Ripening Time and Fiber Formation of Chitosan Spinning Dope

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ABSTRACT: A study was carried out on the wet spinning of chitosan fibers using 2% acetic acid as a solvent, 10% aqueous sodium hydroxide as a nonsolvent, and 4% chitosan solution as a polymer concentration. In this study, we investigated the effect of the ripening time of the spinning dope on the ability of fiber formation (*i*-value), structure, thermal, and mechanical properties (such as fineness, tenacity, elongation, work of rupture, etc.) of chitosan fibers. Based on the results, it can be seen that the ripening time of spinning dope (in days), with the same polymer concentration of spinning dope, changes from 1 to 8, and the *i*-value of the spinning dope increased with an increasing of the ripening time. At the ripening time of 8 days, tensile strength, elongation, and work of rupture showed minimum value attributed to the excessive degradation of the chitosan polymer chains left from the mixing operation that took place at the same time as the ripening time of the spinning dope, which means that the optimum ripening time of the spinning dope is 1 to 7 days. However, the thermal decomposition temperature and the onset of the exothermic temperature of thermal properties decreased with an increased ripening time. On the other hand, tenacity, elongation, and toughness decreased with increasing ripening time, and these qualities radically decreased with an increasing ripening time of more than a week. This indicates that the dispersion of aggregates and the degradation of chitosan polymer chains left from the mixing operation occurred at the same time during the ripening time of the spinning dope. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2870–2877, 2003

Key words: chitin; chitosan; polysaccharides fibers; biopolymers

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 and two hydroxyl groups per hexosamine residue. Chitosan is an underused polymer that possesses many of the desired characteristics for this application; that is, it is readily mineralized in the environment through the actions of microbes and weather. 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.

The main driving force in the development of new applications for chitosan lies in the fact that the polysaccharide is not only naturally abundant, but it is also nontoxic and biodegradable. Unlike oil and coal, chitosan is a naturally regenerating resource (e.g., crab and shrimp shells) that can be further enhanced by artificial culturing. It was reported that chitosan and chitin are contained in cell walls of fungi. Chitin, however, is more widely distributed in nature than chitosan and can be found in mushrooms, yeasts, and the hard outer shells of insects and crustaceans. It was reported, for example, that about 50–80% of the organic compounds in the shells of crustacea and the cuticles of insects consists of chitin. At present, most chitosan in practical and commercial use comes from the production of deacetylated chitin with the crab shell, shrimp, and krill (the major waste byproduct of the shellfish) processing industry being the most readily available sources of chitosan.[1–3]

Strong intra- and intermolecular hydrogen bonds exist in chitosan to form parallel and antiparallel orientations. The dissociation and reorganization of these hydrogen bonds by chemical modification gives rise to novel molecular conformations in the forms of solutions, sols, hydrogels, fibers, films, and sponges.[4–6] In contrast to chitin, chitosan is characterized by its excellent fiber-forming ability. Fiber spun from chitosan can be employed in the manufacture of woven and knitted textile goods used in medicinal dressing materials, and as an exclusive or additional fibrous component.

All commercial chitosan fibers are spun from viscous, concentrated polymer solutions commonly referred to as spinning dope. Melt spinning cannot be used because the chitosan polymers degrade upon heating. The spinning processes most commonly used for chitosan fibers are wet spinning. In wet spinning, the spinning dope is extruded through a multiple-hole spinneret into a coagulation bath containing a nonsolvent.[7–11]

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. 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. After coagulation, the chitosan fiber may be washed to remove excess coagulant and subsequently wound on a bobbin.

The fibers obtained by the coagulation are drawn or stretched in a suitable stretching ratio of, say, up to 300% to improve the tensile properties of the fibers as well as to adjust the fineness of the fibers. Stretching of the fibers must, of course, be carried out in a wet solvent, preferably boiling water.

The spinning dope is ripened by storage. In viscose rayon, when the viscose solution is first made, it is very thick. On standing, it becomes thinner and then, later, more viscous again. This process is known as ripening, which is an essential part of the viscosity process; young viscose cannot be spun satisfactorily, neither can viscose that is even a few hours too old. On the other hand, in the case of the chitosan solution, during the ripening process the viscosity of the spinning dope decreased gradually because of the dispersion of aggregates and the degradation of chitosan polymer chains left from the mixing operation, and also had a significant impact on the fiber formation and mechanical properties of individual fibers. Thus, in this work, the effects of the ripening time of the spinning dope on the fiber formation and the fiber characteristics were the focus of this investigation.

EXPERIMENTAL

Material

Chitin from red crabs was acquired from the Dongbo Chemical Company of Korea. Acetic acid (Aldrich, Milwaukee, WI), sodium hydroxide (Fluka, Milwaukee, WI), urea (Sigma, St. Louis, MO), and distilled water were used in all experiments.

Preparation of chitosan

Chitin was obtained from the Dongbo Chemical Company of Korea as a flake powder that originally came from red crab shells. Chitosans were prepared by deacetylation of chitin in an alkali solution, 50% NaOH, 10% chitin solution, for 1, 2, and 3 h at 110°C, respectively. The solid was filtered and washed thoroughly with distilled water until it attained nearly neutral pH. The solid was dried in a vacuum at room temperature, and finally cut in a knife-milling machine until sieved through a 60-mesh stainless steel filter.

Preparation of chitosan fiber by wet spinning

The fiber-formation process will be described with 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 fiber in the spin bath. Wet spinning is the most widely used spinning process in solution spinning. The fineness of fiber D (denier) in all spinning operations is controlled by the material balance given by the following equation:

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

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

The meaning and usefulness of the above equation can be best conveyed by recognizing that the parameters in the equation can be approximately factored into three groups representing three distinct stages of fiber production: (1) dope preparation (C, ρ); (2) fiber formation in the coagulation bath (Q, V_s); and (3) fiber processing (D_r).

Chitosan fiber was wet spun by general flowing methods described in Figure 2. A spin dope was prepared by dissolving 4% w/v chitosan in a solution of 2% v/v aqueous acetic acid. The chitosan dope was extruded through a stainless steel 300-hole spinneret by means of a variable-speed infusion-metering pump. Spinneret dimensions were 0.1 mm in diameter and a capillary length-to-diameter ratio of 2. Mounted behind the spinneret was a 400-mesh stainless steel filter. Dope solutions were degassed and filtered in a vacuum system and the dope solutions were ripened for 1–8 days at 20 ± 0.01°C in a vacuum-sealed oven. The coagulation bath was a 10 w/w % NaOH aqueous solution. The fibers emerging from the wet-spinning coagulation bath are unoriented and have little strength.

Development of the anisotropic mechanical properties required of textile fibers is accomplished largely in the orientational drawing operation. Therefore, the fibers obtained by the coagulation bath are washed in water and drawn or stretched in a suitable stretching ratio at 99 ± 1°C in a water bath. The takeup velocity at the end of the coagulation bath was maintained at 3.0 m/min for all experiments.

Measurements

Shear viscosities of spinning dopes were measured using a Brookfield viscometer (Tokimec BM). The

TABLE I
Characteristics of Chitin and Chitosan

Reaction time (h)	Degree of deacetylation (%)	Viscosity-average molecular weight (M_v)
0	65.7	—
1	82.1	191,000
2	84.2	173,000
3	85.1	148,000

spinning dopes and controls were placed in an oven at a temperature of 20°C (ripening temperature), and in no case should this temperature be exceeded. Measurements were carried out at a ripening time of 1–8 days at 20°C. Tensile properties and fineness of monofibers were measured using a tensilon (Fafegraph *M*) with a crosshead speed of 20 mm/min at room temperature. The thermal behavior of chitosan fibers was investigated using differential scanning calorimetry (TA Dupont 9900, New Castle, DE). The measurements for the chitosan fiber were performed at a scanning rate of 20°C/min at a temperature range of 35 to 400°C in a nitrogen atmosphere. X-ray diffractograms of the chitosan fiber samples were obtained using a Rigaku (Japan) XG X-ray generator working at 35 kV, 20 mA. The scattered X-ray in WAXD mode was monochromatized to Cu–K$_\alpha$ ray with a graphite monochromater, and counted with a Rigaku Denki scintillation counter at intervals of 2° of scattering angle using a Rigaku Rint 2000 goniometer.

Degree of deacetylation and molecular weight of the chitosan

The degree of free groups in chitosan was determined 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: $NH_2 = (A_{1555}/A_{2867})(1/2.84)100$. The value 2.84 represents the same relationship for completely acetylated chitosan.[12]

The viscometric-average molecular weight (M_v) was determined viscometrically using 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 0.2M acetic acid–0.1M sodium chloride–4M urea mixed aqueous solution.[13,14] The viscometric measurement was done at 25 ± 0.01°C with a Ubbelohode suspended-level dilution viscometer. Molecular weights of the chitosans are summarized in Table I.

RESULTS AND DISCUSSION

Degree of deacetylation and molecular weight of the chitosan

The degree of deacetylation was measured by infrared spectroscopy. The absorbance values found for amide II at 1555 cm^{-1}/methylene groups at 2867 cm^{-1} at reaction times of 0, 1, 2, and 3 h gave 0.634/0.340, 0.786/0.337, 0.792/0.331, and 0.810/0.335, respectively. Degrees of deacetylation of the chitosans and the chitin was calculated by applying these values. On the other hand, the viscosity-average molecular weight was determined by Ubbelohode viscometer. The limiting viscosity number $[\eta]$ of a solution, which has long been called the intrinsic viscosity, is defined as

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_0}{c\eta_0}$$

in terms of the solvent viscosity η_0, the solution viscosity η, and the solute concentration c. The concentration c is expressed in grams of solute per 100 milliliters of solution, the limiting viscosity number being given in the reciprocal of these unit (i.e., mL/g). The limiting viscosity numbers at reaction times of 1, 2, and 3 h gave 5.016, 4.676, and 4.185, respectively. Because of the insolubility of chitin (i.e., at reaction time 0 h), the limiting viscosity number at reaction time 0 h could not be measured. From these limiting viscosity numbers, the viscosity-average molecular weight was calculated by the Mark–Houwink–Sakurada equation. The characteristics of the chitosan and chitin prepared in this experiment are summarized in Table I. As shown in Table I, with no reaction, the degree of deacetylation (%) is 65.7, whereas at reaction times of 1, 2, and 3 h, degrees of deacetylation (%) are 82.1, 84.2, and 85.1, respectively. This suggests that the degree of deacetylation (%) increases with an increased reaction time. On the other hand, the viscosity-average molecular weight decreases with an increase in the reaction time as a result of alkali hydrolysis.

Relationship between ripening time and the viscosity of spinning dope

Figure 1 shows the relationship between the ripening time and the viscosity of the spinning dope. The ripe spinning dope is drawn off to settling tanks in which it is subjected to a vacuum to remove residual air bubbles because these would cause discontinuities in the extruded fibers. The result shows that the viscosity of the spinning dope smoothly decreases with an increased ripening time in these experiments, attributed to the dispersion of aggregates and to the degradation of the chitosan polymer chains during the ripening time of the spinning dope. In the case of molecular weights of 173,000 and 148,000 g/mol; their *i*-values—the ability of fiber formation—is similar. With similar *i*-values at the same spinning conditions, formation of high-tenacity fiber is possible even with retention of a
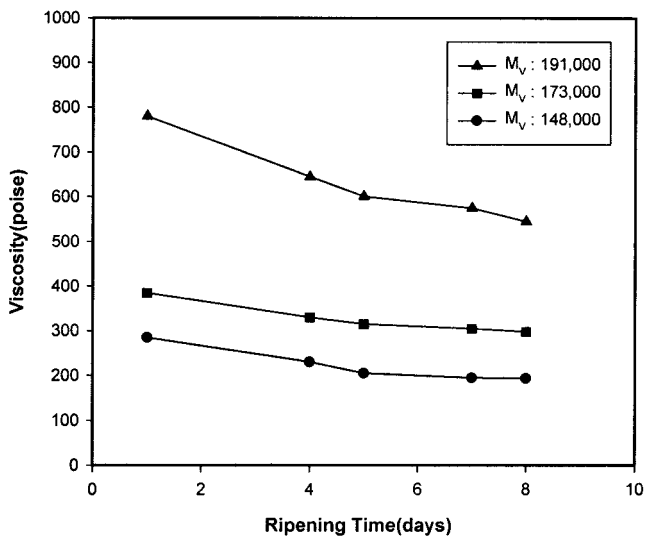
Figure 1 Relationship between ripening time and viscosity of spinning dope.

higher molecular weight.[20] In the case of molecular weight 191,000 g/mol, however, the *i*-value is less than 1, which means that the fiber of desired fineness (denier) cannot be produced. From these results, it was judged that chitosan of molecular weight 173,000 g/mol was suitable to this study. Thus, in this work, the fiber formation and the fiber characteristics of the chitosan of molecular weight 173,000 g/mol were the focus of this investigation.

The wet spinning of chitosan fibers from the chitosan polymer in its bulk form, typically powder or flake, involves dissolution of the polymer in aqueous acetic acid (1–10% by volume glacial acetic acid in water) to form a dope. Because of the solubility of the chitosan, the hydrolysis of the chitosan, the simplification of the spinning process (acetic acid and NaOH minimum consumption) and so forth many investigators have used a 2% aqueous acetic acid solvent, which we also used in this work.[11,16–20]

On the other hand, the physical property of the fiber is characteristically superior as the concentration of polymer increases. Generally, viscosity of the dope increases with an increase in concentration. Because of the physical property of the fiber and the stabilization of the spinning process(deairing, filteration, spinability, etc.), the suitable viscosity of the dope is in the range from 100 to 5000 poise or, preferably, from 200 to 1000 poise. Therefore a 4% chitosan solution as a polymer concentration was used in this study. I do not think that 20°C is the most suitable ripening temperature; thus, in this work, the ripening of chitosan dope was carried out in standard temperature conditions. Investigation of the optimum conditions about concentration of acetic acid, concentration of chitosan polymer, and ripening temperature, for example, will be carried out in future research.

Relationship between spinnability and the molecular weight of chitosan

Most of the fundamental investigations to be discussed here were done using small, laboratory-scale spinning lines that have all of the process stages of their commercial-size counterparts. A schematic diagram of a typical laboratory wet-spinning line used by Lee is shown in Figure 2. A polymer dope with a
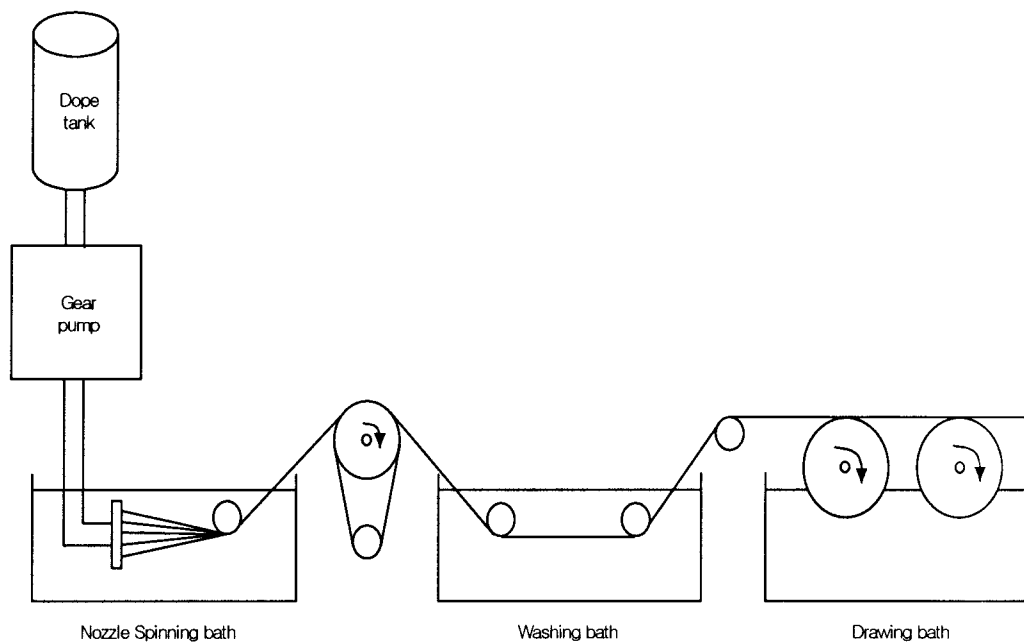

Figure 2 Schematic diagram of wet-spinning apparatus.

viscosity of about 200–800 poise is pumped to a spinneret immersed in a coagulating bath containing an aqueous solution of sodium hydroxide. 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 figure 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 of the spinning dope. The plot of maximum spin draw ratio, i-value, of molecular weight of chitosan versus the ripening time of the spinning dope is shown for the 5 m/min flow rate of the dope in Figure 3. As shown in Figure 3, the i-value increases with the decreasing molecular weight of chitosan polymer and an increase in the ripening time. Generally, in the wet spinning of polymer, the i-value of the spinning dope decreases with an increase in the molecular weight at the same concentration of polymer because of the difficulty of polymer chain extension in the polymer solution. On the other hand, in the case of the chitosan solution, the i-value of the spinning dope gradually increased with the ripening time as a result of the dispersion of aggregates and the degradation of chitosan polymer chains left from the mixing operation.
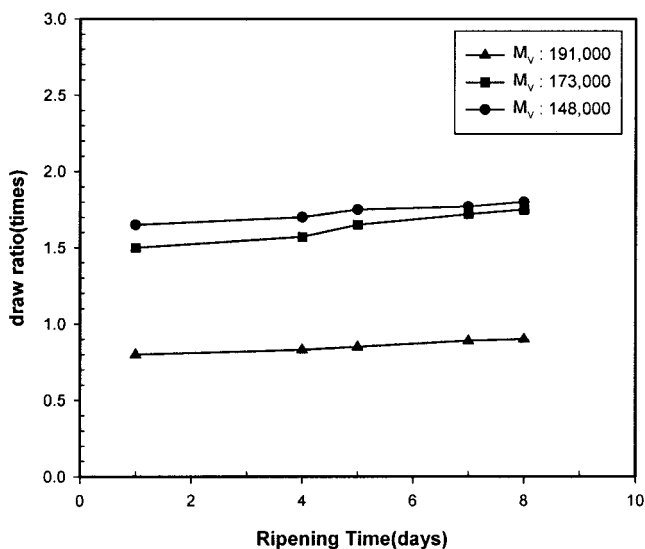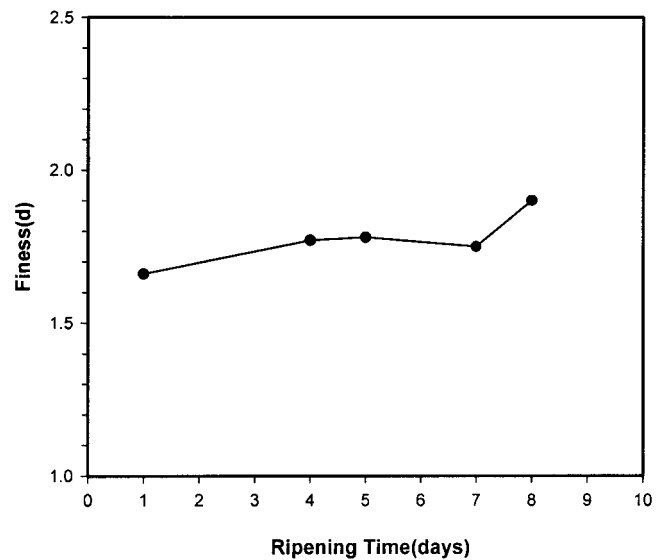

Figure 4 Relationship between ripening time and fineness of dry fiber [viscosity-average molecular weight (M_v) = 173,000].

The fiber is next pulled through a water bath by a second roller at a velocity of V_d to obtain an orientation draw ratio of $D_r = V_d/V_s$. In this study, the protofiber was then drawn to 130% in a second coagulation bath and then was dried on the final roller to give about 1.5–1.9 denier per fiber. The temperature of the water in the draw bath can be adjusted but is most often maintained close to the boiling point.

Relationship between ripening time and fineness of dry fibers

Figure 4 shows the relationship between the ripening time and the fineness of dry fibers (mobility of the spinning dope). This result shows that the fineness of dry fibers increases with an increase in the ripening time of the spinning dope at the same driven motor speed of the gear pump. Because of the degradation and aggregation of chitosan polymer during the ripening time of the spinning dope the mobility of the spinning dope increases in the direction of the spinning process.

Relationship between ripening time and tensile properties of dry fibers

Figures 5, 6, and 7 show tenacity, elongation, and toughness (work of rupture) at breaking point of the ripened chitosan fiber as a function of the ripening time of the spinning dope, respectively. The tenacity at breaking point was decreased with an increase in the ripening time and, in particular, decreased the ripening time of spinning dope beyond 7 days. This result was most significant in the case of chitosan spinning dope resulting from the degradation through chitosan
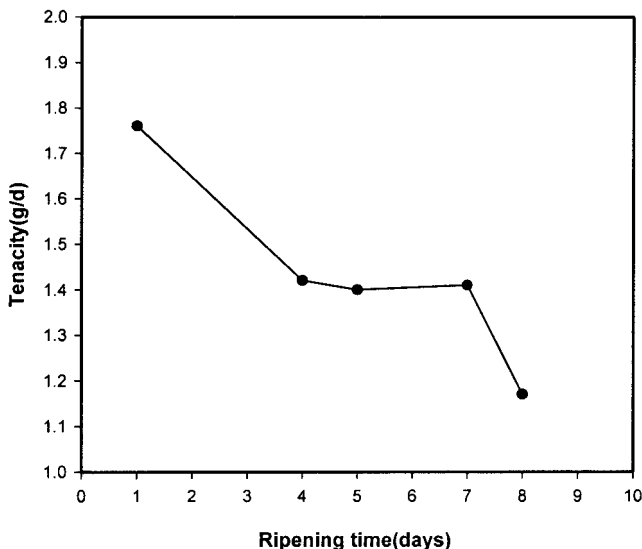

Figure 3 Relationship between ripening time and draw ratio of protofiber.

Figure 5 Relationship between ripening time and tenacity of dry fiber ($M_v = 173,000$).
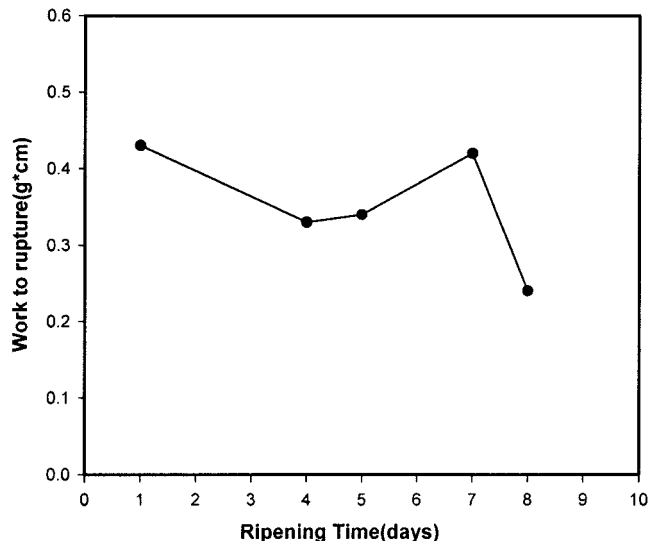

Figure 7 Relationship between ripening time and work of rupture of dry fiber ($M_v = 173,000$).

within an aqueous acetic acid solution, the solvent of chitosan. Typically, during the ripening and ageing of cellulose fibers, there is considerable degradation of the tensile properties through this process.[21] The elongation at breaking point had almost the same value as a function of the ripening time of the spinning dope. On the other hand, the work of rupture of these fibers at breaking point and the integration area of the stress–strain curve up to breaking point are functions of tensile strength and elongation. As shown in Figure 7, the maximum work of rupture appeared at the ripening time of the spinning dope of 1 day and 7 days in this study. At the ripening time of 8 days, tensile strength, elongation, and work of rupture showed

minimum values attributed to the excessive degradation of the chitosan polymer chains left from the mixing operation, which took place at the same time as the ripening time of the spinning dope. From these results, the optimum ripening time of the spinning dope was determined to be 1 to 7 days. Consequently, this means that the wet spinning of the chitosan solution should be carried out after deairing with ripening over 1 to 7 days.
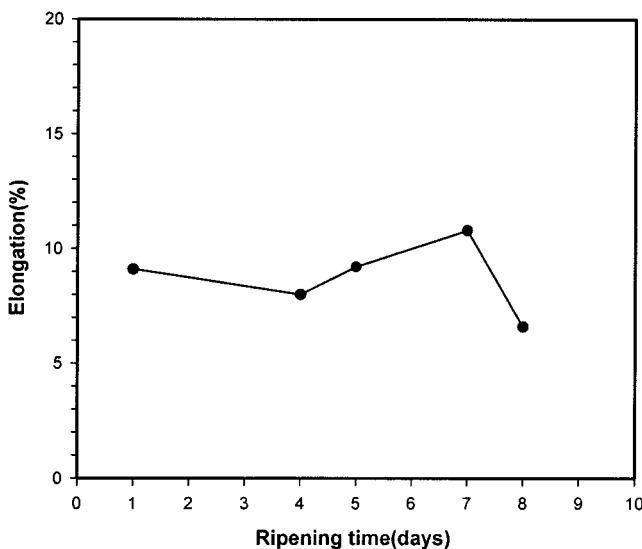
Relationship between ripening time and X-ray spectroscopy

Wide-angle X-ray diffractograms showing radical scans of the intensity versus angle of diffraction (2θ) for chitosan fibers with varying ripening times for the spinning dope are shown in Figure 8. Generally, the 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 (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) orthorhombic or monoclinic diffraction. The degree of crystallinity of chitosan fibers was measured by the method proposed by Hermans.[22] Degrees of crystallinity for chitosan fibers are 0.235, 0.238, 0.239 at ripening times of 1, 5, and 8 days, respectively. As one can see, the chitosan fibers are nearly the same in their degrees of crystallinity and slightly increase with the increase of the ripening time of the spinning dope in the dry fiber. This suggests that the degree of crystallinity of chitosan fibers is independent of the ripening time of the spinning dope.
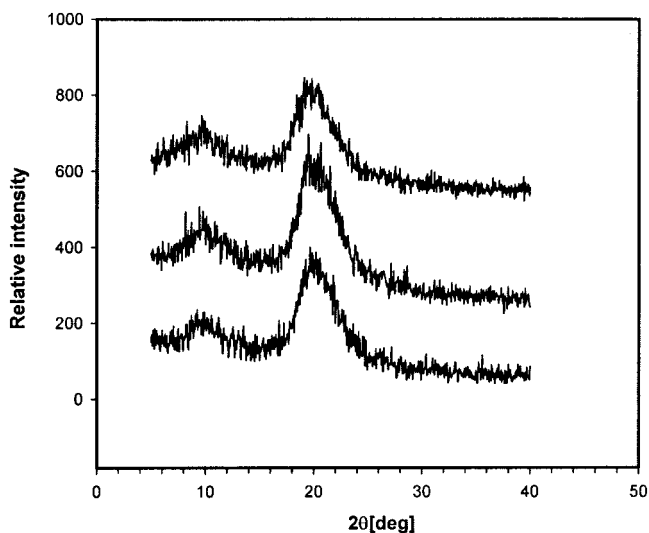

Figure 6 Relationship between ripening time and elongation of dry fiber ($M_v = 173,000$).

Figure 8 X-ray diffractograms of chitsan fiber. Ripening time: top: 8 days; center: 5 days; bottom: 1 day.

Relationship between ripening time and DSC thermogram

Figure 9 shows the DSC curves of various chitosan fibers with different ripening times for the spinning dopes. As shown in Figure 9, chitosan fibers with ripening times of 1, 5, and 8 days differ from each other qualitatively in their thermal properties. In the case of chitosan fibers, a strong exothermal peak (thermal decomposition point) occurs within the temperature interval 300–350°C. In Table II it is shown that the peak temperature decreases as the ripening time of the spinning dope increases and that the onset of the exothermic temperature has the same tendency. This is evidence in the temperature interval 300–350°C of thermal decomposition of the crystalline, and in the
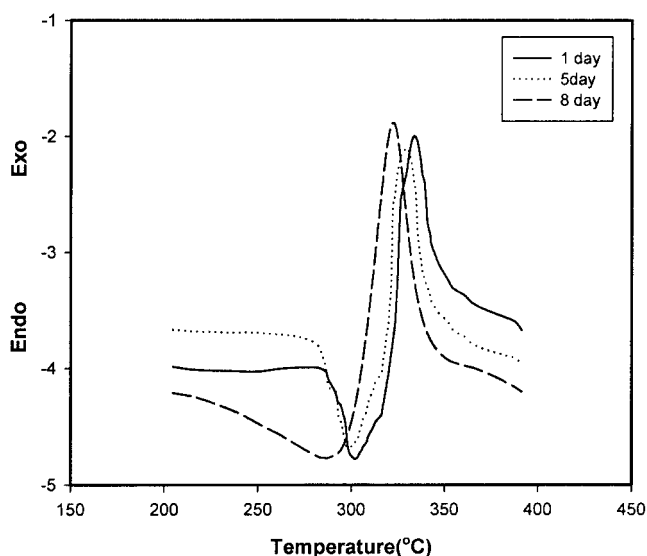
TABLE II
DSC Characterization of Chitosan Fibers

Ripening time of spinning dope (days)	Onset of exothermic temperature (°C)	Peak temperature (°C)
1	302	344
5	299	330
8	287	323

case of chitosan fibers, of an exothermal reaction within the polymer. This is attributed to the fact that the molecular weight of chitosan decreases gradually because of the degradation of the chitosan polymer chains in the ripening process left from the mixing operation.

CONCLUSIONS

The studied fibers regarded as raw materials for the manufacture of medical and textile dressing materials have many advantages. They have relatively high hygroscopicity, that is, considerably large swelling ability in water and in physiological salt solutions. Chitosan fibers are readily prepared with ripening times of 1–8 days, which results in changes in the mechanical properties of these materials. In this study, we investigated the relationship between the ripening time of spinning dope and the fiber formation of the wet spinning system. This was ascertained by spinnability, mechanical properties, X-ray diffractograms, and DSC thermal properties. From this work, the following conclusions were obtained:

1. In this experiment, the plot of maximum spin draw ratio, the *i*-value, increased with the decreasing molecular weight of the chitosan polymer and increasing ripening time.
2. The tenacity at breaking point was decreased with an increase in the ripening time and, in particular, decreased the ripening time of the spinning dope more than 7 days. The elongation at breaking point was almost the same value as a function of the ripening time as the spinning dope. On the other hand, the maximum work of rupture of these fibers at breaking point showed at the ripening times of 1 day and 7 days.
3. The diffractogram of the chitosan fiber shows a moderately sharp intense diffraction at the (040) plane near $2\theta = 20.2°$ and a less-intense diffraction at the (020) plane near $2\theta = 10.2°$. Degrees of crystallinity for chitosan fibers are 0.235, 0.238, and 0.239 at ripening times of 1, 5, and 8 days, respectively.
4. The peak temperature, the thermal decomposition temperature, decreased with an increase in the ripening time of the spinning dope and the

Figure 9 DSC thermograms of dry fiber ($M_v = 173,000$).

onset of the exothermic temperature follows the same tendency.

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