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Effect of the concentration of sodium acetate (SA) on crosslinking of chitosan fiber by epichlorohydrin (ECH) in a wet spinning system

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Abstract

A study has been made of the wet spinning of chitosan fibers using 2% acetic acid as a solvent, 10% aqueous sodium hydroxide as a nonsolvent, 5×10^{-2} M epichlorohydrin as a crosslinking agent, 0–20% aqueous sodium acetate (SA) as a coagulation retardant, and 4.0% chitosan solution as a polymer concentration. This article describes the effect of concentration of aqueous SA on the crosslinking of chitosan fiber by Epichlorohydrin (ECH). ECH was selected as a convenient base-catalyzed crosslinking agent. The coagulation and the crosslinking of chitosan fiber occured simultaneously in the coagulation bath. An investigation was conducted the effect of the concentration of the coagulation retardant, and the SA concentration of the coagulation bath on the thermal, morphology and mechanical properties (such as tenacity, and elongation etc.) of chitosan fibers. The dry and wet tenacity of chitosan fibers were improved by addition of SA to the coagulation bath.

Keywords: Crosslinking; Fibers; Epichlorohydrin (ECH); Sodium acetate (SA); Wet spinning

1. Introduction

Chitosan fibers are typically spun from viscous, concentrated polymer solutions commonly referred to as spinning dopes. Melt spinning cannot be employed because the chitosan polymers degrade upon heating. The spinning process most commonly used for chitosan fibers is wet-spinning. In wet-spinning, the spinning dope is extruded through a spinneret immersed in a coagulation bath containing a nonsolvent (East & Qin, 1993; Knaul, Hooper, Chanyi, & Creber, 1998; Lee, 1997; Lee, 2000; Tokura, Nishi, Tsutsumi, & Somorin, 1983). Wet-spinning of chitosan fibers from the polymer in its bulk form, typically powder or flake, involves the dissolution of the polymer in an aqueous acetic acid (1–10% by volume glacial acetic acid in water) to form the dope (Tokura et al., 1987). This dope is then pumped to a spinneret that is submerged in a high pH bath, known as the coagulation bath. It is in this bath that the polymer is precipitated in fiber form. The bath contains a solution which consists mostly of aqueous alkaline (sodium hydroxide: NaOH) plus 0–20% by weight coagulation retardants (SA:CH_3COONa). The coagulation retardant serves to slow down the chemical change from chitosan spinning dope to chitosan fiber by decreasing the rate of coagulation, and thus the physical property of chitosan fiber is improved (Hirano, Usutani, & Midorikawa, 1997; Hirano, Zhang, Son, Chung, & Kim, 1997; Nishiyama, Kobayashi, Tokura, & Nishi, 1983). Following coagulation, the chitosan fiber may be washed to remove excess coagulant and subsequently wound on a bobbin (Knaul et al., 1998).

This article describes our effort to crosslink chitosan fibers to improve the mechanical properties of this material. Chitosan is less easily defined as it is difficult to fully deacetylate chitin. Chitosan is the preferred form of the

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polymer, as it is more readily processed into fiber and film forms than is chitin. Previous studies have shown that agents containing epichlorohydrin can act as a crosslinking agent to improve the physical properties of chitosan fibers (Lee, Park, & Choi, 2004; Wei, Hudson, Mayer, & Kaplan, 1992). Lee et al. reported that epichlorohydrin(ECH) crosslinked with chitosan fiber in a wet-spinning system, improved the physical properties of the obtained chitosan fiber (Lee et al., 2004). Wei et al. pointed out that a drawback of chitosan fiber is its enhanced hydrophilicity compared to chitin, which results in a considerable loss of tensile strength when chitosan fiber is wet (Wei et al., 1992).

ECH was selected as a convenient base-catalyzed crosslinking agent. An advantage of ECH is that it does not eliminate the cationic amine function of chitosan. The use of ECH to crosslink amylose was reported by Luby and Kuniak (1979). This methodology was adapted to crosslink chitosan films and, in the current study, fibers. Most notably, crosslinking by ECH considerably improves the strength of the chitosan films and fibers (Wei et al., 1992). On the other hand, SA was selected as a coagulation retardant. An advantage of SA is its ability to slow coagulation of the polymer jet by neutralizing the reaction of acetic acid and sodium hydroxide. As a result, the degree of crosslinking by ECH is expected to be improved. In this study, the fiber formation and the fiber characteristics crosslinked by ECH in a wet-spinning system (SA addition to a coagulation bath), a one-step system, have been investigated.

2. Experimental

2.1. Materials

Chitin from red crab of the East Sea of Korea was acquired from the Dongbo Chemical Company of Korea. Acetic acid (Aldrich), sodium hydroxide (Fluka), ECH (Sigma), SA (Sigma), and urea (Sigma) were used as reagent grade. Chitosan was prepared by deacetylation of chitin in an alkali solution of 50 wt% NaOH and 10 wt% chitin solution, which was heated to 110 °C for 4 h. The solid portion was filtered and washed throughly with distilled water until it attained a nearly neutral pH. It was then dried in a vacuum at room temperature, finely cut in a knife-milling machine, and sieved through a 60-mesh screen (pore size, 250 μm).

2.2. Preparation of chitosan fiber by wet spinning

Fig. 1 depicts the wet-spinning system used in this study. A spin dope was prepared by dissolving 4% w/v chitosan in a solution of 2% w/w aqueous acetic acid. To the spinning dope was added the crosslinking agent in the amount 5×10^{-2} M ECH. The solution was mechanically stirred for 60 min in order to be homogenized; then the dope solutions were degassed and filtered in a vacuum system and were left standing for 5 h at 20 °C.

The chitosan dope was extruded through a stainless steel 300-hole spinneret by means of a variable speed infusion metering pump. The spinneret was 0.1 mm in diameter with a capillary length-to-diameter ratio of 2. A 400-mesh (pore size, 37 μm) stainless steel filter was mounted behind the spinnerets. The coagulation bath was a 10% w/w NaOH aqueous solution. To improve the crosslinking efficiency of chitosan fibers SA was added to the coagulation bath, varying in concentration from 0 to 20% w/w, labelled as SAX, $X = 0$, 5, 10, 15, and 20, the number referring to the SA concentration (%). Coagulation and the crosslinking of chitosan fiber occurred simultaneously in this coagulation bath. As a result, the crosslinking reaction started at the surface and worked its way to the core of the fiber

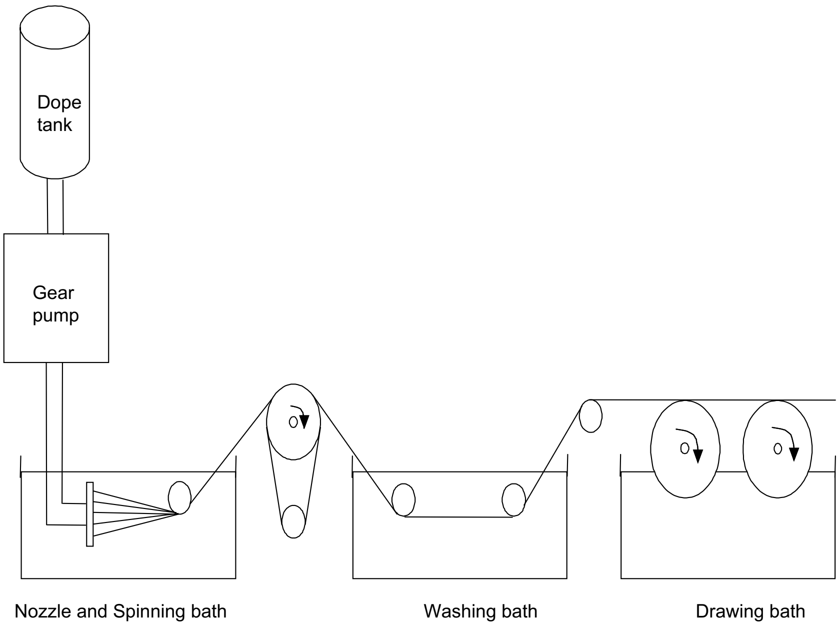

Fig. 1. Schematic diagram of wet-spinning apparatus.

(polymer jet). Depending on the residence time in the coagulation bath, the fiber may not have been crosslinked throughout its entire cross-section. The fibers emerging from the wet-spinning coagulation bath were disoriented and had little strength. Development of the anisotropic mechanical properties required of textile fibers is accomplished largely in the orientational drawing operation (Hirano et al., 1997). Therefore, the fibers obtained from the coagulation bath were washed in water and drawn or stretched in a suitable stretching ratio at 99 ± 1 °C in a drawing bath. The take-up velocity at the end of the coagulation bath was maintained at 3.0 m/min for all experiments.

2.3. Measurement

Tensile properties of monofibers were measured using a tensilon (model Vibrodyn, corrected reference equivalent type, Lenzing Co.) with a crosshead speed of 20 mm/min at standard conditions (temperature 20 °C, relative humidity 65%). The degree of swelling of fiber was measured by a moisture percentage measuring instrument (HR73 Moisture Analyzer, Mettle Toledo) at standard condition. The thermal behavior of the chitosan fibers was investigated using a differential scanning calorimeter, model TA Dupont 9900. The measurements for the chitosan fiber were performed at a scanning rate of 20 °C/min at a temperature range of 35–450 °C in a nitrogen atmosphere. Fractured samples were prepared by stretching the fibers to breaking on a Tensilon at standard condition. Morphologies of the fractured fibers were studied by scanning electron microscopy (SEM, JSM 6400).

3. Results and discussion

3.1. Degree of deacetylation and molecular weight of the chitosan

The degree of deacetylation was measured by infrared spectroscopy. This method is based on the relationship between absorbance values at 1555 cm^{-1}, which is attributed to amide II and the corresponding value of the methylene group at 2867 cm^{-1}, by applying the following equation: $\%\text{NH}_2 = (A_{1555}/A_{2867})(1/2.84) \times 100$. The value 2.84 represents the same relationship for completely acetylated chitosan. The absorbance values found at 1555 cm^{-1} represent the amide II groups, whereas that found at 2867 cm^{-1} are indicative of methylene groups. The degree of deacetylation of the chitosans and the chitin was calculated by applying these values (Nishiyama et al., 1983).

The viscometric average molecular weight (Mv) was determined using the relation $[\eta] = k \cdot \text{Mv}^{\alpha}$, where $[\eta]$ is the limiting viscosity number, and k and α are constants equal to 8.93×10^{-4} and 0.71, respectively, for chitosan in 0.2 M acetic acid-0.1 M sodium chloride-4 M urea mixed in an aqueous solution (Lee et al., 2004; Luby & Kuniak, 1979). The viscometric measurement was done at 25 °C (0.01 °C) with an Ubbelohode suspended level dilution viscometer. The characteristics of the chitosan and chitin prepared in this experiment are summarized in Table 1. As shown in Table 1, before the reaction, the degree of deacetylation (%) was 65.7%, whereas after 4 h of reaction, the degree of deacetylation (%) was 86.7%. This suggests that the degree of deacetylation (%) increased with increased reaction time.

3.2. The relation between spinning speed and SA concentration

A positive displacement gear pump is used to meter the dope volumetric flow rate (Q). For fiber production, the fibers are taken up at a velocity by the first roll (V_s) shown in the Fig. 1 and the fiber is washed with pure water. The spinning dope is pumped through the spinneret capillary hole at a velocity (V), which can be calculated from the following equation:

$V = \frac{Q}{(\pi/4)D^2}$, where Q is the volumetric flow rate per hole and D is the capillary hole diameter. The ratio of V_s to V is referred to as the spin draw ratio. This value is the spinnability (maximum spinning speed) of the spinning dope. The plot of maximum spin draw ratio, *i*-value, of spinning dope versus the SA concentration in coagulation bath is shown for the 3 m/min flow rate of the dope in Fig. 2. As shown in Fig. 2, the i-value increases with the increasing SA concentration of the coagulation bath. Generally, in the wet spinning of polymer, the *i*-value of spinning dope increases

Table 1
The characteristics of chitin and chitosan used in this study

Reaction time (h)	0	2
Degree of deacetylation (%)	65.7	86.7
Viscosity average molecular weight	550,000	112,000
Ash content (%)	1.0 (↓)	0.5 (↓)
Protein content (wt%)	1.0 (↓)	0.5 (↓)

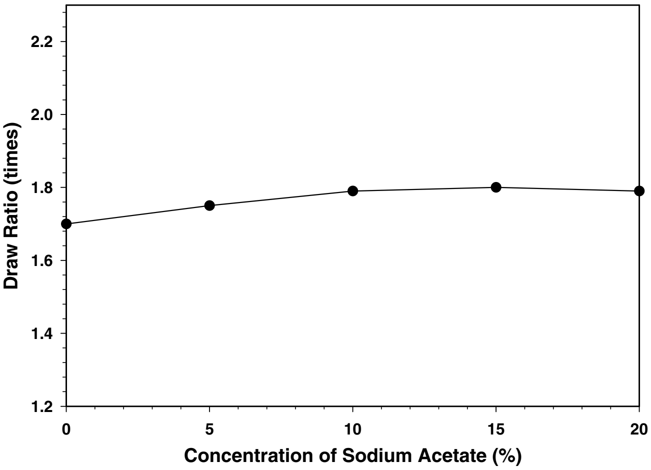

Fig. 2. Relationship between concentration of sodium acetate and draw ratio of protofiber.

with a decrease the solidification rate in coagulation bath because of the ease of polymer chain extension of polymer solution in the coagulation bath (Ziabicki, 1976).

3.3. Degree of swelling

A fiber will swell if it has the capacity to store substances in liquid or vapour form on a temporary basis. Each swelling process is a preparatory stage towards becoming a solution. For a lower packing density and higher amorphous level, there are more free functional groups (-OH, -NH_2, and -$NHCOCH_3$ groups). As a result, the swelling ability is greater and it is easier to dissolve a fibrous material. If the liquid or solvent penetrates through the amorphous areas and between the crystalline zones, temporary (reversible) swelling occurs. Chitosan fibers swell in water, which penetrates the fiber pores; this is not caused by capillary effects alone. The absorption of water is a consequence of molecular solvation forces originating from the free, unbonded hydroxyl and amino groups in the glucosamine. Therefore, swelling in water takes place primarily in the amorphous areas of the fiber, which is why it is known as intermicellary swelling. The water content of fiber increases with swelling. When an uncrosslinked fiber is placed in water, as compared to a crosslinked fiber, it swells to an extent which is dependent upon the interaction between the fiber and the water. The value of the degree of swelling is related to the nature of the fiber-solvent system and provides information concerning the nature of crosslinking and reinforcement.

In order to determine the degree of swelling, it is necessary to make a series of gravimetric measurements and determine the percentage weight decrease as a function of SA concentration. In other words, the degree of swelling decreases in accordance with the degree of crosslinking of chitosan molecules.

The degree of swelling of chitosan fiber in this study is given by

$$\text{Degree of Swelling } (\%) = \frac{\text{WW} - \text{DW}}{\text{DW}} \times 100$$

WW Wet weight after centrifuge(gr)
DW Dry weight(gr)

The weight of the completely dried sample was measured directly, and the sample was dipped into a glass beaker filled with a distilled water for 24 h at 20 °C. The weight of swollen fiber was measured by centrifuge (20,000 rpm for 5 min.). The degree of swelling of chitosan fiber that was crosslinked versus changing concentration of SA is shown in Fig. 3. The degree of swelling decreased by addition of SA when its concentration increase from 0 to 20 wt%. Because of the retardation of coagulation during the fiber formation of the spinning dope, the crosslink of the chitosan fiber increased with an increasing concentration of SA in the coagulation bath. As a result, the degree of swelling decreased when coagulation bath's concentration of SA increased.

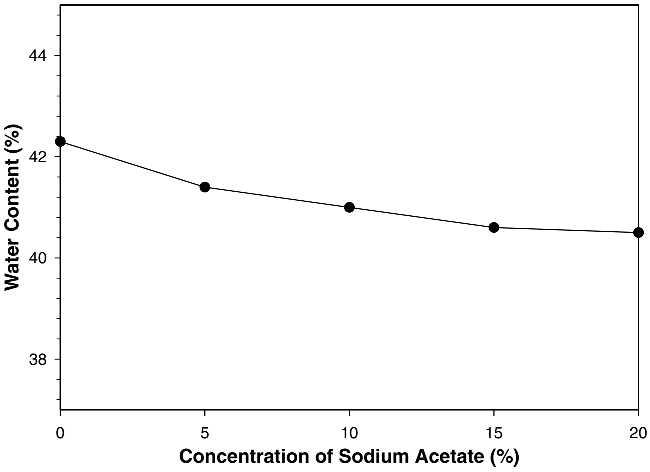

Fig. 3. The effect of concentration of sodium acetate on the water content in chitosan fiber.

On the other hand, a convenient proof of crosslinking is the swelling behavior of the crosslinked fiber in 2% aqueous acetic acid that is the solvent of chitosan. Simple swelling measurements were employed to estimate the extent of crosslinking. A swelling ratio (the ratio of volumes between swollen and unswollen fibers) was determined by examining the diameters of the fibers using optical microscopy. The swelling ratios and soluble phenomena are also reported in Table 2. As shown in Table 2, the swelling ratio and the solubility of chitosan fiber decreases with the concentration of the SA was present in the coagulation bath, not in the dope due mainly to the growing crosslinking density of the chitosan polymer chains (Lee et al., 2004).

3.4. Tensile properties

The structure of the freshly coagulated fiber has a major influence on the tensile properties and abrasion strength of the finished fiber (Hirano et al., 1997; Lee, 2000). The following equations are proposed for the crosslinking reaction mechanism of epichlorohydrin and the fiber formation mechanism at the coagulation bath.

Equation (1) Fiber formation of chitosan (Lee, 2003; Lee et al., 2004; Wei et al., 1992).

Table 2
The effect of concentration on solubility in 2 wt% aqueous acetic acid

SAX	Soluble phenomenon	Swelling ratio
SA0	Non-soluble, and swell	11.0
SA5	Non-soluble, and swell	10.5
SA10	Non-soluble, and swell	10.2
SA15	Non-soluble, and swell	9.4
SA20	Non-soluble, and swell	9.2

(Concentration of ECH: 5×10^{-2} M).

$$\text{Chitosan} + \text{CH}_3\text{COOH(aq)} \frac{+\text{NaOH(aq)}}{\text{Coagulation}}$$
$$\rightarrow \text{Chitosan fiber} + \text{CH}_3\text{COONa(SA)} + \text{H}_2\text{O}$$

Equation (2) Crosslinking of chitosan fiber (Lee et al., 2004; Mark, Wooding, & Atlas, 1971; Mayer & Kaplan, 1991).

$$\text{Chitosan} + \text{CH}_3\text{COOH(aq)}$$
$$+ \text{Epichlorohydrin} \frac{+\text{NaOH(aq)}}{\text{Crosslinking}}$$
$$\rightarrow \text{Crosslinked chitosan fiber} + \text{NaCl(HCl} + \text{NaOH)}$$
$$+ \text{H}_2\text{O}$$

As can be seen from Equation (1) and (2), coagulation retardant SA is product of equation (1). Therefore the SA concentration of the coagulation bath increased, the fiber formation speed of the spinning dope decreased. As a result, the crosslinking speed of chitosan fiber increased. The tensile properties of chitosan fiber prepared in this experiment were summerised in Table 3. The relationship of the tenacity of the crosslinked fiber to the concentration of SA (SAX) used is shown in Fig. 4. Both dry and wet tenacity increased in accordance with an increase in the concentration of SA. It is evident that the strength of the chitosan fiber, its dry and wet tenacity, is improved by increasing the crosslinking (Wei et al., 1992; Lee et al., 2004; Mayer & Kaplan, 1991). As the SA concentration was increased, the dry and wet tenacity increased. However, the increasing dry and wet tenacity are mitigated at SA concentrations higher than 10 wt%.

The change in elongation due to failure with crosslinking, as determined for dry and wet fibers, is presented in Fig. 5. For the dry fibers, it is observed that the elongation decreased by addition of SA when its concentration increased from 0 to 10 wt%. However, the elongation of the chitosan fiber did not increase with concentrations of retardant agent greater than 10 wt% SA. Again, it is noted that there no deleterious effect on the wet fiber properties as a result of the crosslinking.

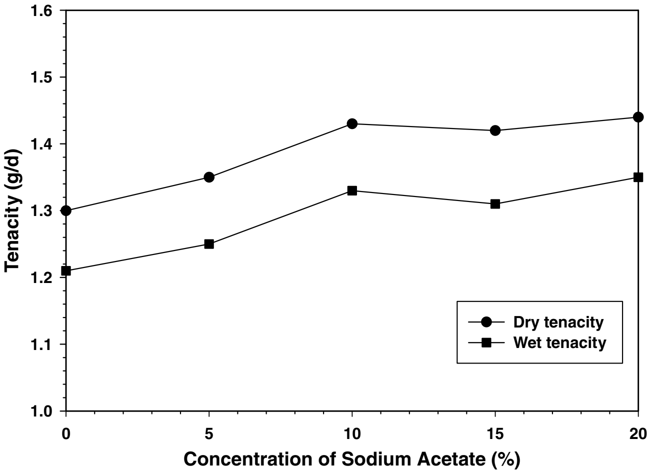

Fig. 4. The effect of concentration of sodium acetate on dry and wet fiber tenacity.

On the other hand, the relationship of the initial modulus of the crosslinked fiber to the concentration of SA (SAX) used is shown in Fig. 6. Both dry and wet tenacity increased in accordance with an increase in the concentration of SA. It is evident that the initial modulus of the chitosan fiber, its dry and wet modulus, is slightly harded by increasing the crosslinking.

3.5. DSC thermogram

Fig. 7 shows the DSC curves of various chitosan fibers with different concentrations of SA in the coagulation bath. In the case of chitosan fibers, a strong exothermal peak occurs within the temperature range of 320–330 °C. There is evidence in the temperature interval 320–330 °C of thermal decomposition of the crystalline structure, and in the case of chitosan fibers, of an exothermal reaction within the polymer. The characteristics of DSC of chitosan fiber summarized at Table 4. As shown in Table 4, the peak of

Table 3
Tensile properties of chitosan fibers

Concentration of sodium acetate (%)	Condition of measurement	Tenacity		Elongation		Initial modulus at 2% extension	
		Mean (g/d)	CV (%)	Mean (%)	CV (%)	Mean (g/d)	CV (%)
0	Dry	1.30	9.3	15.4	10.6	31.9	9.7
	Wet	1.21	5.6	14.6	9.9	23.9	4.3
5	Dry	1.35	8.9	15.4	13.2	32.5	4.3
	Wet	1.25	9.5	14.3	12.8	24.2	9.5
10	Dry	1.43	6.7	13.2	10.9	35.8	5.4
	Wet	1.33	5.6	14.6	12.8	24.0	7.0
15	Dry	1.42	7.9	13.2	11.2	36.1	8.5
	Wet	1.31	4.2	14.2	11.8	25.4	9.9
20	Dry	1.44	6.6	13.6	10.7	36.3	7.8
	Wet	1.35	10.3	14.7	14.4	28.6	9.4

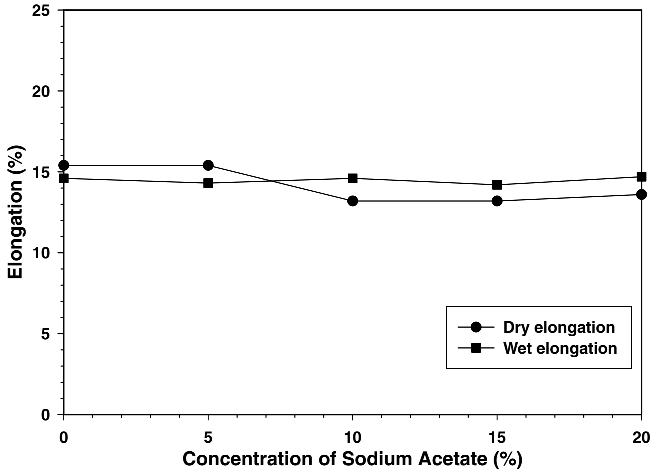

Fig. 5. The effect of concentration of sodium acetate on dry and wet fiber elongation.

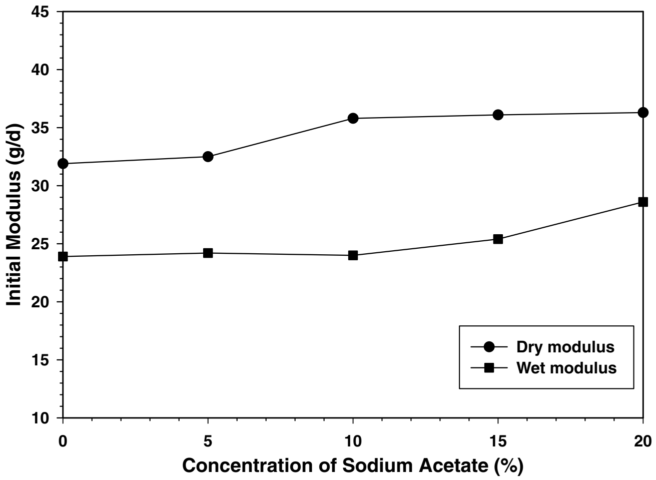

Fig. 6. Relationship between concentration of sodium acetate and initial modulus (at 2% extension).

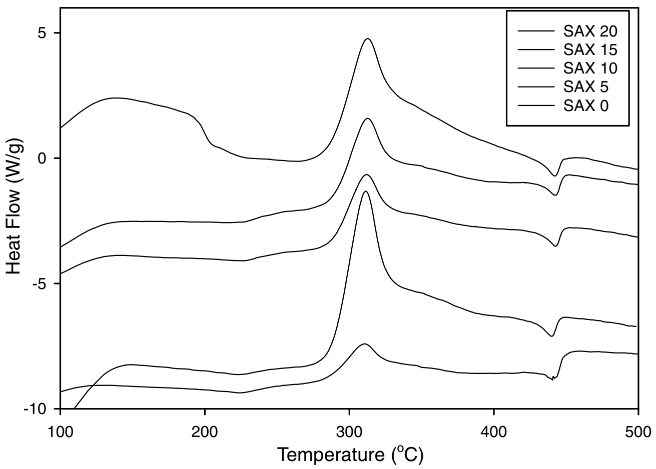

Fig. 7. DSC thermograms of chitosan fiber.

Table 4
DSC characterization of chitosan fibers

SAX	Onset of exothermic temperature (°C)	Peak of exothermic temperature (°C)	Heat of decomposition (J/g)
SA0	286.07	310.47	359.1
SA5	289.44	311.24	408.1
SA10	288.11	311.53	468.1
SA15	289.23	312.55	486.6
SA20	286.51	312.97	712.9

exothermic temperature and the heat of composition increase as the concentration of SA in coagulation bath increases and that the onset of the exothermic temperature does not have this tendency. This is attributable to the fact that the degree of crosslinking of chitosan fiber increases gradually because of the relaxation of coagulation in the coagulation bath by caused the SA.

3.6. Scanning electron microscopy (SEM)

The fracture surface of the fibers after tensile failure in the dry state was observed by SEM. Fig. 8 shows those of fibers fractured under tension in the dry state. The fractured tip of crosslinked chitosan fiber manufactured in the absence of SA (Fig. 8a) showed hard and fragile morphology. However, in the fractured tips of crosslinked chitosan fibers in the presence of SA, hard and fragile structures were not found, and smooth surfaces appeared increasing levels of concentration of SA (Fig. 8b–e). In the case of crosslinked chitosan fibers, a smooth surface in the fractured section is attributable to the formation of bridges between intermicrofibrils preventing fracture of the fibrils (Oh, 1996). Thus, the smooth-faced surface was enhanced by increasing the concentration of SA.

4. Conclusions

Chitosan fibers regarded as raw materials for the manufacture of medical and textile dressing materials have many advantages. They have relatively high hygroscopicity and considerably large swelling ability in both water and physiological salt solutions. Chitosan fibers are readily prepared at concentrations of SA 0, 5, 10, 15, 20 wt%, which results in changes in the mechanical properties of these materials. The coagulation and the crosslinking of chitosan fiber has been shown to occur simultaneously in coagulation bath. In the current study, we analysed the relationship between the SA concentration of the coagulation bath and the resulting fiber characteristics. The fiber characteristics were analysed by degree of swelling, soluble phenomenon, mechanical properties, DSC thermal properties, and SEM morphologies. The following conclusions were obtained:

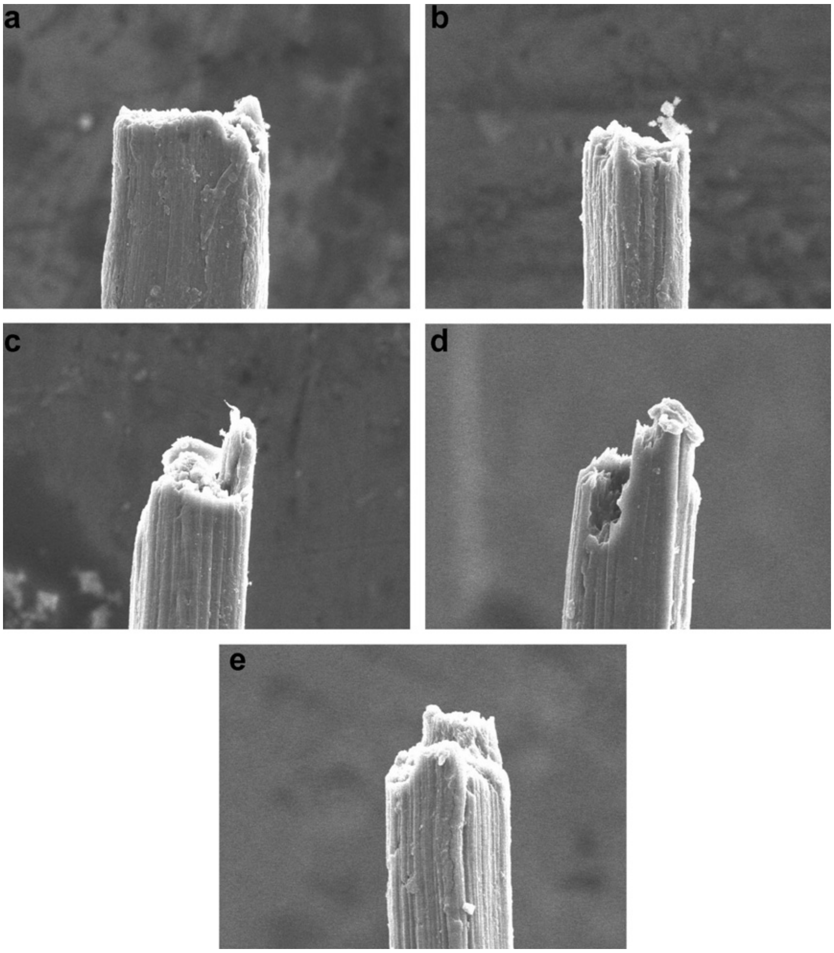

Fig. 8. SEM micrographs of the fracture surface of a dry fiber that failed while under tensile loading. (a) SAX 0, (b) SAX 5, (c) SAX 10, (d) SAX 15, and (e) SAX 20.

1. The maximum draw ratio was increased with increasing the concentration of SA in the coagulation bath. However, the degree of swelling decreased with increasing concentration of SA of the coagulation bath.
2. The fiber properties were affected by the spinning conditions, such as the crosslinking agent (ECH) of the spinning dope, the retardant (SA) of the coagulation bath. The tenacity at breaking point and the initial modulus at 2% extention were increased with increasing the concentration of SA in the coagulation bath. However, the increasing dry and wet tenacity were mitigated at SA concentrations greater than 10 wt%. For the dry fibers, it was observed that the elongation was decreased by addition of SA when its concentration was increased from 0 to 10 wt%. There was no deleterious effect on the wet fiber properties as a result of crosslinking.
3. The crosslinked chitosan fibers showed good thermal stability. The peak of exothermic temperature and the heat of composition increased as the concentration of SA in coagulation bath increased.
4. The fractured tip of crosslinked chitosan fiber manufactured in the absence of SA showed hard and fragile morphology. However, in the fractured tips of crosslinked chitosan fibers in the presence of SA, hard and fragile structures were not found, and smooth surfaces appeared shown with increasing levels of concentration of SA.

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