the NaOH based coagulating systems gave higher values of knot strength and elongation at break than the CaCl_2 based systems, while they showed lower fiber titer or linear density. Higher linear density of fibers from CaCl_2 systems might be resulted from some calcium ions that still remained in the fibers, as determined using atomic absorption spectroscopy (Table 4.2). However, the tensile strength was not considerably affected by the coagulating systems used in the first bath.

Table 4.1 Spinning conditions and mechanical properties of pure chitosan fiber

	Coagulation baths		Drawing [†]	Linear density [‡] (tex)	Tensile strength [§] (cN/tex)	Knot strength [§] (cN/tex)	Elongation at break [§] (%)
	1 st Bath	2 nd Bath					
A	Sat. CaCl ₂ in 50%MeOH	50%MeOH	No	45.7 ± 1.8	7.79 ± 0.47	0.95 ± 0.41	6.53 ± 0.73
B*	Sat. CaCl ₂ in 50%MeOH	50%MeOH	No	40.2 ± 0.7	10.82 ± 0.18	2.13 ± 0.53	6.52 ± 0.42
C*	Sat. CaCl ₂ in 50%MeOH	50%MeOH	Yes	42.8 ± 2.8	8.34 ± 0.55	2.36 ± 0.53	6.48 ± 0.63
D*	Sat. CaCl ₂ in 50%MeOH	70%MeOH	Yes	41.6 ± 4.1	7.89 ± 0.45	1.87 ± 0.52	6.02 ± 0.51
E	1 N NaOH in 50%MeOH	50%MeOH	No	28.1 ± 2.0	11.17 ± 0.62	6.88 ± 0.83	11.91 ± 1.66
F	1 N NaOH	50%MeOH	No	29.6 ± 0.6	9.16 ± 0.61	5.51 ± 0.48	8.11 ± 1.48
G	1 N NaOH	H ₂ O	No	28.0 ± 0.7	8.81 ± 0.82	4.39 ± 0.61	8.45 ± 1.30

* Neutralized by 20/80 (v/v) 1 N NaOH/methanol after spinning and washing with methanol

† 1st roller = 5.7 m/min; 2nd roller = 6.4 m/min; in air at room temperature immediately after exiting the second bath

‡ Average of 50 samples

§ Average of 20 samples

Table 4.2 Calcium content in chitosan fibers prepared by using CaCl₂ saturated 50% aqueous methanol as the first coagulant

Spinning condition	Calcium content* (mg/100 g fiber)
A	20.72
B	663.80
C	160.67
D	173.08

* Measured using atomic absorption spectrophotometer (Varian SpectrAA 300P); wavelength = 422.7 nm; nitrous oxide-acetylene flame; a calibration curve created from 1, 2, and 3 ppm standard Ca solutions.

In corresponding conditions (A and E), NaOH containing coagulating system (condition E) gave chitosan fiber with higher tenacity values—both tensile and knot strengths—than CaCl₂ containing coagulating system (condition A). The explanation might be related to an article of Tamura *et al.* (2002). Being coagulated through calcium ion chelation, the obtained chitosan fiber was still in an acetate salt form, and the relatively bulky groups of acetate might interrupt the arrangement of polymer chain when the force was applied and hence resulted in the lower strength. In contrast, for NaOH coagulating system, chitosan coagulation was induced through the removal of acetic acid or acetate by acid-base reaction with NaOH (Knaul and Creber, 1997b), thus the fiber had already been neutralized while it was travelling in the first coagulation bath. This assumption is confirmed by the results of the spinning condition B, of which the resulted fiber from CaCl₂ system was neutralized by soaking in 20/80 (v/v) 1 N NaOH/methanol after spinning (Table 4.1). With neutralization, the tensile strength of fiber from CaCl₂ system was significantly improved (10.82 cN/tex) to the level comparable to that of fiber from spinning condition E, which gave the highest value of tensile strength (11.17 cN/tex) among all spinning conditions in this study. Knot strength of fiber obtained from CaCl₂ system was also improved about 2 times (from 0.95 cN/tex of condition A to 2.13 cN/tex of condition B) by neutralization, still it was not comparable with those

from NaOH based systems (4.39–6.88 cN/tex). In comparison, mechanical properties of chitosan fibers with various degrees of deacetylation from 45 to 90% were investigated by Tokura *et al.* (1987). The values were reported to be in the range of 6.80–24.72 cN/tex and 6.80–18.19 cN/tex for dry tensile and knot strengths, respectively, while elongation at break varied between 6.6 and 41.4%.

The values of linear density, tenacity and elongation at break of the chitosan fiber were little influenced by the composition of the second bath as comparing between the spinning conditions C and D or between F and G. This might indicate that fiber properties were mainly affected by the coagulation step that occurred in the first coagulation bath, but only slightly affected by the washing step in the second bath.

Interestingly, the addition of methanol to NaOH coagulating solution (condition E) improved both tenacity and elongation at break of the obtained fibers. This might indicate that methanolic NaOH solution (condition E) probably provided more suitable rate of coagulation for the fiber than aqueous NaOH solution (condition F). Hirano *et al.* (1999) has reported the advantage of methanol in improving the spinning of chitosan fiber when methanol was added to the spinning solution. From their results, it was found that 1/1 (v/v) 2% aqueous acetic acid/methanol was an excellent spinning solvent that gave a chitosan solution with a homogeneous molecular distribution at an appropriate viscosity for spinning.

However, the maximum draw ratio that could be applied before the filament breakage was only about 1.11–1.13, and it did not improve any properties of the fibers.

The SEM micrographs of the fibers, as shown in Figure 4.3, indicated that there was no remarkable effect on fiber surface morphology among the different coagulating conditions studied in this work. The surfaces of fibers prepared by using CaCl₂ saturated-coagulant were very similar to those prepared by using alcoholic and aqueous alkaline coagulant, which were rather smooth. However, those from CaCl₂ system might be said to be a little bit rougher.

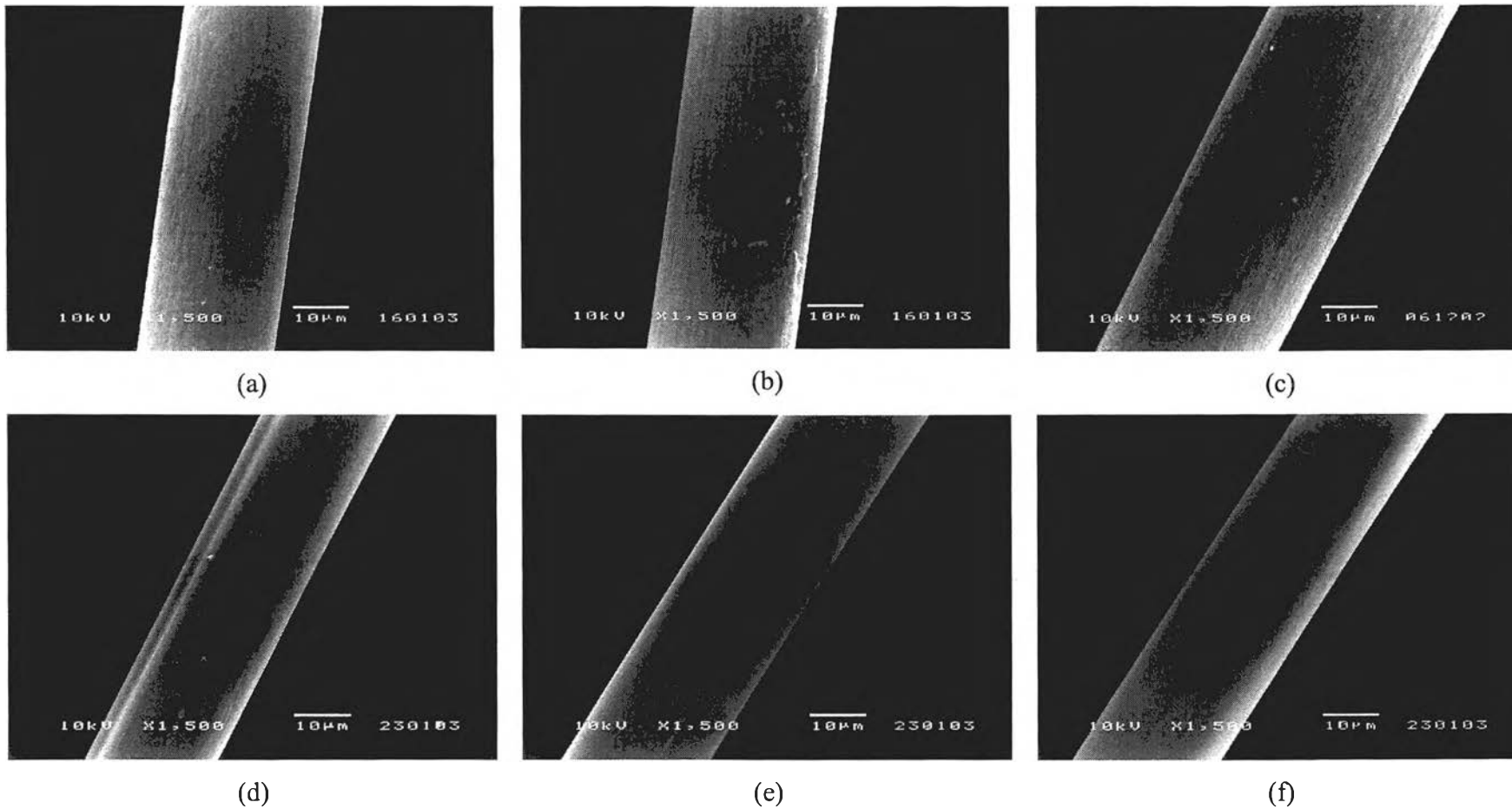


Figure 4.3 SEM micrographs of fibers prepared by (a) condition A, (b) condition B, (c) condition D, (d) condition E, (e) condition F, and (f) condition G.

4.4 Preparation and Characterization of Citrate-Crosslinked Chitosan Fiber

4.4.1 Preparation of Citrate-Crosslinked Chitosan Fiber

As citric acid was soluble both in 4% acetic acid and 1 *N* NaOH aqueous solutions, it could be added either to chitosan dope itself or to the first coagulation bath. Therefore, two separate sets of experiments based on the aqueous NaOH coagulant system (spinning condition F) were conducted: (1) addition of citric acid to chitosan spinning solution and (2) addition of citric acid to the first coagulation bath.

4.4.1.1 *Addition of Citric Acid to Chitosan Spinning Solution*

In order to find an appropriate range of citric acid concentration to be studied, nine sample solutions of chitosan were firstly prepared by dissolving 7% (w/v) chitosan in the mixed solvent of 0.5–15% (w/v) citric acid in 4% (v/v) aqueous acetic acid. After aging overnight at room temperature, the resulted chitosan solutions could be classified into three groups: (A) whitish, turbid solution with a large amount of insoluble part (0.5–3% citric acid); (B) yellowish, clear solution with some insoluble part (7–9% citric acid); and (C) yellowish, clear solution with little insoluble part (11–15% citric acid) as shown in Table 4.3. Anyway, no gelation occurred in any of the samples even after aging for more than three days.

Table 4.3 Solubility of 7% (w/v) chitosan in the mixtures of 0.5–15% (w/v) citric acid in 4% (v/v) aqueous acetic acid after aging overnight

Citric acid concentration (% w/v)	Solubility*
0.5	A
1	A
3	A
5	B
7	B
9	B
11	C
13	C
15	C

* A = Whitish, turbid solution with some insoluble parts; very low viscosity.

B = Yellowish, clear solution with some insoluble parts; quite low viscosity.

C = Yellowish, clear and homogeneous solution.

From the results, chitosan solution containing citric acid concentration less than 9% exhibited a very low viscosity, which was not suitable for being used as a spinning solution due to the limitation of chitosan solubility in the mixed solvent. However, it might be noticed that increasing citric acid content could increase the solubility of chitosan as the residual chitosan flakes gradually reduced with the increasing in citric acid content from 0.5 to 9%, and chitosan was completely dissolved as the citric acid content was 11% and higher. This concentration of citric acid that could completely dissolve chitosan was agreed with what was reviewed in an article of Rathke and Hudson (1994) that chitosan was soluble in formic, acetic, 10% citric, pyruvic, and lactic acids. According to this, an additional experiment was performed by dissolving 7% (w/v) chitosan in 10% (w/v) citric acid. Nonetheless, it was found that an aqueous citric acid alone, without acetic acid, was not a suitable solvent for the preparation of a viscous chitosan solution for spinning since it could not completely dissolve the applied amount of

chitosan even after stirring overnight due to the limited solubility of chitosan. Thus, the solution obtained had a rather low viscosity. With the help of 4% (v/v) acetic acid, chitosan solutions with citric acid ranging from 11 to 15% (w/v) were likely to be suitable for spinning. Therefore, these last three chitosan solutions were measured for their solution viscosities using a Brookfield DV III digital rheometer, and the results are shown in Table 4.4.

Table 4.4 Solution viscosity of 7% (w/v) chitosan in 4% (v/v) acetic acid containing various concentrations of citric acid prepared by method 1*

Citric acid concentration (% w/v)	Solution viscosity (poises) [†]
0	81.50
11	30.52
13	25.59
15	30.61

* Citric acid was dissolved in 4% aq. acetic acid before adding chitosan flakes.

[†] Measured after aging overnight at room temperature.

Despite the viscosity being much lower than 100 poises, the value suggested for wet spinning (East and Qin, 1993), a spinning solution containing 15% (w/v) citric acid was tried. Whitish gum-like filaments were obtained due to melting of each filament, which became very brittle after drying. Thus, a lower range of citric acid concentration might be preferred.

So as to obtain a spinnable chitosan solution and to avoid obtaining brittle chitosan fibers, another way of dissolution was tried by primarily dissolving chitosan flakes completely in 80 parts of 5% (v/v) aqueous acetic acid before adding 20 parts of an appropriate concentrated aqueous solution of citric acid. After vigorous stirring, eight solutions of 7% chitosan in 4% (v/v) acetic acid containing the final concentrations of citric acid of 0.025, 0.125, 0.25, 0.5, 1, 2, 2.5, and 5% (w/v) were achieved. Table 4.5 shows the effect of citric acid on the chitosan solution prepared by this method.

Table 4.5 Effect of citric acid on 7% (w/v) chitosan in 4% (v/v) acetic acid solution prepared by method 2*

Citric acid concentration (% w/v)	Solution viscosity (poises) [†]
0	81.50
0.025	72.25
0.125	75.23
0.25	82.50
0.5	61.81
1	Gelled after aging overnight
2	Gelled within an hour
2.5	Gelled within an hour
5	31.13

* Chitosan flakes were dissolved in 80 parts of 5% aq. acetic acid before adding 20 parts of aq. citric acid solution.

[†] Measured after aging overnight at room temperature.

A viscous clear solution of chitosan with citric acid of 0.5% (w/v) and lower could be obtained. However, 1, 2, and 2.5% (w/v) citric acid in the spinning solution brought about a creamy white chitosan gel, which could not be used as a spinning solution after stirring and aging. Interestingly, although 5% of citric acid yielded a whitish liquid also, it did not become a gel, but gave too low solution viscosity to be spun. This might be implied that the addition of citric acid probably led to crosslinking, especially at about 1–2.5% (w/v) citric acid, while higher content of citric acid might induce the degradation of chitosan molecules, or citric acid itself might act as a solvent instead of a crosslinker at a higher concentration.

Therefore, five spinning solutions containing citric acid ranging from 0 to 0.5% (w/v), which gave spinnable chitosan dopes, were chosen to be used in this study. The chitosan spinning solutions were successfully prepared by

the second method that chitosan flakes were dissolved in 80 parts of 5% (v/v) aqueous acetic acid to obtain a homogeneous chitosan solution before 20 parts of an appropriate concentrated aqueous solution of citric acid was added and mixed thoroughly. After filtration and aging overnight without gelation, each spinning solution was wet spun into the first coagulation bath of 1 N NaOH followed by the second bath of 50% aqueous methanol. After that, the obtained fiber was then wound up on a bobbin, washed extensively in methanol until the pH was neutral, dewatered in methanol overnight, and dried in air.

4.4.1.2 Addition of Citric Acid to the First Coagulation Bath

A spinning solution of 7% (w/v) chitosan in 4% (v/v) acetic acid was spun into each of the first coagulation bath containing 900 mL of 0–5% (w/v) citric acid in 1 N NaOH. The citric acid concentration higher than 5% (w/v) could reduce the alkalinity of the coagulating solution that its pH should be higher than 12 to obtain the solidified fiber. Following the first coagulation bath, the resulted filaments were passed through the second bath containing 50% aqueous methanol, wound up on a bobbin, washed several times with methanol, dewatered in methanol overnight, and dried in air.

4.4.2 Fiber Properties

Addition of various concentrations of citric acid to chitosan dope for the preparation of citrate-crosslinked chitosan fiber, yellowish fibers were obtained with mechanical properties as shown in Table 4.6 and Figure 4.4–4.7.

Table 4.6 Effect of citric acid content in the spinning solution on mechanical properties of chitosan fiber

Item	Citric acid concentration (% w/v)	Linear density* (tex)	Tensile strength [†] (cN/tex)	Knot strength [†] (cN/tex)	Elongation at break [†] (%)
1	0	29.6 ± 0.6	9.16 ± 0.61	5.51 ± 0.48	8.11 ± 1.48
2	0.025	30.3 ± 0.6	10.14 ± 0.28	4.04 ± 0.37	13.08 ± 0.98
3	0.125	28.4 ± 0.8	10.11 ± 0.58	4.79 ± 0.42	12.07 ± 1.84
4	0.25	35.2 ± 0.6	9.11 ± 0.62	4.62 ± 0.52	12.34 ± 1.95
5	0.5	40.3 ± 1.1	8.95 ± 0.69	5.32 ± 0.57	11.61 ± 1.68

* Average of 50 samples.

[†] Average of 20 samples.

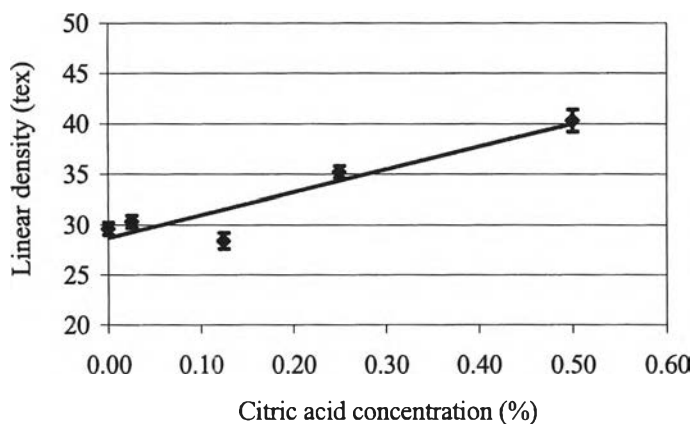


Figure 4.4 Effect of citric acid content in the spinning solution on linear density of chitosan fiber.

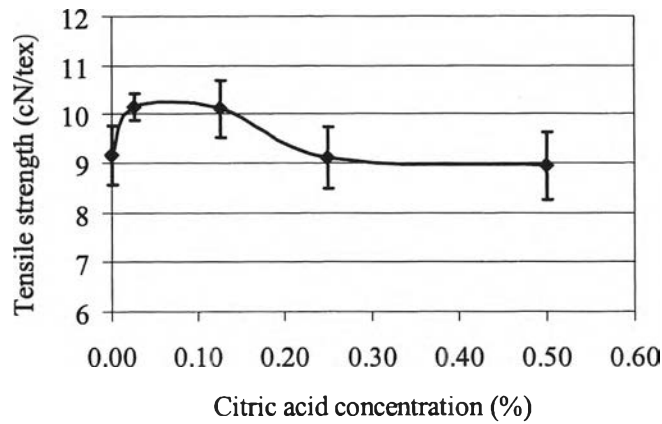


Figure 4.5 Effect of citric acid content in the spinning solution on tensile strength of chitosan fiber.

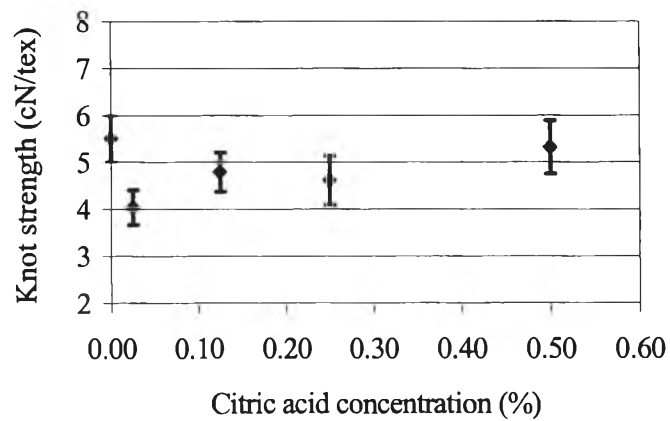


Figure 4.6 Effect of citric acid content in the spinning solution on knot strength of chitosan fiber.

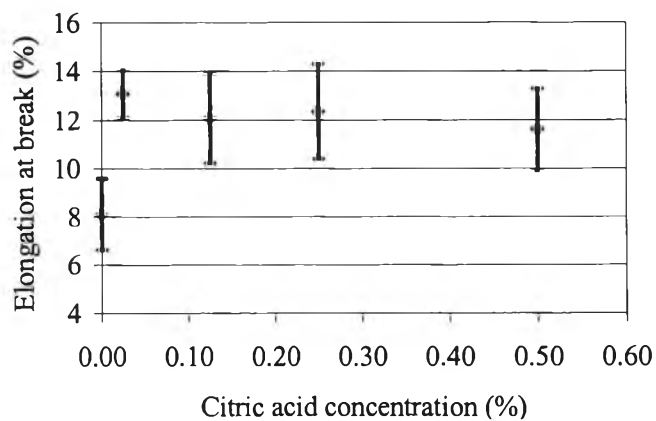


Figure 4.7 Effect of citric acid content in the spinning solution on elongation at break of chitosan fiber.

The elongation at break increased from about 8% in the control (0% citric acid) to about 11–13% (0.025–0.5% citric acid). The fiber titer or linear density increased with increase in citric acid concentration. The reason might be due to the association of the citric acid molecules in the fiber structure. The tensile strength was also slightly better up to a point (about 10 cN/tex at 0.025 and 0.125% citric acid), after which it began to reduce to that of the control. Knot strength was not improved as comparing with the control.

Table 4.7, Figure 4.8 and Figure 4.9 presents the mechanical properties of the chitosan fibers obtained by the addition of citric acid to the first coagulation bath.

Table 4.7 Effect of citric acid content in the first coagulation bath on mechanical properties of chitosan fiber

Item	Citric acid concentration (% w/v)	Linear density* (tex)	Tensile strength† (cN/tex)	Knot strength† (cN/tex)	Elongation at break† (%)
1	0	29.6 ± 0.6	9.16 ± 0.61	5.51 ± 0.48	8.11 ± 1.48
2	0.025	36.7 ± 2.5	8.87 ± 0.54	5.79 ± 0.65	9.74 ± 1.66
3	0.125	32.4 ± 1.2	9.53 ± 0.59	4.55 ± 0.61	7.75 ± 1.67
4	0.25	35.2 ± 1.0	9.14 ± 0.61	4.63 ± 0.48	11.60 ± 1.76
5	0.5	31.1 ± 0.8	10.38 ± 0.61	3.96 ± 0.42	9.84 ± 1.92
6	1.25	27.2 ± 0.5	11.03 ± 0.28	4.24 ± 0.57	14.11 ± 1.13
7	2.5	37.8 ± 1.3	9.01 ± 0.68	4.17 ± 0.66	9.49 ± 1.76
8	3.75	36.0 ± 1.9	9.04 ± 0.46	4.16 ± 0.78	11.74 ± 1.38
9	5	36.3 ± 0.9	7.45 ± 0.14	2.39 ± 0.55	13.35 ± 1.09

* Average of 50 samples.

† Average of 20 samples.

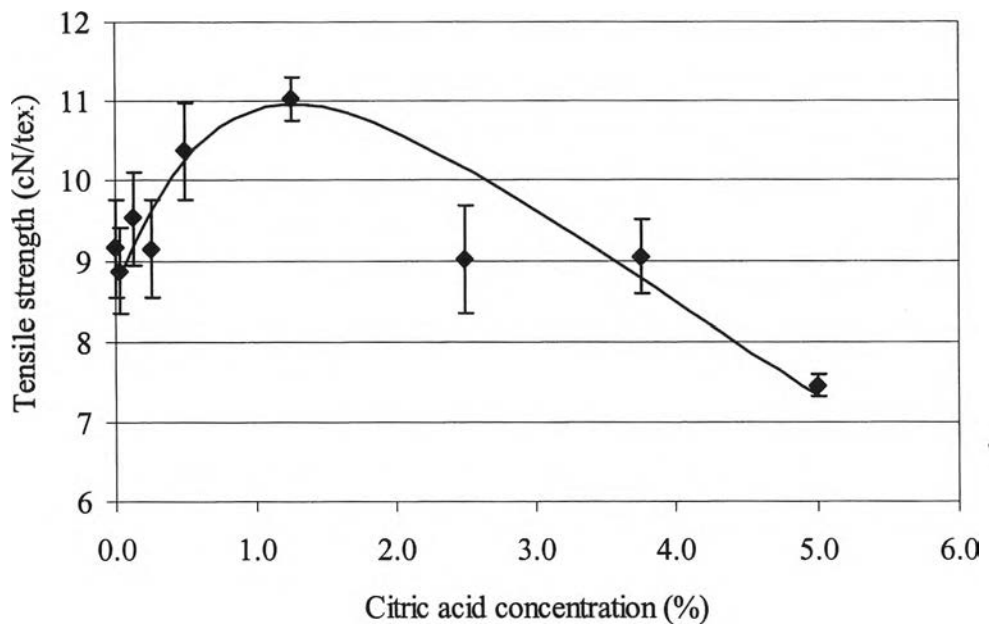


Figure 4.8 Effect of citric acid content in the first coagulation bath on tensile strength of chitosan fiber.

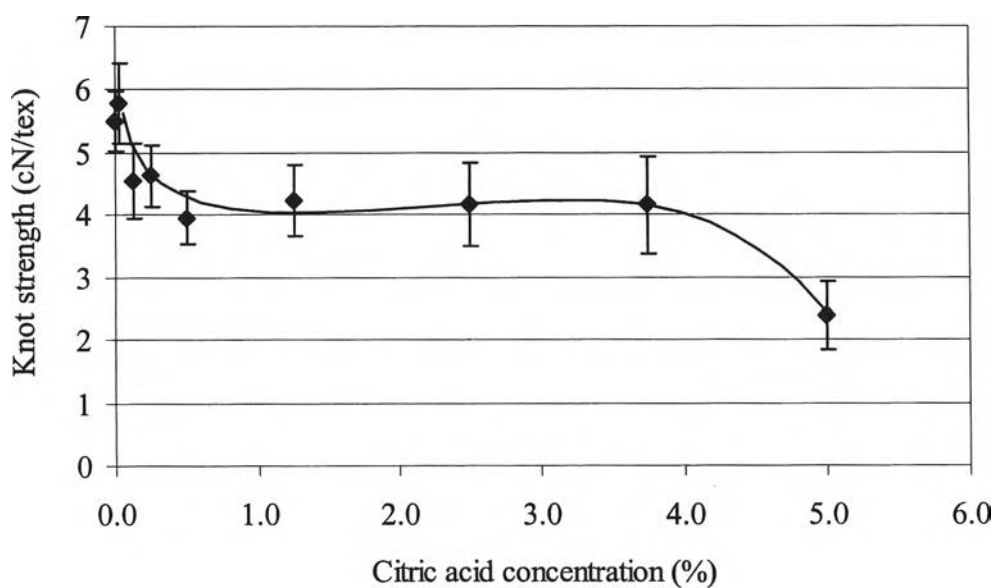


Figure 4.9 Effect of citric acid content in the first coagulation bath on knot strength of chitosan fiber.

Tensile strength of the fibers, although the values were rather fluctuated, showed the same trend as the addition of citric acid to chitosan dope. As can be seen in Figure 4.8, tensile strength increased when citric acid concentration was increased from 0.025 to 1.25% (w/v) and then began to decrease as citric acid concentration was higher than 1.25% (w/v). Nevertheless, the maximum value (about 11 cN/tex) was obtained at citric acid concentration of 1.25% (w/v) citric acid which was quite higher than that applied for chitosan dope (0.025% citric acid). The explanation might be that, by mixing citric acid with chitosan dope, it was easier for citric acid to react thoroughly with chitosan than adding it to the coagulating media. Moreover, mixing citric acid with chitosan and then aged overnight provided longer time for the interaction to occur and partial crosslinking might be able to take place. Therefore, lower citric acid content was enough for the improvement of the strength of fiber by adding it to the dope than to the coagulation bath. However, by adding citric acid to chitosan dope, acid hydrolysis of chitosan chains might also occur during aging and thus gave the lower maximum value of tensile strength (about 10 cN/tex) than by adding citric acid to the first coagulation bath (about 11 cN/tex).

It was also clearly concluded for the values of knot strength that the addition of citric acid to the first coagulation bath reduced knot strength of the fiber as can be seen obviously in Figure 4.9. Especially, the value obtained at 5% (w/v) citric acid (2.4 cN/tex) was about half of the control with no addition of citric acid (5.5 cN/tex).

Similar to the addition of citric acid to the spinning solution, the results in Table 4.7 shows that, by adding citric acid to the first coagulation bath, the linear density as well as the elongation at break of the chitosan fiber was higher than that of the control (0% citric acid). However, the increase in both properties did not noticeably relate to the acid content in the coagulation bath.

The increment in breaking strength and elongation at break as a result of crosslinking was also observed in the work of Knaul *et al.* (1999b). In 1999, Knaul *et al.* crosslinked chitosan fiber by immersing the fiber in a buffered solution containing either phosphate ions or phthalate ions. Maximum values of mechanical properties were exhibited at pH 4.5–5.5 for phthalate buffer (17.73 cN/tex) and about 5.4 for phosphate buffer (15.88 cN/tex), while the control condition was performed at

pH 7 (13.16 cN/tex). Furthermore, all fiber samples showed an increase in elongation at break over the control at all pH values (from 23.1% of the control to 26.7–32.5%). Nonetheless, no obvious correlation of elongation at break with pH, temperature, or reaction time could be concluded. The improvement in mechanical properties may be attributed to the crosslinked network that might be set up whereby the ions establish bridges in between the chitosan molecules.

The fluctuation of the data for mechanical properties of the fibers might be explained by the reason that there was no addition of fresh coagulating solution to the coagulation bath during the spinning process. As chitosan solution was continuously extruded into the bath, the compositions of the coagulant gradually changed, and this might affect the properties of coagulated fiber. In particular, in the case where a small amount of citric acid was added to the coagulation bath, citric acid or citrate salt might be used up before the spinning process was completed. Moreover, another reason might be that there was no specific device, such as a metering pump, to control the flow rate of the spinning solution except a gas regulator, and the pressure applied might not be exactly the same in all experimental runs.

4.4.3 Fiber Appearance and SEM Micrographs

Most citrate-crosslinked chitosan fibers prepared by the addition of citric acid to chitosan dope or the addition of citric acid to the first coagulation bath were rather transparent and hardly seen in the first bath, but they gradually became cloudy, yellowish, and seemed to be luster during the spinning path. Interestingly, only chitosan fiber produced from a coagulating medium containing 5% (w/v) citric acid was whitish and relatively matt when exiting from the spinneret and even after drying. This correlated with the SEM micrographs shown in Figure 4.10 and 4.11 for chitosan fibers prepared by adding citric acid to the chitosan dope and to the first coagulation bath, respectively.

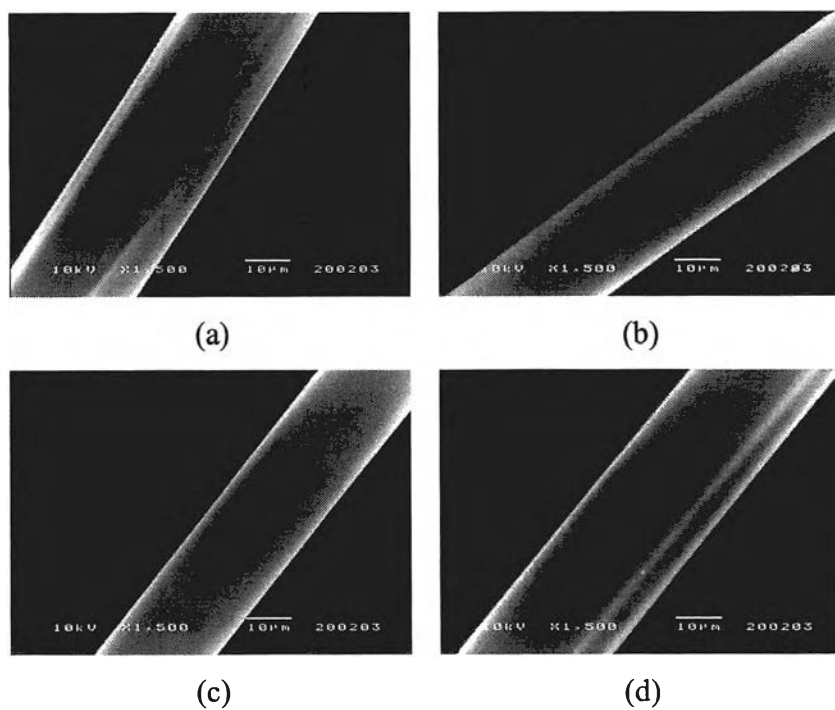


Figure 4.10 SEM micrographs of fibers prepared from chitosan dope consisting of (a) 0.025%, (b) 0.125%, (c) 0.25%, and (d) 0.5% (w/v) citric acid.

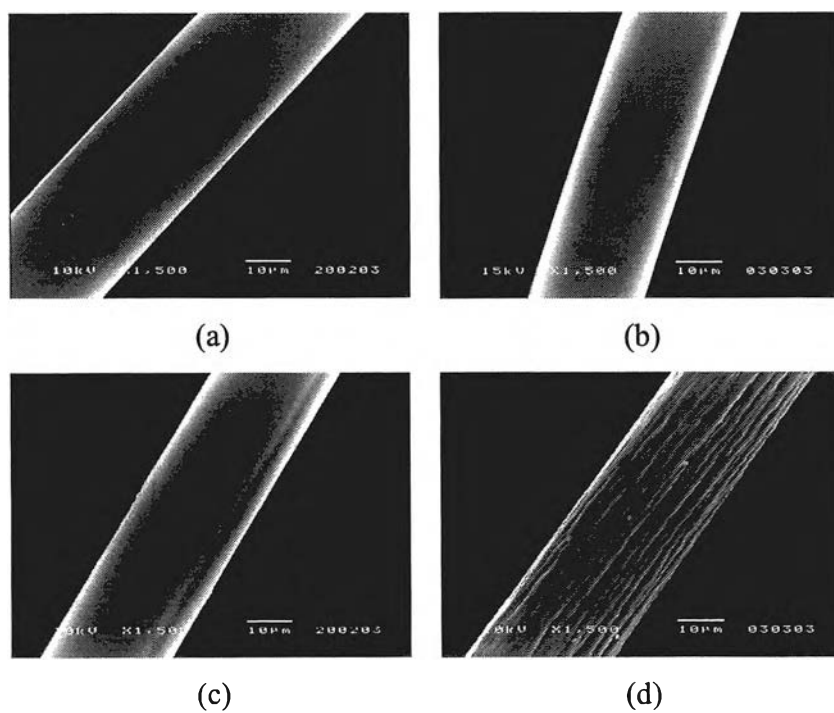


Figure 4.11 SEM micrographs of fibers coagulated in 1 N NaOH containing (a) 0.025%, (b) 0.25%, (c) 2.5%, and (d) 5% (w/v) citric acid.

It can be clearly seen in Figure 4.11c that a rough surface appeared on the fiber prepared by using 5% (w/v) citric acid in the first coagulation bath instead of the smooth surface as appeared on the others. Such characteristics as fiber appearance and SEM micrograph were also observed in the fiber prepared from chitosan dope containing 15% citric acid, of which the SEM micrograph is shown in Figure 4.12.

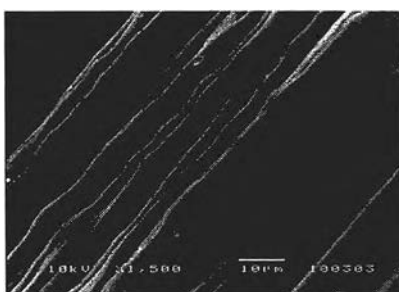


Figure 4.12 SEM micrograph of fiber prepared from chitosan dope consisting of 15% (w/v) citric acid.

According to these evidences, it might confirm the effect of citric acid on chitosan fiber, particularly at high citric acid content, both in the coagulation bath and chitosan dope.

The reason for the rough surface might be explained by the very different in coagulation rate between the outer skin and the inner core of the extruded fiber. In the case of adding 5% (w/v) citric acid to the first coagulation bath, as soon as the extrudate contacted with the coagulant, crosslinking might occur very fast at the surface or skin of the fiber due to the relatively high concentration of citric acid or citrate salt in the bath. After the residual solvent that was held inside the skin of the fiber was leached out, space that previously occupied by the solvent was left in the core of the fiber and caused the skin to collapse and gave the rough surface. In the case of adding 15% (w/v) citric acid to chitosan dope, the explanation might be the same. As citric acid was in the chitosan dope, the crosslinking might occur very fast at fiber surface where citric acid in chitosan dope reacted with NaOH in the coagulation bath to form citrate salt that could crosslink the chitosan molecules.

Tokura *et al.* (1987) studied the preparation of chitosan fiber by using several coagulant systems, such as copper-ammonia ($\text{CuSO}_4\text{-NH}_4\text{OH}$), alcoholic NaOH, and acidic coagulant ($\text{CuSO}_4\text{-H}_2\text{SO}_4$). The SEM micrograph of chitosan fiber prepared by using a copper-ammonia coagulant of 1/1 (v/v) 2 M CuSO_4 /conc. NH_4OH showed the rough surface of chitosan fiber. Whereas, the chitosan fibers produced by alcoholic alkaline coagulant of 7/3 (v/v) 5% aqueous NaOH solution/ethanol or acidic coagulant of 1/1 (v/v) 2 M CuSO_4 /1 M H_2SO_4 had smooth surface.

4.5 Preparation and Characterization of Glutaraldehyde-Crosslinked Chitosan Fiber

In addition to citric acid, glutaraldehyde, a widely used crosslinking agent, was used to compare with the results obtained by using citric acid. It was mixed in the spinning solution for the preparation of crosslinked chitosan fiber. Before being added to a chitosan dope, it was necessary for glutaraldehyde to be diluted otherwise a gel droplet would be produced as soon as glutaraldehyde was in contact with the chitosan solution, and this was in spite of the vigorous stirring. This was because the chitosan concentration used for fiber spinning (7% w/v) was quite high compared to chitosan solution generally used for film casting. Despite dilution, glutaraldehyde contents of 0.0025% and higher gave highly viscous liquids which became dark brown, but transparent, jelly-like gels after aging overnight (Table 4.8). As a result, glutaraldehyde contents of 0.002% and lower were chosen.

The preparation of the spinning solution was similar to that for citric acid except that 20 mL of distilled water containing 1, 2, and 4 μL of glutaraldehyde (50% in water) solution was used, instead of 20 mL of aqueous citric acid, in 100 mL of total spinning solution. Thus, the final glutaraldehyde concentrations in 7% (w/v) chitosan solutions in 4% (v/v) acetic acid were 0.0005, 0.001, and 0.002% glutaraldehyde, respectively. After aging overnight at room temperature, the viscosity of each chitosan dope was measured and presented in Table 4.8. It was found that the viscosity of the spinning solutions remarkably increased as

glutaraldehyde contents increased. This might be a good evidence for the occurrence of crosslinks in the aged solution.

Table 4.8 Effect of glutaraldehyde content on 7% (w/v) chitosan in 4% (v/v) acetic acid solution after aging overnight at room temperature

Glutaraldehyde concentration (%)	Solution viscosity (poises)
0	81.50
0.0005	88.84
0.001	101.02
0.002	121.10
0.0025	Gelled after aging
0.005	Gelled after aging
0.0125	Gelled after aging
0.025	Gelled after aging
0.05	Gelled after aging
0.125	Gelled after aging

Table 4.9 Effect of glutaraldehyde content in the spinning solution on mechanical properties of chitosan fiber

Item	Glutaraldehyde concentration (%)	Linear density* (tex)	Tensile strength [†] (cN/tex)	Knot strength [†] (cN/tex)	Elongation at break [†] (%)
1	0	29.6 ± 0.6	9.16 ± 0.61	5.51 ± 0.48	8.11 ± 1.48
2	0.0005	34.3 ± 0.6	10.27 ± 0.25	5.48 ± 0.78	14.87 ± 1.24
3	0.001	24.6 ± 2.3	10.71 ± 0.42	5.23 ± 0.86	13.53 ± 1.25
4	0.002	26.3 ± 1.0	10.03 ± 0.76	4.47 ± 1.04	11.42 ± 1.58

* Average of 50 samples.

[†] Average of 20 samples.

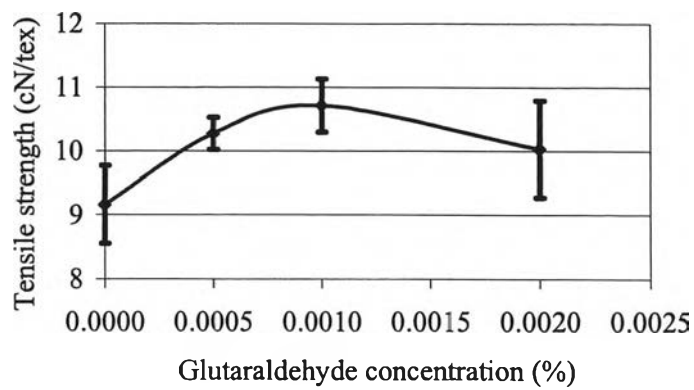


Figure 4.13 Effect of glutaraldehyde content in the spinning solution on tensile strength of chitosan fiber.

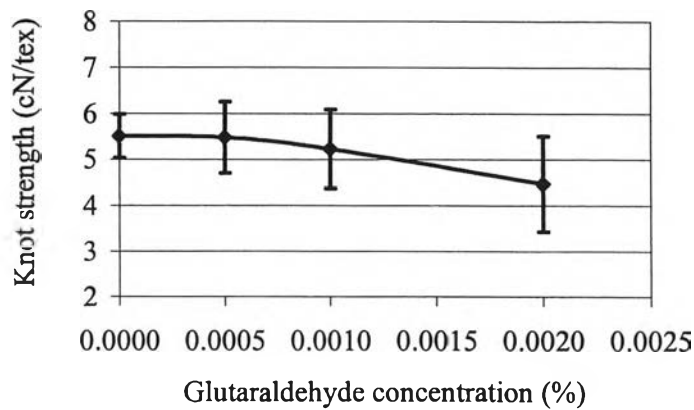


Figure 4.14 Effect of glutaraldehyde content in the spinning solution on knot strength of chitosan fiber.

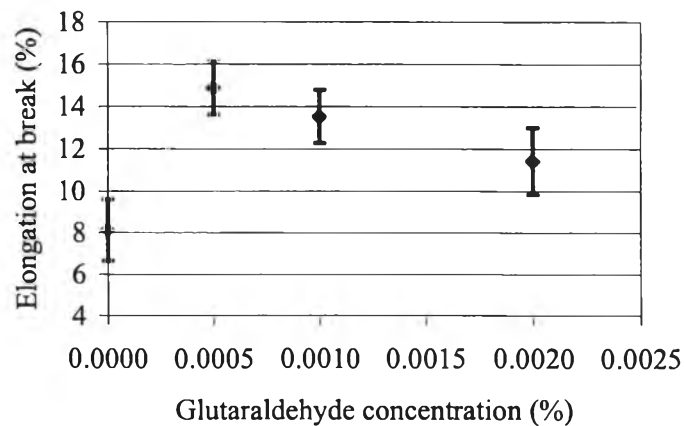


Figure 4.15 Effect of glutaraldehyde content in the spinning solution on elongation at break of chitosan fiber.

Chitosan dopes containing the three different glutaraldehyde concentrations were successfully spun. The resulted fibers were fairly luster but not so bright as the noncrosslinked or citrate-crosslinked chitosan fibers. The linear density and mechanical properties of glutaraldehyde-crosslinked fibers are shown in Table 4.9 and also graphically illustrated in Figure 4.13–4.15.

Tensile and knot strengths of glutaraldehyde-crosslinked chitosan fibers have the same trends as those of citrate-crosslinked chitosan fibers, i.e. the tensile strength increased to a maximum point before decreasing, while knot strength was gradually decreased as glutaraldehyde content increased. Maximum dry tensile strength of 10.71 cN/tex was obtained at 0.001% glutaraldehyde in chitosan dope. The breaking elongation of the chitosan fibers was also considerably enhanced from 8% to about 15% with the addition of 0.0005% glutaraldehyde. In spite of that, as glutaraldehyde content increased, the values of elongation at break decreased from 15% to 11% as illustrated in Figure 4.15.

On the other hand, Knaul *et al.* (1999a) studied the crosslinking of chitosan fibers with two types of dialdehydes, glutaraldehyde and glyoxal, by immersing dried chitosan fiber in an aqueous solution containing glutaraldehyde or glyoxal, while the control was immersed in water (12.71 cN/tex). In the case of glutaraldehyde, the same tendency for the tensile strength was also reported, i.e. it was better up to a point (19.69 cN/tex), after which it began to decrease as the amount of crosslinking agent was higher. The reason suggested for this effect was that the dialdehyde might degrade the molecular structure at high concentration, or cause stress in the fiber. Nevertheless, with an increasing amount of dialdehyde, the elongation at break of the fiber was greatly decreased from about 27% in the control to about 2–12% in the crosslinked fibers. This is in contrast to what was found in this work (Table 4.9). However, the disagreement might be due to the different ranges of glutaraldehyde concentrations and also the method of crosslinking used in the studies. In the work of Knaul *et al.* (1999a), chitosan fiber was submersed in an aqueous glutaraldehyde solution after spinning, and the glutaraldehyde contents ranged from about 0.007 to 22%. While in this work, glutaraldehyde was added directly to the chitosan dope and the range of glutaraldehyde concentration was from 0.0005 to 0.002% (Table 4.9).

The elongation at break might be increased by a small amount of crosslinking, caused by low glutaraldehyde concentration. Whereas, the higher concentration of glutaraldehyde might lead to higher degree of crosslinking and the decreasing in elongation at break.

No markedly distinctive surface morphology appeared on any glutaraldehyde-crosslinked fiber as compared with the fiber without crosslinking.