Chitosan: Aspects of Fiber Spinnability

Khaled El-Tahlawy,[1] Samuel M. Hudson[2]

[1]*Textile Division National Research Center, Dokki, Cairo, Egypt*
[2]*Fiber and Polymer Science Program, Box 8301, North Carolina State University, Raleigh, North Carolina 27695-8301*

ABSTRACT: The preparation of useful fibers from chitosan remains an interesting challenge. Chitosan is easily solubilized in aqueous acids, but these solutions generally have high solution viscosities because of the polyelectrolyte effect. The high viscosity affects the processibility of chitosan during extrusion by wet-spinning techniques. The coagulation rate, which also includes the regeneration of the free amine form of chitosan is also expected to be influenced by viscosity. In this study, the solution rheology of chitosan solutions was examined; our aim was to find the optimum compositions, in terms of chitosan, acid, and added salts, for spinnability. The diffusion of coagulants into chitosan spinning solutions is also reported. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1162–1168, 2006

Key words: chitosan; extrusion; polyelectrolytes; rheology

INTRODUCTION

The preparation of useful fibers from chitosan remains an interesting challenge.[1] Chitosan is the deacetylated form of chitin. Chitin is an important organic resource, and it is available from the shells of marine invertebrates.[2] These invertebrates include crab, shrimp, and lobster. Chitosan is primarily 2-amino-2-deoxy-β-D-glucopyranose with a few molar percentages of 2-acetamido-2-deoxy-β-D-glucopyranose residues. Currently, chitosan is the preferred form of this polymer, as it is more tractable to solution processes than chitin. Chitosan's primary usefulness is a result of its ability to act as a cationic polyelectrolyte, its bioactivity, and its biocompatibility.

Chitosan is easily solubilized in aqueous acids, but these solutions generally have high solution viscosities because of the polyelectrolyte effect. The high viscosity affects the processibility of chitosan during extrusion by wet-spinning techniques. The coagulation rate, which also includes the regeneration of the free amine form of chitosan, is also expected to be influenced by viscosity. In this study, the solution rheology of chitosan solutions was examined; our aim was to find the optimum compositions, in terms of chitosan and acid, for spinnability. The diffusion of coagulants into the chitosan spinning solutions is also reported.

Chitosan and chitin can be converted to fibers by the dissolution of the polymer in a spinnable solvent and the coagulation of the solution in a bath by the wet-spinning process.[3,4] Ziabicki[5] provided an overview of the wet-spinning process. Usually, the spin solution is extruded under pressure out a spinneret. The liquid jet may be immersed directly into a coagulation bath, or it can go through an air gap first. The coagulation bath solidifies the fiber by setting up a skin through which the solvent diffuses into the fiber. The fiber may travel over rollers to be drawn or attenuated. One or two additional baths can be used for solvent removal and washing. They can also be used to provide additional fiber draw. The draw step imposes orientation on the polymer chain alignment. The dimensions of the spinneret, the composition of the coagulation bath and solvent system, and the draw ratio are the most important spinning parameters. In the case of chitosan, a convenient solvent is aqueous acetic acid, and the coagulation bath is aqueous sodium hydroxide.

Flow curves of chitosan viscosity as a function of shear rate were measured on capillary and cone/plate rheometers. These data are reported and were used to gauge the spinnability of various chitosan compositions. The diffusion coefficients of various coagulants for chitosan, such as alkali metal hydroxides, are reported. They were determined by a microprecipitation technique within small-diameter capillary tubes.

EXPERIMENTAL

Materials

Chitosan was obtained as a 60-mesh powder from Vanson, Inc. (Raymond, WA). This batch was a crab-

based chitosan with a degree of deacetylation (DD%) of 83.5%. The following chemicals were all reagent grade and were obtained from Fisher Scientific: glacial acetic acid; lithium, potassium, and sodium hydroxide; and sodium acetate.

Deacetylation of chitosan

The as-received chitosan (200 g) was further deacetylated by stirring in 50 wt % sodium hydroxide for 2 h at 100°C in a glass reaction vessel purged with gaseous nitrogen. The reaction product was subsequently washed in distilled water until it exhibited a neutral pH; it was then air-dried for 2 days. The process was repeated a second time under the same conditions to obtain chitosan with a high DD%. This product was also washed with distilled water until it became neutral, and then, it was dried for 24 h at 50°C in a convection oven.

Determination of the deacetylation ratio

The DD% of chitosan can be measured by acid–base titration because chitosan dissolves in an acidic solution by protonation of its amine groups.[6] In this method, chitosan dissolved in a known excess of acid is titrated conductometrically with a standard NaOH solution.

A known weight of chitosan (0.094 g) was transferred to a 150-mL beaker and completely dissolved in 10 mL of 0.1N HCl, and then, 90 mL of distilled water and several drops of phenolphthalein as an indicator were added. The temperature was kept at 20°C with a water bath. In this solution, a conductivity probe (Orion conductivity cell, model 013030) was submerged, and the solution was stirred until the temperature became constant. The chitosan solution was titrated with 0.1N NaOH standard solution with a 10-mL buret. Conductivity readings were obtained within 3–5 s after each addition of NaOH. The data were polled as conductivity versus volume of NaOH added (Fig. 1). The titration curve showed two deflection points.

The number of moles of NaOH between the two deflections points was proportional to the number of moles of amino groups of chitosan samples, which was calculated as follows:

No. of Moles of amino groups =

$$M_{\text{NaOH}}(\text{mol/L}) \times V_{2-1}(\text{mL})/1000 \quad (1)$$

where M_{NaOH} is the molarity of the standard NaOH solution and V_{2-1} is the difference in volume between the two inflection points. DD% of the chitosan was found to be 97.7%.
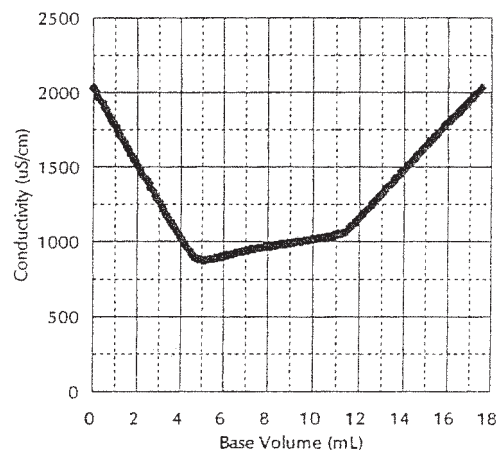

Figure 1 Conductometric titration curve for the chitosan sample.

Determination of the molecular weight

The average molecular weight was determined on the basis of intrinsic viscosity ($[\eta]$) as measured in an Ubbelohde viscometer with a solvent of $0.1M$ acetic acid/$0.2M$ sodium chloride and was calculated to be 7.6×10^5 g/mol with a degree of polymerization (DP) of 4700. This was calculated with the Mark–Houwink equation:

$$[\eta] = KM^\alpha \quad (2)$$

Wang et al.[7] established the functional relationships for the Mark–Houwink constants K and α as a function of the DD% of chitosan:

$$K = 1.64 \times 10^{-30} \times \text{DD\%}^{14} \quad (3)$$

$$\alpha = (-1.02 \times 10^{-2} \times \text{DD\%}) + 1.82 \quad (4)$$

The viscosity sample was prepared by the dissolution of 0.0374 g of chitosan in 25 mL of $0.2M$ aqueous acetic acid/O.1M sodium acetate to give the desired concentration of l.5 mg/mL. A Cannon-Ubbelohde semimicro viscometer was charged with 5 mL of the solution and equilibrated to 30°C in a water bath. The solution was diluted four times, and 10 flow times were recorded at each concentration and averaged. Specific viscosities were obtained, and $[\eta]$ was determined.

Rheological measurements

Chitosan solutions were prepared in aqueous solutions of acetic acid as a solvent. The ratio of acetic acid used to chitosan ([A/C]) was defined by a molar ratio:
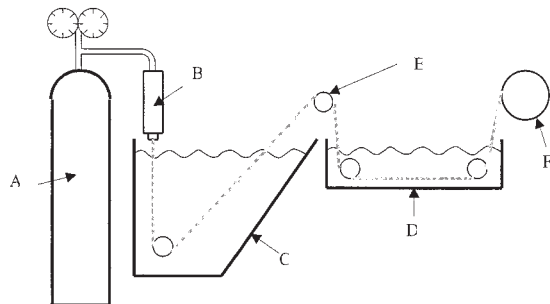
Figure 2 Schematic of a bench-top scale apparatus for the capillary rheometer measurements and extrusion by wet spinning: (A) nitrogen gas cylinder, (B) polymer solution in the spin cell, (C) coagulation bath, (D) wash bath, (E) draw rolls, and (F) take-up roll.

Figure 3 Apparatus for the coagulation boundary movement measurement.

$$[A/C] = \text{Molarity of acetic acid}/$$
$$\text{Molarity of the glucosamine unit} \quad (5)$$

The ratio of added sodium acetate salt to chitosan ([S/C]) was also defined as a molar ratio:

$$[S/C] = \text{Molarity of the salt}/$$
$$\text{Molarity of the glucosamine unit} \quad (6)$$

The viscosity of the dope solution at zero shear rate was calculated by extrapolation of the viscosity data measured by a Brookfield DV-E digital rheometer. The viscosity data were collected within a torque range between 10 and 90% for data reliability. Shear rate values were limited to $100 \ s^{-1}$ or less. Data at higher shear rates were obtained from the capillary of the wet-spinning device shown in Figure 2. Volumetric flow rates (Q's in mL/s) were obtained against pressure (Pa). Shear stress at the wall (τ) was calculated by

$$\tau = R\Delta P/2L \quad (7)$$

where L is the length of the capillary, R is the capillary radius, and P is the pressure. The apparent shear rate ($\dot{\gamma}_{app}$) was calculated from

$$\dot{\gamma}_{app} = 4Q/\pi R^3 \quad (8)$$

Coagulation rate of the chitosan solution

To determine the coagulation rate of the chitosan solution in 5% aqueous acetic acid, a capillary and a polarizing microscope were used. The measuring apparatus illustrated in Figure 3 was used to determine the rate of diffusion of the coagulant (aqueous KOH) into the chitosan dope. As KOH diffused into the capillary, chitosan precipitated. The moving boundary was observed by a polarizing microscope equipped
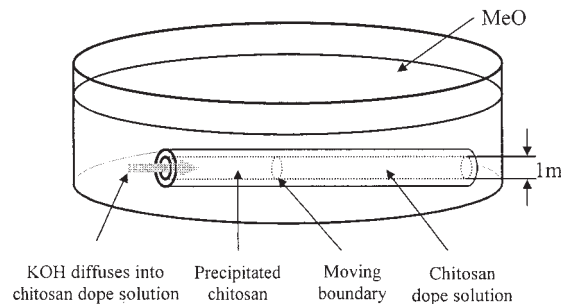
with an eyepiece graticule, and the boundary distances were recorded with time.

The Stoke–Einstein equation was used to calculate the diffusion coefficient of K^+ ions:

$$D = \frac{k_B T}{6\pi\eta R_0} \quad (9)$$

where D is the diffusion coefficient, k_B is Boltzmann's constant (1.381×10^{-23} J/K), T is the temperature, η is the solvent viscosity, and R_0 is the radius of the solute molecule. This equation can be applied to a small and rigid sphere solute diffusing into a solvent. Liu et al.[8] with a cellulose solution and Knaul and Creber[9] with a chitosan solution demonstrated the reliability of the Stoke–Einstein equation for this type of coagulant and polymer solution system.

Fiber spinning

A schematic of the wet-spinning apparatus is shown in Figure 2. Aqueous hydroxide solutions were used as coagulants. Chitosan was dissolved in aqueous acetic acid by stirring at room temperature overnight. The solution was filtered and put in an ultrasonic bath to remove the air bubbles. The polymer cell was charged
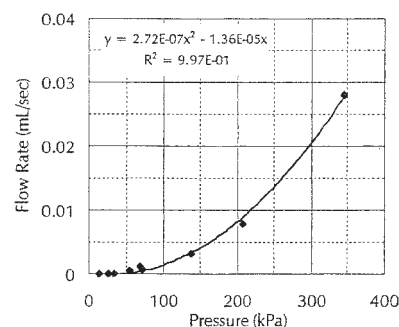

Figure 4 Capillary flow rate data. The capillary dimensions were as follows: $D = 0.127$ mm; $L = 0.635$ mm; $L/D = 5$. The chitosan solution was 5.0 wt % in 5% v/v aqueous acetic acid at 20°C.
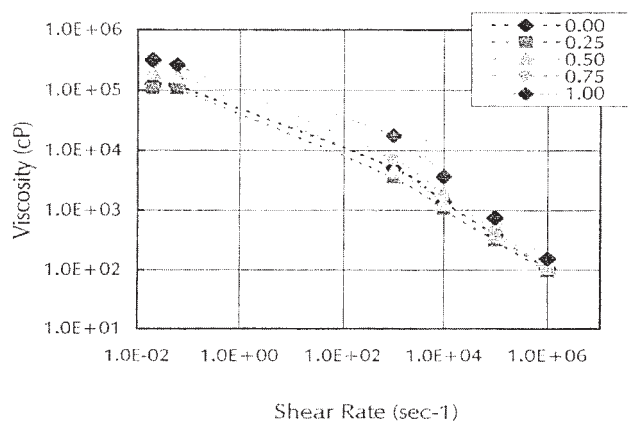
Figure 5 Effect of added salt on the flow curve of chitosan. The data labels indicate [S/C]. The viscosity data is shown in Table I.

Figure 6 Plot of the boundary position against time at 20°C. The chitosan solution was 5 wt % with [A/C] = 1 and [S/C] = 0.0. The coagulant was 1.0M KOH.

with 50 mL of solution and pressurized. We determined volumetric flow by collecting solution in a beaker below the capillary and weighing it. The density of the solution was determined in a pycnometer and used to obtain the volumetric flow value. Jet velocity (JV) was calculated from the capillary dimensions and the volumetric flow:

$$JV = 4Q/D^2 \qquad (10)$$

where Q is the volumetric flow rate and D is the diameter of the capillary. The wind-up velocity was measured with a digital tachometer and was used to calculate the draw ratio (Wind-up speed/JV).

RESULTS AND DISCUSSION

A number of factors are involved in the conversion of chitosan to filament via the wet-spinning process. These include:

The shear flow characteristics of the solution.
The coagulation rate for regeneration of fiber in the bath.
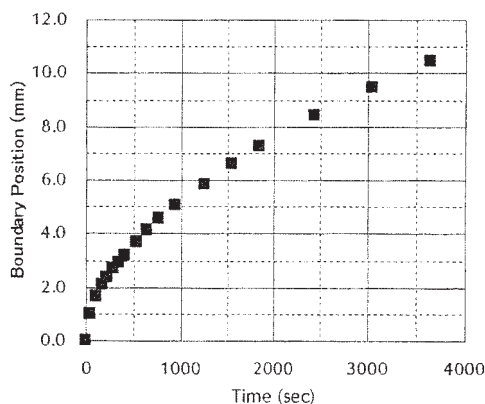The extensional flow characteristics of the chitosan solution jet.

Hydraulic drag of the threadline through the coagulation bath.

Chitosan solution rheology

A chitosan sample with a molecular weight of 7.6 × 10^5 or a DP of 4700 was obtained. It had a DD% of 97.7. A high DD% value should contribute to a higher crystallinity level in the fibers and lead to improved mechanical properties from chitosan. Solutions were prepared in an aqueous acidic acid solvent, which had many advantages for use as a spinning solvent compared to chitin solvents such as trichloroacetic acid. Typical capillary flow data is shown in Figure 4.

These data were used to construct a flow curve of log viscosity versus log shear rate with eqs. (6) and (7). Sodium acetate was added to the solutions to screen the ionic charges of the chitosan in acidic solution. A [S/C] value of 0.25 gave a consistent minimum in the viscosity of the chitosan solution at each shear rate measured. This meant that the chitosan chains were in a less expanded conformation and may have been less entangled. By lowering the viscosity this way, we could then increase the chitosan concentration to bring the viscosity back up. Increasing the concentration of chitosan in the spinning solution favored the over all

TABLE I
Viscosity Data in the Presence of Added Salt

Shear rate	0.00	0.25	0.50	0.75	1.00
2.0×10^{-2}	1.27×10^5	1.07×10^5	1.95×10^5	2.79×10^5	3.16×10^5
6.0×10^{-2}	1.19×10^5	1.05×10^5	1.76×10^5	2.55×10^5	2.64×10^5
1.0×10^3	5.07×10^3	3.47×10^3	4.60×10^3	7.01×10^3	1.77×10^4
1.0×10^4	1.40×10^3	1.05×10^3	1.33×10^3	1.78×10^3	3.65×10^3
1.0×10^5	3.86×10^2	3.15×10^2	3.86×10^2	4.55×10^2	7.57×10^2
1.0×10^6	1.07×10^2	9.50×10^1	1.12×10^2	1.16×10^5	1.57×10^2

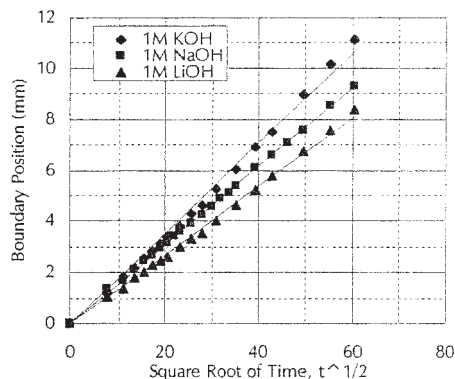The chitosan solution was 6.0 wt % chitosan in 5 v% aqueous acetic acid at 20°C.

Figure 7 Square root of time (s) versus the boundary position (SRT-BP) at 20°C. The chitosan solution was 5 wt % with [A/C] = 1 and [S/C] = 0.0. The dependence of the coagulation rate on the counterion is shown.

(a) [A/C]: 1.0

Figure 9 Dependence of the coagulation rate on the KOH concentration at 20°C. The chitosan solution was 5 wt % with [A/C] = 1.

economics of the process. Figure 5 and Table I show these results. On the other hand, lowering the viscosity of the spinning solution for a high-molecular-weight chitosan may also lessen the potential for chaotic flow, which is known as solution fracture.[5] This would allow higher extrusion speeds and possibly improved fiber tensile properties from higher orientation effects. Also, it takes less energy to extrude a lower viscosity solution.

Chitosan coagulation rate

Figure 6 shows the time-dependent relationship of the boundary movement of precipitated chitosan in the capillary. The boundary distance was linearly proportional to the square root of time, which is illustrated in Figure 7.

The use of small and large capillaries indicated that the movement of the boundary position was by diffusion and not capillary action. The use of the phenol red indicator, which had a yellow to red change by pH 8.3, demonstrated that the chitosan was precipitated
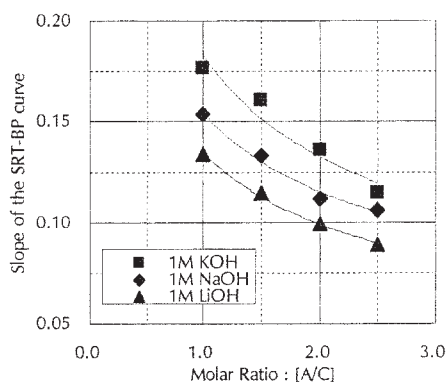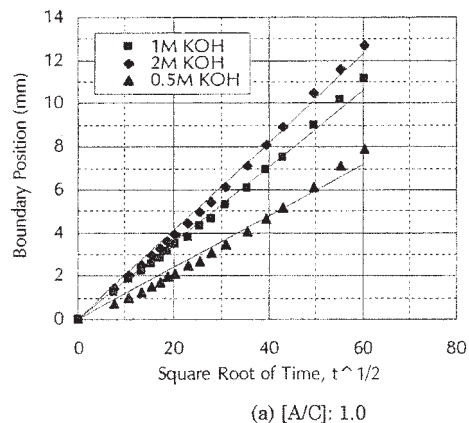
by pH 8.3. The boundary front of the precipitated chitosan coincided with the change in the phenol red indicator added to the chitosan solution. This validated these measurements for use as probes of the coagulation rates of the chitosan solution.

We desired the regeneration or coagulation of chitosan from solution to be as rapid as possible. This would have allowed for a shorter coagulation bath length and would result in less hydraulic drag on the threadline, and thus, higher extrusion speeds would be possible. With the coagulation rate determination method described previously, the boundary position versus time was determined for lithium, sodium, and potassium hydroxide solutions (see Fig. 7). These results followed the trend of ionic radius in aqueous solution at 25°C, which was $Li^+ = 6$Å, $Na^+ = 4$Å, and $K^+ = 3$Å. Potassium hydroxide was selected for all of the following spinnability measurements.

The acidity of the chitosan solution should have also had an effect on the viscosity and coagulation rate of chitosan. [A/C] was varied, and the coagulation rate
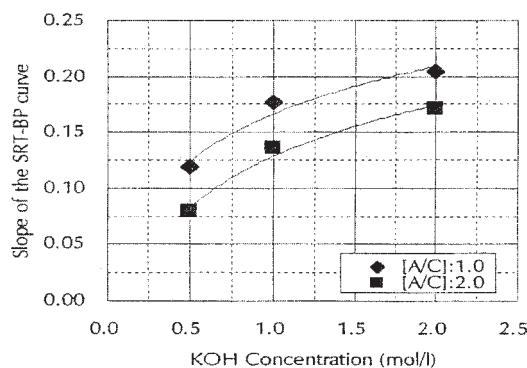

Figure 8 Plot of [A/C] versus the slope of the SRT-BP curves for the different counterions.

Figure 10 Plot of the slope of the SRT-BP curve against the KOH concentration. The chitosan solution was 5 wt % at 20°C.
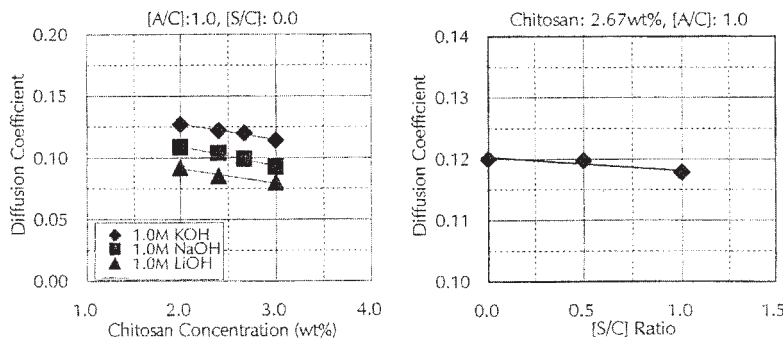
Figure 11 Plots of diffusion coefficients for different chitosan concentrations and potassium hydroxide at different salt ratios.

was determined. These data are presented in Figure 8. As shown, the potassium ion consistently led to the fastest coagulation rates. However, as expected, the presence of excess acid retarded coagulation by potassium hydroxide.

The dependence of the coagulation rate on the KOH concentration in the bath is shown in Figure 9. The coagulation rate increased with KOH concentration but approached an asymptotic limit. This is more clearly shown in Figure 10. In Figure 10, the relative change in slope is shown to have decreased as the KOH concentration increased. The increase in acid, [A/C], did not seem to have an effect on the rate of the decrease.

Figure 11 shows that the diffusion coefficient of all three ions was affected by the chitosan concentration. This was presumably due to the increase in the bulk viscosity of the solutions and of the interaction of the ion with chitosan. The presence of added salt also had a negligible effect on the diffusion of potassium hydroxide.

Chitosan spinnability

Chitosan spinnability is determined by a number of factors. In the case of the wet spinning of chitosan, these include:

The shear flow characteristics of the solution.
The coagulation rate in the bath.
The extensional flow characteristics of the chitosan solution jet.
Hydraulic drag of the threadline through the coagulation bath.

Here, the combined effect of hydraulic drag in the bath and the extensional characteristics of the chitosan jet as it was hardening in the coagulation bath were examined. We anticipated that the hydraulic drag would be the dominating factor for imposition of tension on the threadline. At a critical value, the filament would break. This would interrupt the spinning process and decrease the overall spinnability of the chitosan solution. The extensional ability of the thread and jet would determine the maximum spin draw, that is, the maximum ratio of JV to the wind-up ve-
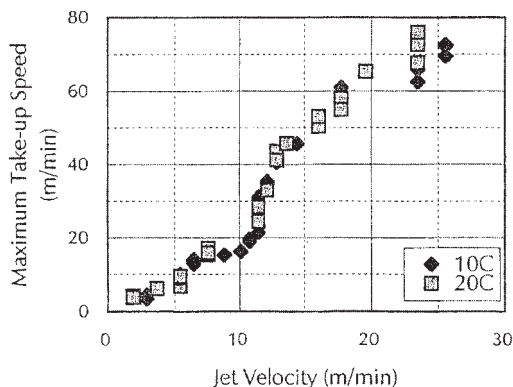

Figure 12 Maximum take-up speed as a function of JV at 20°C. The chitosan solution was 5 wt % with [A/C] = 1 and [S/C] = 0.0. The capillary dimensions were as follows: D = 0.127 mm; L = 254 mm; L/D = 2. The coagulant was 1.0M KOH.
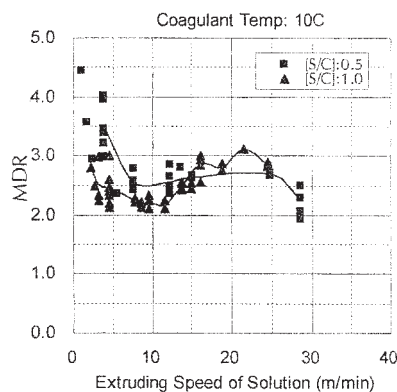

Figure 13 MDR as a function of the JV at 10°C. The chitosan solution was 5 wt % with [A/C] = 1. The capillary dimensions were as follows: D = 0.25 mm; L = 2.54 mm; L/D = 10. The coagulant was 1.0M KOH.
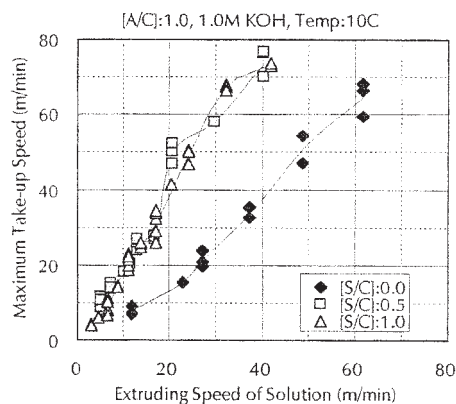
Figure 14 Effect of salt concentration on the maximum take-up speed against extrusion speed. The capillary dimensions were as follows: $D = 0.203$ mm; $L = 0.203$ mm; $L/D = 1$.

locity. As noted, the maximum spinning speed was ultimately limited by the hydraulic drag.

Figure 12 illustrates the relationship between the maximum take-up speed and JV. At higher JVs, the maximum take-up speed was limited to about 75 m/min. Beyond this speed, the hydraulic drag increased the tension on the threadline to its breaking point.

The ratio of the maximum take-up speed to JV, or the maximum draw ratio (MDR), is shown in Figure 13. At low JVs, it was possible to get high draw ratios before the wind-up velocity reached a critical value and the filament broke. In this region, characterized by low extrusion velocities, the hardening of the fiber by coagulation predominated, and a decrease in MDR was seen with increasing tension on the threadline as the JV increased. A minimum was reached, beyond which the higher extrusion speeds resulted in a shortened time for coagulation. A more plastic filament resulted, which allowed for a higher MDR. At the highest JVs, hydraulic drag became dominant again, and the fiber began to fall to lower draw ratios.

The effect of added salt to the chitosan solution also had an effect on the draw characteristics of the fiber.

Figure 14 shows that the added salt made the filament more plastic and able to reach higher draw ratios than in the absence of the salt. By analogy, the salt seemed to act as a plasticizer within the formation of the chitosan filament and allowed for more draw. The temperature effect on data obtained at 10 and 20°C was negligible.

CONCLUSIONS

The optimization of the chitosan spinning process has been reported. The solution rheology of chitosan in aqueous acetic acid was modified by the addition of sodium acetate. At a [S/C] of 0.25, the viscosity was minimized at all chitosan concentrations. The viscosity was lowered by the polyelectrolyte screening effect. Coagulation rate studies as a function of [A/C] and [S/C] revealed that potassium hydroxide was the best alkaline coagulant for chitosan, as it had the highest diffusion rate into chitosan. Added salt also had a beneficial effect on the MDR that could be obtained. Maximizing the draw ratio should maximize the potential tensile properties of these fibers.

References

1. Rathke, T. D.; Hudson, S. M. J Macromol Sci Rev Macromol Chem Phys 1994, 34, 375.
2. Hudson, S.; Smith, C. In Biopolymers from Renewable Sources; Kaplan, D., Ed.; Springer Verlag: Heidelberg, 1998; p 96.
3. Wei, Y. C.; Hudson, S. M.; Meyer, J. M.; Kaplan, D. L. J Polym Sci Part A: Polym Chem 1992, 30, 2187.
4. Knaul, J.; Hudson, S.; Creber, K. J Appl Polym Sci 1999, 72, 1721.
5. Ziabicki, A. Fundamentals of Fiber Formation; Wiley-Interscience: New York, 1976.
6. Lim, S.-H.; Hudson, S. M. Carbohydr Res 2004, 339, 313.
7. Wang, W.; Bo, S.; Li, S.; Qin, W. Int J Biol Macromol 1991, 13, 281.
8. Liu, C. K.; Cuculo, J. A.; Smith, B. J Polym Sci Part B: Polym Phys 1989, 27, 2493.
9. Knaul, J. Z.; Creber, K. A. M. J Appl Polym Sci 1997, 66, 117.