Improved Mechanical Properties of Chitosan Fibers

JONATHAN Z. KNAUL,¹ SAMUEL M. HUDSON,² KATHERINE A. M. CREBER¹

¹ Department of Chemistry and Chemical Engineering, Royal Military College, P.O. Box 17000, Station Forces, Kingston, ON, K7K 7B4, Canada

² Fiber and Polymer Science Program, Box 8301, Centennial Campus, North Carolina State University, Raleigh, North Carolina 27695-8301

Received 25 March 1998; accepted 11 October 1998

ABSTRACT: A highly deacetylated chitosan from shrimp with a degree of deacetylation of 95 \pm 3% was prepared and spun into a monofilament fiber using a solution of 5% by weight chitosan in 5% by volume aqueous acetic acid. Samples of the spun fibers were immersed in separate solutions containing phosphate ions and phthalate ions, and subsequently washed and dried. The various solutions ranged in pH from 4.12 to 7.75. The highest dry mechanical properties resulted from solutions containing phthalate ions between 4.5-5.5 pH, and from solutions containing phosphate ions at pH 5.4. Immersion time was varied between 1 and 60 min at 25.8°C, and temperature was varied between 25.8 and 70.0°C, in the phosphate ion solutions at a pH of 5.8. Dry mechanical properties were highest at 25.8°C and after 1 h of treatment. Chitosan films were subjected to similar treatments in phosphate and phthalate ion solutions. Fourier transform infrared data (FTIR) on the films suggest that some interaction is occurring between the phosphate ions and the amine group on the chitosan backbone. An additional experiment was performed whereby the same chitosan was used to prepare a dope of 4% by weight chitosan in 4% by volume aqueous acetic acid with 30% by volume methanol. This solution was spun into fibers, but was subjected to a "final draw" by increasing the speed of the winder. With increasing the final draw, denier and elongation-at-break decreased, while the other mechanical properties showed a marked increase. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1721-1732, 1999

Key words: chitosan; fiber; mechanical; films; FTIR; wet spinning

INTRODUCTION

Chitosan, a (1-4)-linked 2-amino-2-deoxy- β -D-glucopyranose, is derived from chitin, (1-4)-linked 2-acetamido-2-deoxy- β -D-glucopyranose. The chitin polymer is typically extracted from the shells of crustaceans such as shrimp, crab, lobster, and squid. This same polymer may also be found in the shells of some insects such as beetles, and in some fungi. Chitin is typically prepared after the shells are separated from the sea animal, ground, then deprotenized in a hot 5% aqueous NaOH bath, and finally demineralized in a cold 2% aqueous HCl bath. Chitosan is the *N*-deacetylated form of chitin that is obtained after treating the chitin with hot 50% aqueous NaOH. The term chitosan is usually reserved for chitin molecules that are deacetylated to the point where they become soluble in dilute aqueous acidic systems (e.g., 1–10% by volume aqueous acetic acid). One hundred percent *N*-deacetylation of chitin is very difficult to achieve. Molecular illustrations of chitin, chitosan, and the structurally similar biopolymer cellulose can be found in Figure 1.

Correspondence to: J. Z. Knaul.

Journal of Applied Polymer Science, Vol. 72, 1721–1732 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/131721-12



Figure 1 Segments of cellulose, chitin, and chitosan polymers.

To prepare fibers from chitosan, 3-10% by weight of the polymer is typically dissolved in solvents such as 2-10% by volume aqueous acetic acid. The resulting solution, known as a dope solution, will exhibit a viscosity on the order of 100,000 cP. The dope is then extruded into a basic coagulation bath where the solvent is drawn off and the chitosan will precipitate in the form of a fiber. Subsequent to coagulation, the spun fiber may be washed, chemically modified, dried, and taken up on a winder.¹

The copolymeric structure of partially deacetylated chitosan generally lowers the dry/wet strength properties of chitosan fibers.² There are numerous methods available for improving the mechanical properties of chitosan fibers, in particular, the initial modulus, tenacity, and breaking strength. These methods can follow one of two approaches, either one of a physical or a chemical application to the fibers. By virtue of a physical application, improvements to a fiber's mechanical properties can be rendered by applying a stretch to the yarn in the coagulation step of wet spinning, by applying a stretch to the yarn after coagulation but while it is still wet and swollen with water, or by applying a stretch to the yarn after it is dried and just prior to being wound up.³ In 1993, East and Qin reported on the effects on fiber mechanical properties of increasing jet stretch ratio in relation to the maximum draw ratio in the

wash and draw bath. The authors demonstrated a decrease in the maximum draw ratio with increasing jet stretch ratio. East and Qin also reported on the resulting fiber mechanical properties when jet stretch ratio was varied at a fixed draw ratio, and the resulting properties when draw ratio was varied at a fixed jet stretch ratio. The authors were able to show a dramatic decline in breaking strength, and only minimal changes in tenacity, with increasing jet stretch and draw ratios. Minimal changes in extensibility were also in evidence.^{4,5}

Using a chemical approach, fiber mechanical properties can be altered by reaction with another compound—usually this involves crosslinking the polymer chains. Wei et al. (1992) crosslinked chitosan fibers using epichlorohydrin. Results demonstrated a significant increase in wet mechanical properties with increasing reaction time, reaction temperature, and concentration of epichlorohydrin. Dry mechanical properties improved only slightly under the same reaction conditions, and in some cases, these properties were degraded. In both the dry and wet cases, elongation at break remained constant or decreased under all reaction conditions. The dry mechanical values reported in Wei et al.'s 1992 study were a modulus of between 48.1-73.4 g/denier, a tenacity of 1.19-1.46 g/denier, and an elongation at break of 11.2–7.5%. The results of Wei et al. are the

highest modulus values reported to date for chitosan fibers.⁶ Tokura and coworkers have reported the highest tenacity values for a highly deacetylated chitosan fiber (90% deacetylated) at 2.56 g/denier.⁷ Rathke and Hudson's review concerning chitin and chitosan as fiber and film formers covers all of the reported information regarding chitosan fiber results up to 1994.⁸

Chemical methods used to improve the mechanical properties of chitosan fibers usually involve a treatment applied to the fiber after it has been spun, dried, and packaged. In 1991, Minami and coworkers made claims regarding the production of "artificial hairs" from blends of chitosan and polyvinyl alcohol. To make these fibers resistant to water, they were treated with epichlorohydrin and formaldehyde, which added hydrophobic groups to the chitosan molecule.⁹ Other authors have made claims that involve postspinning chemical modifications to chitosan fibers. Typically, such treatments have used toxic agents as crosslinking agents.^{10,11} Many more authors have reported on postcasting modifications to chitosan films and capsules using aldehydes and other $agents.^{12-24}$

In this article we report on the changes in the mechanical properties of chitosan fibers using buffered solutions based on potassium dihydrogen phosphate and also based on potassium hydrogen phthalate. Our aim has been to improve the initial modulus of chitosan fibers through the application of crosslinking agents that are considered to be relatively nontoxic in comparison to most aldehydes.

EXPERIMENTAL

Materials

Chitosan, lot # P59san3, was obtained in the form of flake from Novachem Limited of Dartmouth, Nova Scotia, Canada. This batch was a shrimpbased product obtained from the Gulf of the St. Lawrence. The chitosan was received with a claimed viscosity of 740 cP for a 1% by weight chitosan solution in 1% by volume aqueous acetic acid. The degree of deacetylation as reported by the supplier was 74.0%. The following chemicals were all obtained and used as reagent grade from Sigma-Aldrich Canada Ltd.: glacial acetic acid, sodium hydroxide pellets, potassium hydroxide pellets, methanol, potassium dihydrogen phosphate powder, and potassium phthalate crystals.

Chitosan Characterization

Degree of Deacetylation

The chitosan as received was further deacetylated by heating in 50% by weight sodium hydroxide, for 1 h, at 100°C, in a resin kettle purged with gaseous nitrogen. The reaction product was subsequently washed in distilled water until it exhibited a neutral pH, and then dried in an oven at 50°C for 16 h. The entire process was repeated a second time. The final degree of deacetylation was shown to be 95 \pm 3%, as determined by UV spectrometry, following the method of Muzzarelli et al.²⁵ The water content of the chitosan sample was determined using a Texas Instruments 2050 TGA Thermogravimetric Analyser. The sample was heated from room temperature to 300°C at 10°C per minute under nitrogen. The loss in weight of the chitosan sample up to 180°C was taken to be the result of water evaporation. Repeated TGA runs on the same chitosan sample showed a difference of as much as 1% loss in weight due to water. This relatively large error in the water content value of the chitosan was the largest contributing factor to the error in the % DDA calculation.

Molecular Weight

The viscosity average molecular weight, M_v , was determined by the method of Wang et al. (1991).²⁶ Intrinsic viscosity was measured in a Ubbelohde tube viscometer with a solvent of 0.2*M* acetic acid/ 0.1*M* sodium acetate at 30°C, and M_v was calculated to be $1.13 \pm 0.05 \times 10^6$ g \cdot mol⁻¹. The experiment was repeated three times with five dilutions for each run. The viscosity average molecular weight, M_v , was further measured using the method of Knaul and coworkers²⁷ in a solvent system of 0.25*M* CH₃COOH/0.25*M* CH₃COONa at 25°C. Using the following Mark-Houwink equation, also developed by Kassai and coworkers,²⁸

$$[\eta] = 1.40 \times 10^{-4} M_v^{0.83} \tag{1}$$

the M_v was determined to be $6.99 \pm 3.00 \times 10^5$ g/mol. The molecular weight distribution was additionally analyzed in the solvent system 0.25MCH₃COOH/0.25M CH₃COONa with a TSK-gel column at 35°C using a procedure outlined by Knaul et al. The number-average molecular weight was calculated to be 2.08×10^5 g/mol, the weight-average molecular weight was found to be 3.07×10^5 g/mol, and the polydispersity index



Figure 2 Illustration of the wet spinning system.

was determined to be 1.48. The difference in M_{ν} values between the method of Knaul and coworkers, and Wang et al., most probably lies in the fact that Wang's equation accounts for differences in degree of deacetylation, which is not the case with Kassai's equation.

Method of Fiber Fabrication

Run 1—Fibers from This Run Were Used in Chemical Modification Experiments with Phophate and Phthalate Ions

Chitosan fibers were produced using the method of wet spinning. This method was similar to the method of East and Qin.⁴ A dope was prepared by dissolving 5% by weight of chitosan in a solution of 5% by volume aqueous acetic acid at room

temperature. The dope was prefiltered under a pressure of 150 psi of nitrogen gas, through a 40- μ m stainless steel filter. The dope was then centrifuged to remove all air bubbles, and left to stand for 48 h at 9°C to allow for further dissolution of the chitosan. The apparent viscosity of the dope was estimated to be 140,000 ± 1400 cP at 25°C using a Brookfield RVDV I+ viscometer with a small sample adapter and a # 29 spindle at 10 rpm.

After 48 h at 9°C, the dope was placed in a stainless steel vessel. By applying a nitrogen pressure of 70 psi, the polymer was passed from the vessel to a constant volume metering pump, from the metering pump through a $40-\mu m$ stainless steel filter, and then to a single-hole stainless steel spinneret. The dimensions of the spinneret included a coning angle of 60°, and a diameter of 250 μ m, with a capillary length of 500 μ m, giving a spin-draft ratio of 2 : 1. The spinneret was immersed in a coagulation bath of length 2.1 m containing a solution of 1M KOH. The linear extrusion rate at the spinneret was maintained at $4.8 \text{ m} \cdot \text{min}^{-1}$. After exiting the coagulation bath, the fiber was advanced into a 1 m-long bath containing distilled water at 40°C. From the water bath the fiber was advanced into a 1 m-long bath containing methanol. From the third bath, the fiber proceeded across another advancing roller to a hot roller at 50°C, and then to a winder where the fiber was collected on a bobbin. A diagram of the wet spinning system is found in Figure 2. As

Conditions	$ m pH~\pm 0.05$	Modulus (g/Denier)	Std. Dev.	Breaking Strength (g Force) ^d	Std. Dev.	Elongation at Break (%)	Std. Dev.
Control	7.00	54.32	2.16	40.67	0.76	23.05	0.79
KH phthalate	4.12	66.26	4.61	53.41	2.35	32.10	1.00
KH phthalate	4.58	69.62	6.36	54.44	1.30	31.72	1.26
KH phthalate	5.00	75.73	2.11	54.81	1.21	28.43	0.71
KH phthalate	5.33	71.15	8.01	53.33	0.30	31.12	3.11
Phosphate	5.39	66.26	1.40	49.07	1.17	31.85	2.68
Phosphate	5.68	63.49	6.74	48.73	1.56	32.53	1.53
Phosphate	6.16	63.82	1.40	46.89	1.38	28.03	0.53
Phosphate	6.64	56.67	2.11	42.98	1.18	26.66	0.95
Phosphate	7.25	54.05	1.59	42.31	0.79	27.12	1.19
Phosphate	7.75	49.59	1.65	40.13	0.61	30.33	1.53

Table I The Variance of Mechanical Properties with pH, at 25.8°C^{a,b,c}

^a Fiber denier = 27.29 denier.

 $^{\rm b}$ Testing conditions were at 65% RH and 20°C.

^c Gauge length was set at 2.3 cm.

^d Tenacity, in grams/denier, is calculated by dividing breaking strength by the denier.

per Figure 2, roller number 2 was advanced faster than roller number 1, roller number 1 was run faster than the extrusion rate of the polymer at the spinneret face. As a result, a jet-stretch ratio of $1.03 \ (2.50\%)$ was applied to the coagulating fiber, and a draw ratio of $1.12 \ (11.70\%)$ was applied to the fiber in the water bath. The bobbin of collected fiber was stored in a sealed plastic bag with a dessicant pack at room temperature.

Run 2—Fibers from This Run Were Used in Analysis of Physical Treatments Used to Increase Mechanical Properties

This dope was prepared, filtered, and centrifuged in the same manner as was the dope in run 1, except that the concentration was different. In this case, 4% by weight of chitosan was dissolved in 4% by volume aqueous acetic acid containing 30% by volume of methanol. The apparent viscosity of this dope measured at $84,750 \pm 8475$ cP, also using a Brookfield RVDV I+ viscometer under the same conditions as for the dope of run 1. The method of wet spinning was virtually the same as run 1. However, in this case, the extrusion rate was set at 3.6 m \cdot min⁻¹. An experiment was then conducted whereby the winder was run at increasing speed to change the mechanical properties of the chitosan monofilament by applying a final draw to the dried fiber. The initial draw ratio was set at 1.00 (i.e., no draw applied) and increased over seven steps to 1.18. No jet stretch or draw in the wash bath was applied in this run; only a final draw between the heated roller and the winder (see Fig. 2).

Reaction of Chitosan Fibers with Buffered Solutions

Depending on the desired pH, solutions were prepared using a 0.1M KH phthalate/0.1M NaOH solution for pH values less than 5.8, and a 0.1MKH₂PO₄/0.1M NaOH solution for pH values of 5.8 and greater. The pH value of all solutions was verified using a model 955 Accumet Mini pH Meter provided by Fisher Scientific. The probe was a gel-filled model # 13-620-108, also made by Fisher Scientific. The metered pH values are listed with the mechanical results in Table I. Fiber samples from run 1 were wrapped onto bent glass rods. One hundred milliliters of buffered solution was placed into a glass test tube that was submerged in a constant temperature bath. The fiber sample wrapped on the glass rod was then immersed in the solution for the required time. After removal from the buffered solution, the fiber was rinsed with distilled water for approximately 30 s and then placed in an oven at 50°C for 16 h to dry. Control samples underwent the same procedure except that they were immersed in distilled water rather than a buffered solution.

Mechanical Testing

Mechanical testing of fiber samples was performed at the facilities of DuPont Canada Inc. (Kingston, ON) using an 1120 Series Instron tensiometer. Gauge length was set at 23 mm, the crosshead speed was 23 mm \cdot min⁻¹, and the chart speed was 1000 mm \cdot min⁻¹. All samples were preconditioned at 20°C and 65% relative humidity for 24 h prior to mechanical testing. Yarn count was determined to be 27.29 denier based on the weights of 9 cm lengths of yarn averaged over five measurements.

Film Preparation

A low viscosity chitosan solution was prepared by dissolving 0.5 g of chitosan in 100 mL of 1% by volume aqueous acetic acid at room temperature. Films were cast by pouring the 0.5% chitosan solution into Petri dishes and allowing the poured solutions to dry overnight, also at room temperature. After 24 h, the films were immersed in a solution of 1M KOH for 15 min at room temperature, rinsed in distilled water for 1-2 min, and then left to dry again overnight. Three films were reacted in buffered solutions at pH 4.6 in potassium hydrogen phthalate, and three other films were immersed in buffered solutions at pH 5.8 in KH₂PO₄ for 24 h at 25.8°C. After removal from the buffered solutions, the films were again rinsed in distilled water and left to dry overnight at room temperature. In total, there were seven films: the "control," which was immersed in distilled water; three films immersed at pH 4.6; and three films immersed at pH 5.8.

Fourier Transform Infrared Analysis

The IR spectra of the films were obtained with a Nicolet A 510 P FTIR spectrometer in transmission mode. The sample chamber was purged with dry nitrogen gas.



Figure 3 (a) The variance of initial modulus and breaking strength with pH, in phosphate buffer at 25.8° C for 1 h. (b) The variance of elongation at break with pH, in phosphate buffer at 25.8° C for 1 h.

RESULTS AND DISCUSSION

In total, five chemical modification experiments were conducted: three separate experiments involving run 1 fibers in which pH, then temperature, and then time were independantly varied to see the resulting effects on mechanical properties; and one experiment involving films in order to spectroscopically analyze the reaction results on the chitosan molecule. The fifth experiment involved physical modifications applied to the spun fiber during run 2.

Altered Mechanical Properties with pH, Temperature, and Time

The variance of initial modulus, breaking strength, and tenacity with increasing pH at 25.8°C is illustrated in Figure 3, and the values are listed in Table I. The total time of the experiment was 1 h. It is evident from these graphs that the highest values for mechanical properties are exhibited between a pH of 4.5 and 5.5 pH using a potassium hydrogen phthalate buffer



Figure 4 (a) The variance of initial modulus and breaking strength with temperature, at pH 5.8 and 1 h. (b) The variance of elongation at break with temperature, at pH 5.8 and 1 h.

Temperature (°C)	Modulus (g/Denier)	Std. Dev.	Breaking Strength (g Force) ^d	Std. Dev.	Elongation at Break (%)	Std. Dev.
Control	47.27	1.39	40.25	0.97	32.28	3.35
25.8	66.69	2.73	51.29	1.13	33.22	2.05
30.0	67.79	2.99	50.15	0.69	35.67	1.79
40.0	63.62	4.13	48.12	0.52	45.33	4.73
50.0	59.30	2.01	47.12	2.12	35.57	7.86
60.0	61.91	2.05	45.84	2.29	33.54	5.83
70.0	59.36	2.23	46.44	0.17	35.57	1.76

Table II The Variance of Mechanical Properties with Temperature in 0.1M KH₂PO₄/0.1M NaOH at pH 5.8, and a Time of 1 h^{a,b,c}

^a Fiber denier = 27.29 denier.

 $^{\rm b}$ Testing conditions were at 65% RH and 20°C.

^c Gauge length was set at 2.3 cm.

^d Tenacity, in g/denier, is calculated by dividing breaking strength by the denier.

treatment. The graphical results also suggest that the best mechanical properties using the KH_2PO_4 buffer can be achieved at approximately pH 5.4. One explanation for the improvement in mechanical properties is that a crosslinked network may be set up whereby the phosphate ions or the phthalate ions, depending on the experiment, establish bridges in between the chitosan molecules. The FTIR film data that is presented later in this report suggest that there is an association between the chitosan and the phosphate ions that may be crosslinking the chitosan chains.

The elongation-at-break results are presented Figure 3(b), and are also included in Table I. All of the elongation values show an increase over the control at all pH values. There is, however, no apparent correlation of elongation-at-break results with pH.

Based on these results, we further investigated the change in mechanical properties over increasing temperature using the phosphate buffer at pH 5.55. These results are presented graphically in Figure 4, and the values are listed in Table II. Accordingly, it would appear that the highest mechanical properties are seen at 25.8°C, and followed by degradation at higher temperatures. The elongation-at-break results are similar to those in Figure 3(b) insofar as an increase has occurred with the application of a buffer; however, there would seem to be no correlation with temperature.

With increasing time, the mechanical properties of initial modulus, breaking strength, and tenacity are shown to increase until a maximum occurs at 60 min. This experiment was conducted using a phosphate buffer at pH 5.8 at 25.8°C. A further experiment was conducted whereby fiber samples were immersed over the course of 24 h. There was no significant change in fiber mechanical properties between 1 and 24 h, and thus it would appear that an equilibrium is reached after 1 h in the reaction between chitosan and phosphate ions. The relationship of reaction time over 1 h to mechanical properties is illustrated in Figure 5, and the values are listed in Table III. There is an apparent increase in elongation at break with temperature, but this phenomenon dropped off at 60 min. The correlation between the elongation at break and time is also elusive.

One would expect that in the reaction involving chitosan and a salt, an increase in the weight of the fiber might be apparent. Three fiber samples were reacted in the maximum amount of phthalate salt solution, and another three samples in the maximum concentration of phosphate salt solution. Nine centimeter lengths of the samples were weighed before and after immersion, and in all cases, the change in weight was negligable. Thus, the denier of the bulk unreacted yarn was the value used to calculate the mechanical properties of all the reacted samples.

FTIR Study on Reacted Chitosan Films

Figure 6 shows a comparison between FTIR spectra on (a) chitosan film, (b) chitosan film immersed for 24 h in 0.1M KH₂PO₄/0.1M NaOH at pH 5.8, and (c) chitosan film immersed for 24 h in 0.1M potassium hydrogen phthalate/0.1M NaOH at pH 4.6. Both experiments were run at 25.8°C.



Figure 5 (a) The variance of initial modulus and breaking strength with time, at pH 5.8 and 25.8 °C. (b) The variance of elongation at break with time, at pH 5.8 and 25.8 °C.

The spectrum of the chitosan film exhibits an absorption at 1650 cm⁻¹, which represents the amide I carbonyl stretch as the shoulder on the amine deformation peak at 1600 cm⁻¹. This is characteristic of a chitosan film, and is in agreement with the results of Samuels (1981), who has presented results on the solid-state characterization of chitosan film structures.²⁹ In the case of the chitosan film that was reacted with the phosphate buffer, the shoulder at 1650 cm⁻¹ has developed into a peak at 1635 cm⁻¹, and the amine deformation peak has shifted to 1540 cm⁻¹. This

peak indicates that an interaction is occurring at the amine group on the chitosan, and this could represent the binding of phosphate to this site. Bae and Hudson completed a study where they analyzed the binding behavior of sodium dodecyl sulfate to crosslinked chitosan films. Their FTIR results gave rise to a peak at 1626 cm⁻¹, which they assigned to the binding of the dodecyl sulphate ion with the amine group.³⁰

In 1994, Lee and coworkers crosslinked chitosan films and then phosphorylated the crosslinked films with P_2O_5 . The authors suggested a binding mechanism whereby the phosphate ions bound themselves to the "OH" groups on the chitosan backbone. Lee et al.'s FTIR spectra exhibit the development of a broad peak at approximately 1650 cm⁻¹ in the case of crosslinked chitosan films reacted with phosphate pentoxide. Such an FTIR result also suggests that the binding is occurring at the free amine group.³¹

In the case of Figure 6(c) involving the chitosan film in potassium hydrogen phthalate at room temperature (pH 4.6) and 24 h of immersion, we see no evidence to support any sort of binding behavior between the phthalate ion and the amine or "OH" groups on the chitosan backbone. This does not confirm that binding has not occurred; it may be that crosslinking has occurred in amounts large enough to produce a mechanical change, but too small to be detectable by FTIR. The phthalate salt is organic, and contains a benzene ring that must contribute greatly to the strength of a supposed phthalate crosslinkage as opposed to a crosslinkage involving a phosphate ion. Furthermore, the organic nature of the phthalate ion suggests that the chemical binding will take place more readily than in the case of the phosphate ion. Accordingly, it is suggested that the phthalate salt reacted with the chitosan backbone in quantities sufficient to provide improvements to mechanical properties, but insufficient to be apparent through FTIR analysis of reacted films.

Final Draw Applied to Monofilament During Run 2

For run 2, we chose to use a dope concentration different of that in run 1. The fibers of run 1 were smooth, and exhibited a negligible variation in fiber diameter. However, all wet spinning runs subsequent to run 1 that used a 5% chitosan/5% aqueous acetic acid dope produced fibers with surface bulges and significant variations in fiber diameter. The explanation for this could lie in a

Time	Modulus (g/Denier)	Std. Dev.	Breaking Strength (g Force) ^d	Std. Dev.	Elongation at Break (%)	Std. Dev.
Control	40.13	0.41	35.96	0.49	32.25	0.61
1	52.81	2.67	39.83	1.14	27.30	3.37
5	54.89	2.03	41.19	0.68	38.17	3.08
10	55.27	2.68	41.45	1.36	33.66	2.32
20	57.27	2.84	42.85	0.71	40.60	1.75
30	54.05	2.42	42.45	0.33	43.15	0.69
60	63.65	2.85	48.73	1.56	32.53	1.53

Table III The Variance of Mechanical Properties with Time in 0.1M KH₂PO₄/0.1M NaOH at pH 5.8 and $25.8^{\circ}C^{a,b,c}$

^a Fiber denier = 27.29 denier.

^b Testing conditions were at 65% RH and 20°C.

^c Gauge length was set at 2.3 cm.

^d Tenacity, in g/denier, is calculated by dividing breaking strength by the denier.

melt-fracture effect that results when extruding a high molecular weight polymer at a relatively high concentrations and throughputs.³² We can offer no explanation as to why the run 1 fibers were relatively smooth, yet all subsequent runs using the same conditions yielded fibers exhibiting the melt fracture effect. In an effort to eliminate the problem, we elected to use a lower con-



Figure 6 FTIR results on films of (a) chitosan, (b) chitosan after 24 h of immersion in a phosphate ion buffer solution at room temperature, and (c) chitosan film after 24 h of immersion in a phthalate ion buffer solution, also at room temperature.

centration dope for the experiment involving physical modifications to the spun fibers.

As stated in our introduction, there is published data concerning the effects of jet stretch and draw on chitosan fiber mechanical properties.⁴ However, there are no published results focusing on the effects of final draw. Figure 7(a)-(c) illustrates the variation in mechanical properties, including denier, of the chitosan monofilament when subjected to a final draw. The values that go with Figure 7 are also provided in Table IV. Straight lines have been drawn through some of the figures, but the regression values, as also noted on the figures, are too low to confirm a linear correlation. The decrease in denier with final draw ratio makes sense, as the fiber diameter must decrease with an applied stretch, even when dry. The increase in mechanical properties with final draw ratio is accorded to a corresponding increase in molecular chain orientation. It is doubtful, however, that there is any change to the crystallinity. This has been explained by Ziabicki,³ who stated that undrawn amorphous samples can remain amorphous even after drawing. Ziabicki further quoted the work of Kratky and Sekora,³³ who observed that drawing of highly swollen cellulose fibers affords no change in the degree of cystallinity even while crystallites rotate and orient themselves along the fiber axis. Last, the decrease in elongation at break, as seen in Figure 7(c), suggests that a plastic deformation has been applied to the fiber through the application of a final draw. It is to be expected that with increasing modulus, the elongation at break must be reduced as the fibers become more brittle, as in



Figure 7 (a) The variation in denier with increasing final draw ration. (b) The variation in initial modulus and breaking strength with increasing final draw ratio. (c) The variation in elongation at break with increasing final draw ratio.

evidence by the results. At draw ratios exceeding 1.18, the fiber broke before it could be wound up.

CONCLUSIONS

Chitosan fibers were successfully spun from a highly deacetylated chitosan of 95 \pm 3%. After immersal in solutions containing 0.1*M* KH₂PO₄/0.1*M* NaOH at pH values varying from 5.39 to 7.75, at room temperature, for 1 h, initial modulus, breaking strength, and tenacity of the spun

fibers were all seen to increase. The greatest values occurred at pH 5.39, and then steadily degraded back down to that of the control at pH 7.75. When a buffer solution of potassium hydrogen phthalate was used, a definite increase in mechanical properties was also seen over the pH range of 4.12 to 5.33. A similar experiment was followed with the phosphate solution at pH 5.8 where the temperature was varied from 25.8 to 70°C, and it was demonstrated that the properties of initial modulus, tenacity, and breaking strength were all greatest at 25.8°C. A third ex-

Final Draw Ratio	Denier (dtex)	Initial Modulus (g/Den)	Std. Dev. (g/Den)	Breaking Strength (g Force) ^d	Std. Dev. (g Force)	Elongation at Break (%)	Std. Dev. (%)
1.00	25.00	45.80	1.71	32.68	0.27	36.32	0.81
1.03	23.89	48.85	2.04	32.76	0.41	30.63	1.32
1.05	23.11	54.70	1.99	32.77	0.17	24.26	1.51
1.08	22.78	54.33	0.60	33.04	0.18	23.02	0.76
1.10	21.89	59.95	3.51	33.90	0.42	20.35	0.66
1.13	21.89	64.41	1.32	33.81	0.39	17.21	0.36
1.18	20.78	73.27	4.39	34.47	0.30	14.14	1.48

Table IVComparison of Mechanical Properties under Conditions of Increased Final Draw RatioApplied to a Dry Chitosan Monofilament between the Hot Roller and the Winder^{a,b,c}

^a Fiber denier = 25.03 denier.

^b Testing conditions were at 65% RH and 20°C.

^c Gauge length was set at 2.3 cm.

^d Tenacity, in g/denier, is calculated by dividing breaking strength by the denier.

periment involving the phosphate solution again at pH 5.8 and room temperature demonstrated that the highest mechanical properties were achieved after 60 min of immersal. FTIR data of chitosan films that were immersed in the phosphate solutions for 24 h exhibited a peak at 1635 cm^{-1} and a shift of the amine deformation peak to 1540 cm^{-1} . This is indicative of an interaction at the amine group of the chitosan monomer unit, which in all likelihood, is an association between the phosphate ion and the free amine group on the chitosan. In addition, the application of phosphate ions to the chitosan network is a relatively nontoxic approach to mechanical improvements compared to the crosslinking of chitosan through the use of epichlorohydrin or other toxic agents such as glutaraldehyde and glyoxal.

An additional experiment was conducted whereby a final draw was applied to spun chitosan monofilament between the heated roller and wind up. With increasing final draw ratio, a corresponding decrease in filament denier, and a corresponding increase in mechanical properties is noted.

REFERENCES

- Knaul, J.; Hooper, M.; Chanyi, C.; Creber, K. A. M. J Appl Polym Sci 1998, 69, 1435.
- Hudson, S. M. In Proceedings of the 7th International Conference on Chitin and Chitosan; Domard, A.; Roberts, G. A. F.; Varum, K. M. Eds.; Jacques Andre: Lyon, France, 1997, p. 592.
- 3. Ziabicki, A. Fundamentals of Fiber Formation; Wiley: London, 1976.

- 4. East, G. C.; Qin, Y. J Appl Polym Sci 1993, 50, 1773.
- East, G. C.; McIntryre, J. E.; Qin, Y. In Chitin and Chitosan; Skjak-Braek, G. Ed.; Elsevier: New York, 1989, p. 757.
- Wei, Y. C.; Hudson, S. M.; Mayer, J. M.; Kaplan, D. L. J Polym Sci Part A Polym Chem 1992, 30, 2187.
- Tokura, S.; Nishimura, S.; Nishi, N.; Nakamura, K.; Hasegawa, O.; Sashiwa, H.; Sashiwa, H.; Seo, H. Sen'i Gakkaishi 1993, 43, 288.
- Rathke, T. D.; Hudson, S. M. JMS Rev Macromol Chem Phys 1994, C34, 375.
- Minami, T.; Kobayashi, T.; Horiguchi, S. Dainichiseika Color and Chemicals Mfg. Co., Ltd., Jpn. Pat. 03 47 263 (1991).
- Yoshida, H.; Okamoto, A.; Yamasaki, H.; Kataoka, T. Fundam Adsorp 1993, 80, 767.
- 11. Kishimoto, N.; Yoshida, H. Separa Sci Technol 1995, 30, 3143.
- Nakatsuka, S.; Andrady, A. L. J Appl Polym Sci 1992, 44, 17.
- Yao, K. D.; Peng, T.; Goosen, M. F. A.; Min, J. M.; He, Y. Y. J Appl Polym Sci 1993, 48, 343.
- Groboillot, A. F.; Champagne, C. P.; Darling, G. D.; Poncelet, D.; Neufeld, R. J. Biotechnol Bioeng 1993, 42, 1157.
- Yao, K. D.; Peng, T.; Feng, H. B.; He, Y. Y. J Polym Sci Part A Polym Chem 1994, 32, 1213.
- 16. Suto, S.; Kan, R. Sen'i Gakkaishi 1995, 51, 361.
- Ahmad, M. B.; O'Mahony, J. P.; Huglin, M. B.; Davis, T. P.; Ricciardone, A. G. J Appl Polym Sci 1995, 56, 397.
- 18. Suto, S.; Ui, N. J Appl Polym Sci 1996, 61, 2273.
- Guan, Y. L.; Shao, L.; Yao, K. D. J Appl Polym Sci 1996, 61, 2325.
- Paradossi, G.; Lisi, R.; Paci, M.; Crescenzi, V. J Polym Sci Part A Polym Chem 1996, 34, 3417.
- Chen, X.; Li, W.; Zhong, W.; Lu, Y.; Yu, T. J Appl Polym Sci 1997, 65, 2257.

- 22. Andrady, A. L.; Xu, P. J Polym Sci Part B Polym Phys 1997, 35, 517.
- 23. Zhang, Q.; Liu, L.; Ren, L.; Wang, F. J Appl Polym Sci 1997, 64, 2127.
- 24. Wang, H.; Li, W.; Lu, Y.; Wang, Z. J Appl Polym Sci 1997, 65, 1445.
- Muzzarelli, R. A. A.; Jeuniaux, C.; Gooday, G. W. Chitin in Nature and Technology; Plenum: New York, 1986.
- Wang, W.; Bo, S.; Li, S.; Qin, W. Int J Biol Macromol 1991, 13, 281.
- 27. Knaul, J.; Kassai, M. R.; Bui, V. T.; Creber, K. A. M. Can J Chem Mater Sci (Special Issue) Nov. 1998, accepted.
- Kassai, M. R.; Arul, J. A.; Charlet, G. In Proceedings of the 7th International Conference on Chitin and Chitosan; Domard, A.; Roberts, G. A. F.; Varum, K. M. Eds.; Jacques Andre: Lyon, France, 1997, p. 421.
- Samuels, R. J. J Polym Sci Part B Polym Phys 1981, 19, 1081.
- Bae, H.-S.; Hudson, S. M. J Polym Sci Part A Polym Chem 1997, 35, 3755.
- Lee, J. S.; Hong, S. I.; Jeon, D. W. J Korean Fiber Soc 1994, 31, 966.
- 32. Denn, M. M. Process Fluid Mechanics; Prentice-Hall Inc: Hillsdale, NJ, 1980.
- 33. Kratky, O.; Sekora, A. Kolloid Z 1955, 108, 169.