Fiber Formation and Physical Properties of Chitosan Fiber Crosslinked by Epichlorohydrin in a Wet Spinning System: The Effect of the Concentration of the Crosslinking Agent Epichlorohydrin

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Received 3 December 2002; accepted 4 December 2003

ABSTRACT: The wet spinning of chitosan fibers was studied with 2% acetic acid as the solvent, 10% aqueous sodium hydroxide as the nonsolvent, and a 4% chitosan solution as the polymer. This article describes the crosslinking of the chitosan fibers. Epichlorohydrin (ECH) was selected as a convenient base-catalyzed crosslinking agent. The coagulation and crosslinking of the chitosan fibers occurred simultaneously in the coagulation bath. In this study, we investigated the effect of the concentration of the crosslinking agent, ECH, in the spinning dope on the structural, thermal, morphological, and mechanical properties (e.g., the tenacity, elongation, and work of rupture) of chitosan fibers. The tenacity of the chitosan fibers, especially the wet tenacity, was improved by crosslinking. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2054–2062, 2004

Key words: crosslinking; fibers; epichlorohydrin; wet spinning; tenacity

INTRODUCTION

Chitin [(1,4)-linked 2-acetamido-2-deoxy-β-D-glucan] has two hydroxyl groups, and its *N*-deacetylated derivative, chitosan, has one reactive amino group and two hydroxyl groups per hexosamine residue. Chitosan is an underused polymer that possesses many of the desired characteristics for fiber applications; that is, it is readily mineralized in the environment through the actions of microbes and weathering.[1] These biopolymers are biocompatible, biodegradable, and biofunctional and are, therefore, used to good effect as special products in the surgical treatment of the human body.

Strong intramolecular and intermolecular hydrogen bonds exist in chitosan to form random orientations. The dissociation and reorganization of these hydrogen bonds by chemical modification give rise to novel molecular conformations in the forms of solutions, sols, hydrogels, fibers, films, and sponges.[2–4] In contrast to chitin, chitosan is characterized by excellent fiber-forming abilities. Fiber spun from chitosan can be used in the manufacture of woven and knitted textile goods used in medicinal dressing materials and as an exclusive or additional fibrous component.

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Journal of Applied Polymer Science, Vol. 92, 2054–2062 (2004)

Chitosan fibers are typically spun from viscous, concentrated polymer solutions commonly called *spinning dopes*. Melt spinning cannot be used 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.[5–9]

The wet spinning of chitosan fibers from the polymer in its bulk form, typically a powder or flakes, involves the dissolution of the polymer in aqueous acetic acid (1–10 vol % glacial acetic acid in water) to form the dope. This dope is then pumped to a spinneret that is submerged in a high-pH coagulation bath. In this bath, the polymer is precipitated in the fiber form. After coagulation, the chitosan fiber may be washed for the removal of excess coagulant and subsequently wound on a bobbin.[8]

Fibers obtained by coagulation are drawn or stretched at a suitable stretching ratio of up to 300% to improve the tensile properties of the fibers and to adjust the fineness (denier) of the fibers. The stretching of the fibers can be carried out in water, preferably boiling water.[10]

This article describes our work in crosslinking chitosan fibers. It is our objective to improve the functional properties of this material. Chitosan is not easily defined because it is difficult to fully deacetylate chitin. Chitosan is the preferred form of the polymer because it is more readily processed into fiber and film

forms than chitin. A drawback of chitosan is its enhanced hydrophilicity in comparison with chitin, which results in a considerable loss of tensile strength when chitosan is wet.[1]

Epichlorohydrin (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.[11] This methodology has been adapted to crosslink chitosan films and, in this work, fibers. Most notably, crosslinking by ECH considerably improves the strength of chitosan films and fibers.[1,12] In this work, the formation and characteristics of fibers crosslinked by ECH in a one-step wet-spinning system have been investigated. A similar study is also described here for crosslinked fibers.

EXPERIMENTAL

Materials

Chitin from red crabs of the East Sea was acquired from Dongbo Chemical Co. (Sekcho, Korea). The acetic acid (Aldrich, Milwaukee, WI), sodium hydroxide (Fluka, Buchs, Switzerland), ECH (Sigma, St. Louis, MO), and urea (Sigma) that were used were reagent-grade.

Preparation of chitosan

Chitin was obtained from Dongbo Chemical Co. as a flake powder that originally came from red crab shells. Chitosan was prepared by the deacetylation of chitin in an alkali solution of 50 wt % NaOH and 10 wt % chitin, which was heated to 110°C for 2 h. The solid was filtered and washed thoroughly with distilled water until a nearly neutral pH was attained. The solid was dried *in vacuo* at room temperature, cut in a knife-milling machine, and sieved through a 60-mesh screen (pore size = 250 μm).

Preparation of the chitosan fibers by wet spinning

The fiber formation process is described with an emphasis on the development of the optimum fiber structure for commercial applications. By fiber formation, we mean the process by which the spinning dope is converted into fibers in the spin bath. Wet spinning is the most widely used spinning process in solution spinning. The fiber denier in these spinning operations is controlled by the material balance given by the following equation:

$$D\ (\text{denier}) = \frac{Q \times C \times \rho \times 9000}{V_s \times D_r \times n}$$

where Q is the volumetric flow rate per spinneret hole (mL/s), C is the concentration of the spinning dope (%/100), ρ is the spinning dope density (g/mL), V_s is the first roller speed [the linear speed (m/s) at which the fibers leave the coagulation bath], D_r is the overall stretch ratio including any relaxation, and n is the number of holes.

The meaning and usefulness of this equation can be best conveyed if we recognized that the parameters in the equation can be approximately factored into three groups representing three distinct stages of fiber production. These are dope preparation (C and ρ), fiber formation in the coagulation bath (Q and V_s), and fiber processing (D_r).

Figure 1 depicts a schematic drawing of the wet spinning system used in this study. A spin dope was prepared by the dissolution of 4% (w/v) chitosan in a solution of 2% (w/w) aqueous acetic acid. To a set of chitosan samples was added ECH, varying in concentration from 0.0 to 25.0 $\times$ $10^{-2}M$; the samples were labeled CEX 0.5, CEX 1.0, CEX 2.5, CEX 5.0, CEX 10.0, and CEX 25.0, the numbers referring to the ECH concentration (M). The solutions were mechanically stirred for 60 s to be homogenized; then, the dope solutions were degassed and filtered with 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 with a variable-speed infusion metering pump. The spinneret was 0.1 mm in diameter and had a capillary length-to-diameter ratio of 2. A 400-mesh (pore size = 37 μm) stainless steel filter was mounted behind the spinneret. The coagulation bath was a 10% (w/w) aqueous NaOH solution. The coagulation and crosslinking of the chitosan fibers occurred in this coagulation bath at the same time. As a result, the crosslinking reaction started at the surface and worked its way to the core of the fibers (polymer jet). Depending on the residence time in the coagulation bath, the fibers may not have been crosslinked throughout their entire cross section. The fibers emerging from the wet-spinning coagulation bath were unoriented and had little strength. The development of the anisotropic mechanical properties required of textile fibers is accomplished largely in the orientational drawing operation.[13] Therefore, the fibers obtained from the coagulation bath were washed in water and drawn or stretched to a suitable stretching ratio at 99 $\pm$ 1°C in a water bath. The take-up velocity at the end of the coagulation bath was maintained at 3.0 m/min for all the experiments.

Measurements

The tensile properties of the monofibers were measured with a tensilon (Fafegraph M) at a crosshead speed of 20 mm/min at room temperature. The degree of swelling of the fibers was measured with a moisture percentage measuring instrument (HR73 moisture analyzer, Mettler–Toledo) under standard conditions. The thermal behavior of the chitosan fibers was inves-

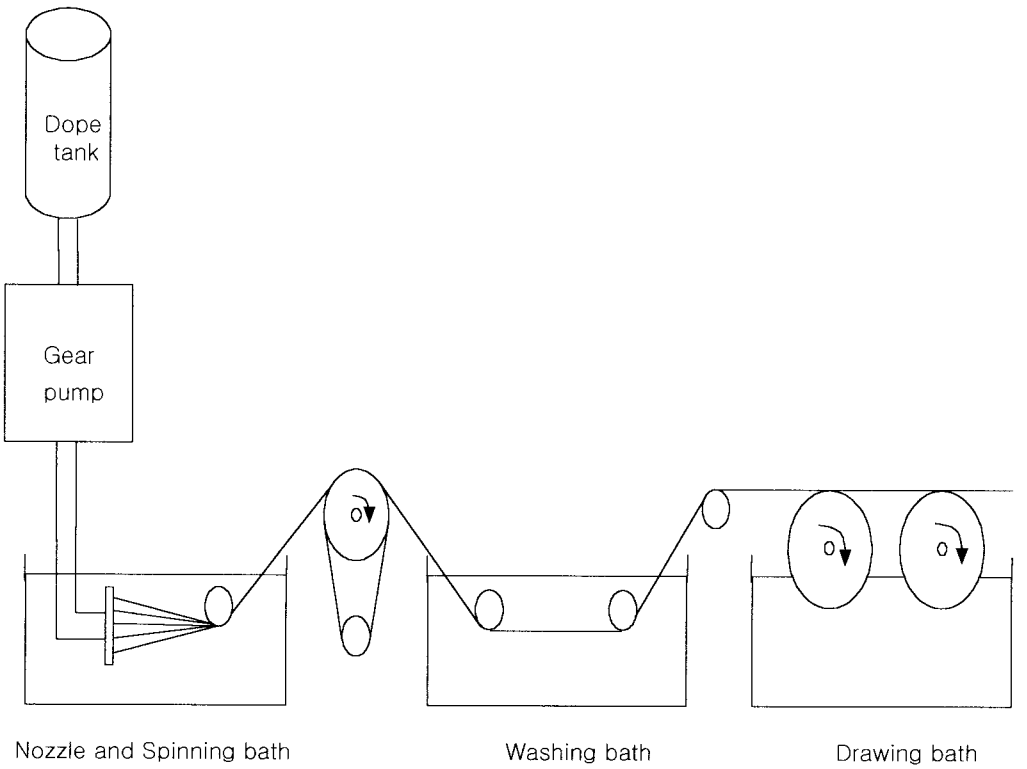

Figure 1 Schematic diagram of the wet-spinning apparatus.

tigated with a TA Dupont 9900 differential scanning calorimeter. The measurements of the chitosan fibers were performed at a scanning rate of 20°C/min from 35 to 450°C in a nitrogen atmosphere. X-ray diffractograms of the chitosan fiber samples were obtained with a Rigaku XG X-ray generator working at 35 kV and 20 mA. The scattered X-ray in the wide-angle X-ray diffraction mode was monochromatized to a Cu Kα ray with a graphite monochromator and counted with a Rigaku Denki scintillation counter at intervals of 2° of the scattering angle with a Rigaku Rint 2000 goniometer. The fractured samples were prepared by the stretching the fibers to the breaking point on a tensilon under standard conditions. The morphologies of the fractured fibers were studied with scanning electron microscopy (SEM; JSM 6400).

RESULTS AND DISCUSSION

Degree of deacetylation and molecular weight of chitosan

The degree of deacetylation was measured with infrared spectroscopy. This method is based on the relationship between the absorbance value at 1555 cm^{-1}, which is attributed to amide II, and the corresponding value of the methylene group at 2867 cm^{-1}, by the use of the following equation : NH_2 (%) = $(A_{1555}/A_{2867})(1/2.84) \times 100$. The value 2.84 represents this relationship for completely acetylated chitosan. The absorbance values found at 1555 cm^{-1} represent the amide II groups, whereas those found at 2867 cm^{-1} are indicative of methylene groups. The degree of deacetylation of the chitosan and chitin was calculated with these values.[14]

The viscometry-average molecular weight (M_v) was determined viscometrically with the relation $[\eta] = kM_v^{\alpha}$, 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, and 4*M* urea mixed in an aqueous solution.[15,16] The viscometric measurements were performed at 25 ± 0.01°C with an Ubbelohde suspended-level dilution viscometer. Because of the insolubility of chitin, that is, at a reaction time of 0 h, the limiting viscosity number at that reaction time could not be measured. The characteristics of the chitosan and chitin prepared in this experiment are summarized in Table I. As shown in Table I, before the reaction, the degree of deacetylation was 65.7%, whereas after 2 h of reaction, the degree of deacetylation was 84.3%. This suggests that the degree of deacetylation increases as the reaction time increases.

Degree of swelling

A fiber swells if it has the capacity to store substances in a liquid or vapor form on a temporary basis. Each

TABLE I
Characteristics of Chitin and Chitosan Used in this Study

	Reaction time (h)	
	0	2
Degree of deacetylation (%)	65.7	84.3
M_v	550,000	191,000
Ash content (%)	1.0 (↓)	0.5 (↓)
Protein content (wt %)	1.0 (↓)	0.5 (↓)

swelling process is a preparatory stage toward it becoming a solution. A lower packing density and a higher amorphous level are provided by more free functional groups (—OH, —NH_2, and —$NHOCOCH_3$ groups). As a result, the swelling ability is greater and it is easier to dissolve such 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 result 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 fibers; this is why it is known as intermicellary swelling. The water content of fibers increases with swelling. When an uncrosslinked fiber is placed in water, in comparison with a crosslinked fiber, it swells to an extent that is dependent on 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 on the nature of the crosslinking and reinforcement.

To determine the degree of swelling, we must make a series of gravimetric measurements and determine the weight reduction percentage as a function of the ECH concentration. In other words, the degree of swelling decreases with the degree of crosslinking of chitosan molecules.

The degree of swelling of a chitosan fiber in this study is calculated as follows:

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

where WW is the wet weight after centrifugation (g) and DW is the dry weight (g). The weight of a completely dried sample was measured directly, and the sample was dipped into a glass beaker filled with distilled water for 24 h at 20°C. The weight of the swollen fiber was measured by centrifugation (20,000 rpm for 5 min). The degree of swelling of the crosslinked chitosan fiber versus the changing concentration of ECH is shown in Figure 2. The degree of swelling decreased with the addition of ECH when its concentration increased from 0 to $5 \times 10^{-2}M$. There was no increase in the degree of swelling beyond a concentration of $5 \times 10^{-2}M$, and this suggests that a limit of crosslinking was reached.

However, a convenient proof of crosslinking is the swelling behavior of the crosslinked fiber in 2% aqueous acetic acid, which is a solvent of chitosan. Simple swelling measurements were used to estimate the extent of crosslinking. A swelling ratio (the ratio of the

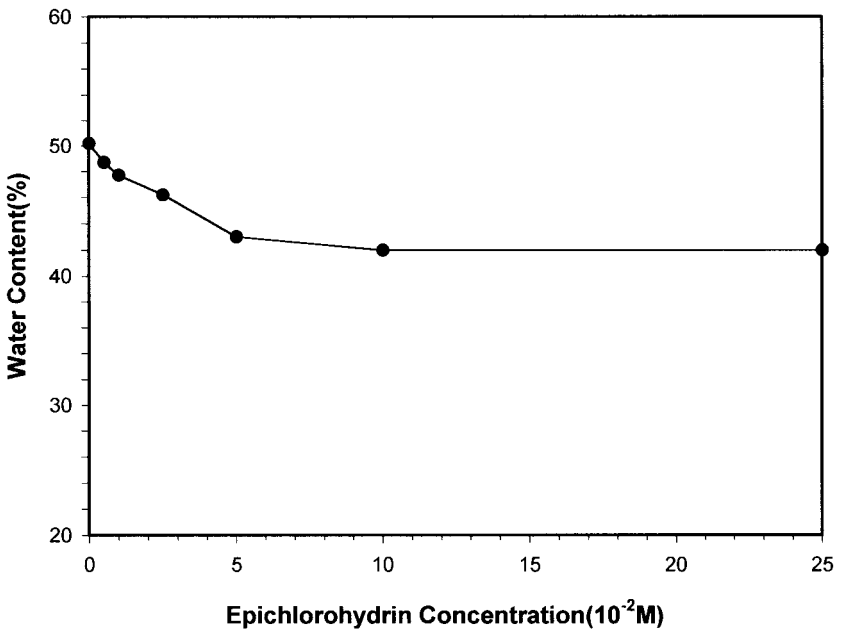

Figure 2 Effect of the ECH concentration on the water content in the chitosan fiber.

TABLE II
Effect of the Concentration on the Solubility in 2 wt % Aqueous Acetic Acid

[ECH] $\times 10^2 M$	Solubility characteristics	Swelling ratio
0	Soluble	—
0.5	Partially soluble	—
1	Nonsoluble and swollen	52.0
5	Nonsoluble and swollen	11.2
25	Nonsoluble and swollen	10.6

volumes of the swollen and unswollen fibers) was determined by an examination of the diameters of the fibers with optical microscopy. The swelling ratios and solubility characteristics are also reported in Table II. At ECH concentrations of 0 and $0.5\times 10^{-2}M$, the measurement of the swelling ratio was impossible because the chitosan fiber dissolved. As shown in Table II, the swelling ratio and solubility of the chitosan fiber decreased with the concentration of ECH in the spinning dope, mainly because of the growing crosslinking density of the chitosan polymer chains.[1,17]

Tensile properties

The relationship of the tenacity of the crosslinked fiber with the ECH concentration is shown in Figure 3. It is evident that the strength of the chitosan fiber, especially its wet tenacity, is improved by crosslinking.[12] However, the tenacity in the dry state decreases with an increase in the ECH concentration. Typically, during the pad bake crosslinking of cellulose fibers, there is considerable degradation of the tensile properties throughout the process.[18] As the ECH concentration is increased, the wet tenacity increases and the dry tenacity decreases. However, increasing the concentrations above $5.0 \times 10^{-2}M$ does not produce a further increase in the wet tenacity or a further decrease in the dry tenacity.

The changes in the elongation with crosslinking, as determined for dry and wet fibers, are presented in Figure 4. For the dry fibers, the elongation decreases with the addition of ECH when its concentration increases from 0 to $5 \times 10^{-2}M$. However, the elongation of the chitosan fiber does not decrease further with concentrations of the crosslinking agent ECH greater than $5 \times 10^{-2}M$. Again, there is not a deleterious effect on the wet fiber properties as a result of crosslinking.

The change in toughness, also known as the work to rupture, with increasing amounts of the crosslinking agent, as determined for dry and wet fibers, is presented in Figure 5. The toughness decreases with an increasing amount of the crosslinking agent up to $5 \times 10^{-2}M$. However, regardless of the presence or absence of the crosslinking agent, the work to rupture in the dry state is higher than that in the wet state.

X-ray spectroscopy

Wide-angle X-ray diffractograms showing radical scans of the intensity versus the angle of diffraction (2θ) for chitosan fibers with various concentrations of ECH for the spinning dope are shown in Figure 6. Generally, a diffractogram of chitosan fibers shows a moderately sharp intense diffraction at the (040) plane near $2\theta = 20.2°$ and a less intense diffraction at the

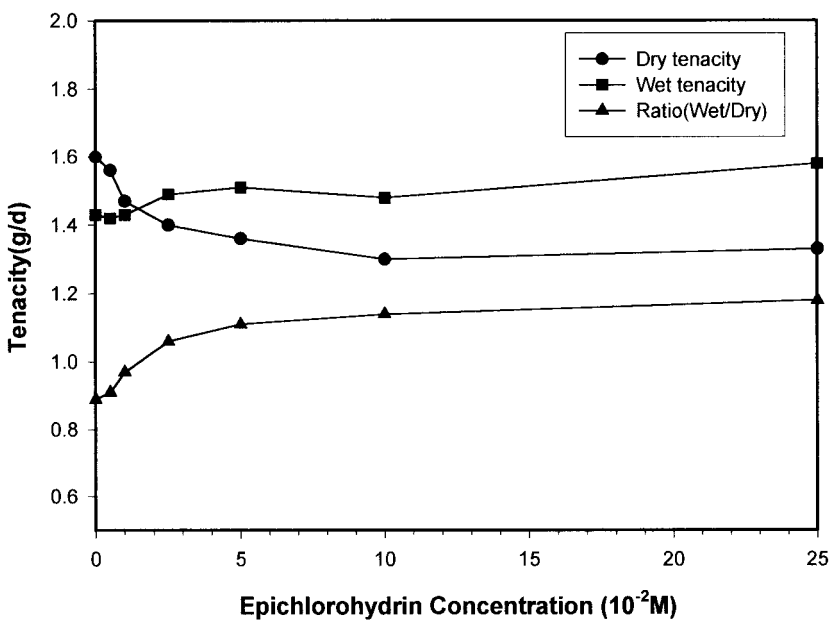

Figure 3 Effect of the ECH concentration on the dry and wet fiber tenacity.

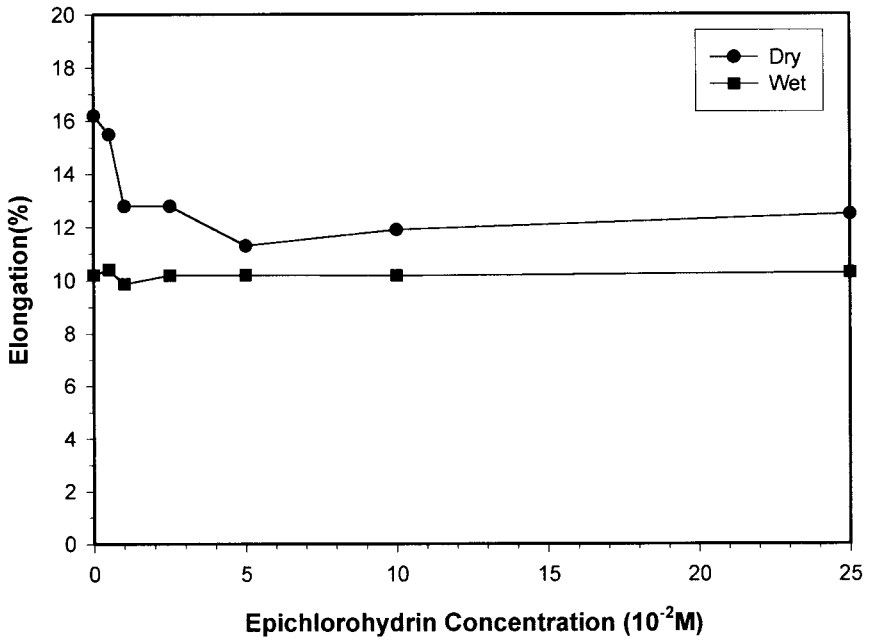

Figure 4 Effect of the ECH concentration on the dry and wet fiber elongation.

(020) plane near $2\theta = 10.2°$. The sharp, intense diffraction corresponds to a lateral repeat distance, or Bragg spacing, and has been represented as the (040) diffraction of orthorhombic or monoclinic structures. As shown in Figure 6, the wide-angle X-ray diffractograms of the chitosan fibers are nearly the same in their profile and intensity. This result leads to the conclusion that the crosslinking agent does not affect the formation of the crystalline structure within the extent of this study.

Differential scanning calorimetry (DSC) thermograms

Figure 7 shows the DSC curves of various chitosan fibers with different concentrations of ECH for the

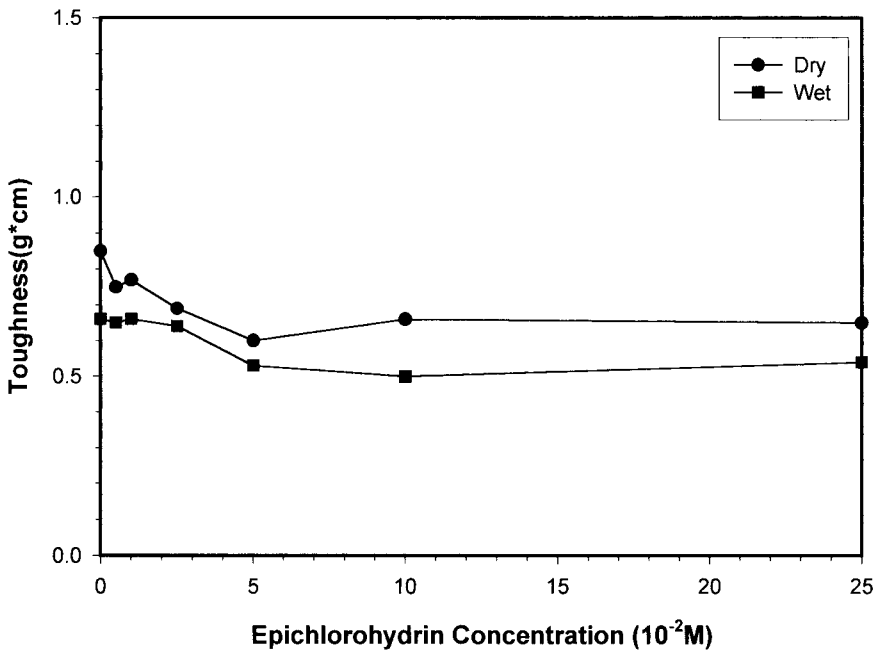

Figure 5 Effect of the ECH concentration on the dry and wet fiber toughness.

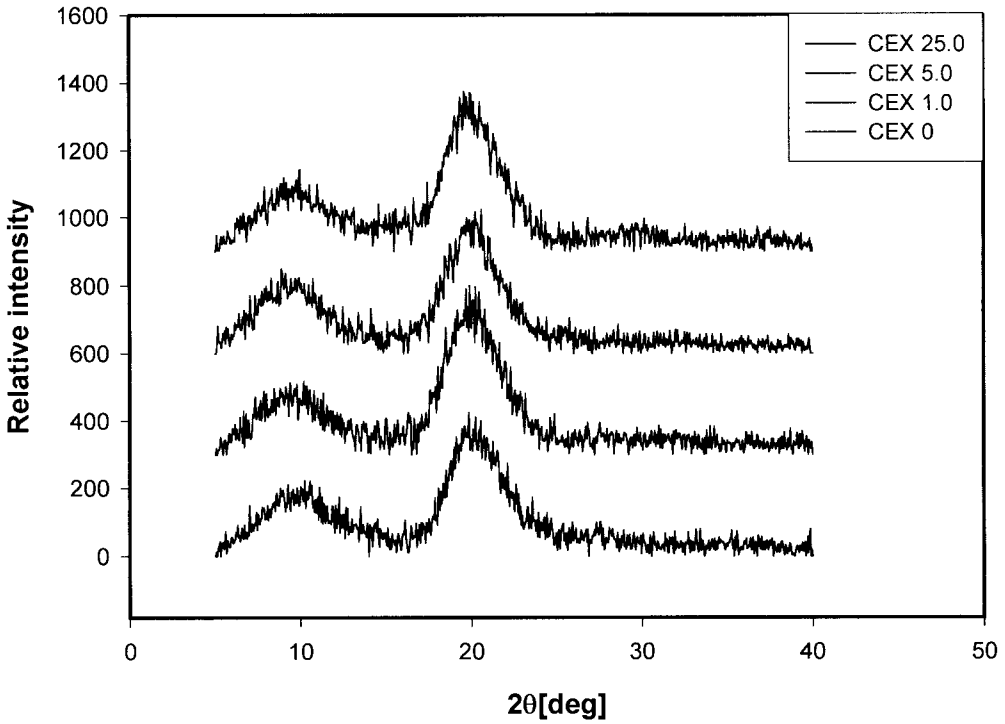

Figure 6 Effect of the ECH concentration on the X-ray diffractograms of the chitosan fiber.

spinning dopes. In the case of chitosan fibers, a strong exothermic peak occurs within the temperature interval of 320–330°C. There is evidence in this interval of the thermal decomposition of the crystalline structure and, in the case of chitosan fibers, of an exothermic reaction within the polymer. As shown in Figure 7, the DSC curves of the chitosan fibers are nearly the same in their profile and intensity. This suggests that the crosslinking by ECH hardly affects the thermal decomposition of the chitosan fibers within the extent of this study.

SEM

The fracture surfaces of the fibers after tensile failure in the dry state were observed by SEM. Figure 8 shows SEM images of fibers fractured under tension in the dry state. The fractured tips of the noncrosslinked

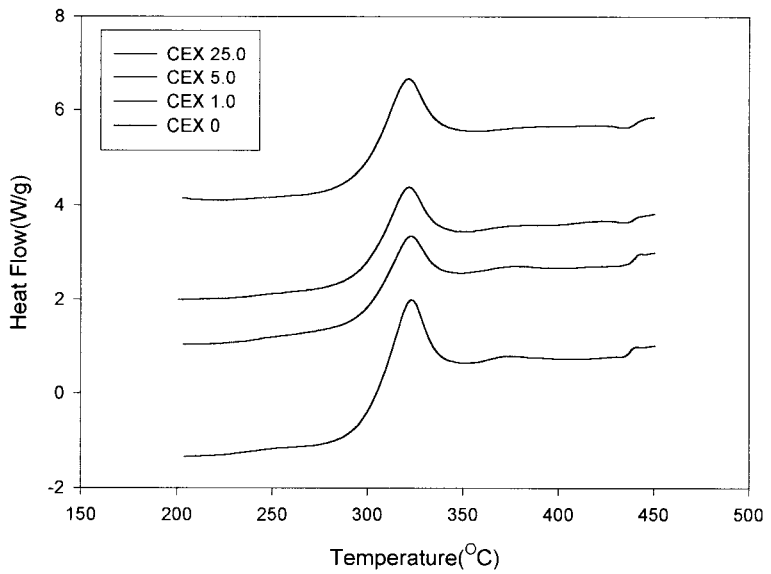

Figure 7 DSC thermograms of the chitosan fiber.

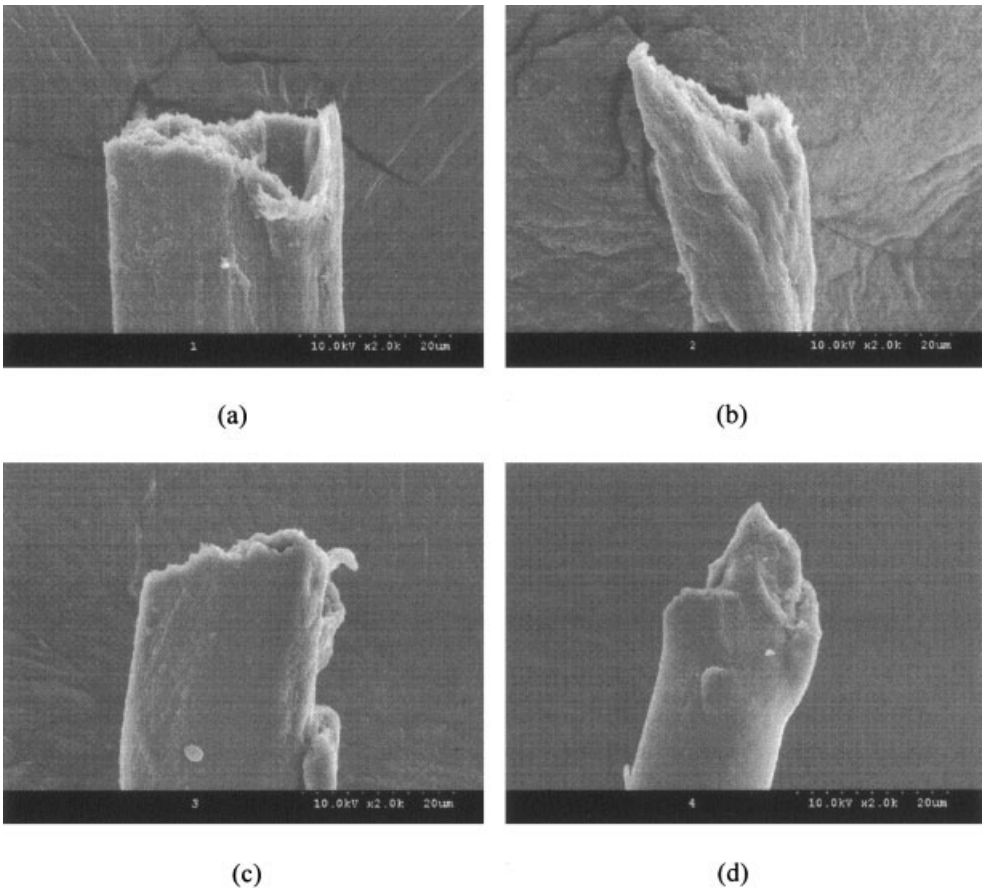

Figure 8 SEM micrographs of the fracture surfaces of dry fibers that failed under tensile loading: (a) CEX 0, (b) CEX 1.0, (c) CEX 5.0, and (d) CEX 25.0.

chitosan fibers [Fig. 8(a)] showed a hard and fragile, glasslike morphology. However, in the fractured tips of crosslinked chitosan fibers, hard and fragile structures were not found, and smooth surfaces were shown with increasing concentrations of ECH [Fig. 8(b–d)]. In the case of crosslinked chitosan fibers, a smooth surface in the fractured section was due to the formation of bridges between intermicrofibrils preventing the fracture of the fibrils.[19] Thus, the smooth-faced surface was enhanced with an increased concentration of ECH.

CONCLUSIONS

The studied fibers, potential raw materials for the manufacture of medical and textile dressing materials, have many advantages. They have relatively high hygroscopicity and a considerable swelling ability in water and in physiological salt solutions. Chitosan fibers are readily prepared with ECH concentrations of 0, 0.5 1.0 2.5 5.0, 10.0, and 25.0 $\times 10^{-2}M$; this results in changes in the mechanical properties of these materials. The coagulation and crosslinking of chitosan fibers have been shown to occur in the coagulation bath simultaneously. In this study, we have analyzed the relationship between the concentration of ECH in the spinning dope and the resulting fiber characteristics. The fiber characteristics were analyzed with infrared spectrophotometry, the degree of swelling, the solubility, the mechanical properties, X-ray diffractograms, DSC thermal properties, and SEM morphologies. From this work, the following conclusions were obtained:

1. The degree of swelling decreases as the concentration of ECH increases in the spinning dope.
2. The wet tenacity at the breaking point increases somewhat as the concentration of ECH increases in the spinning dope. However, the dry tenacity decreases significantly with an increasing concentration of ECH in the spinning dope. For the dry fibers, the elongation decreases with the addition of ECH. There is no deleterious effect on the wet fiber properties as a result of crosslinking. The work to rupture decreases with the addition of ECH. The saturated concentration of ECH is about 5 $\times 10^{-2}M$.

3. The wide-angle X-ray diffractograms and the DSC curves of the chitosan fiber and crosslinked chitosan fibers are nearly the same in their profile and intensity.
4. The fractured tip of a noncrosslinked chitosan fiber has a hard and fragile, glasslike morphology. However, in the fractured tips of crosslinked chitosan fibers, hard and fragile structures disappear, and smooth surfaces are found with an increasing degree of crosslinking.

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