# Improvements in the Drying Process for Wet-Spun Chitosan Fibers

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**ABSTRACT:** Chitosan fibers were wet spun from a 6% by weight chitosan in 3% by volume acetic acid solution. The fibers were collected as a 20 filament yarn intended for use as a chaff substrate. The yarn had to be sufficiently dry following spinning to allow for winding and subsequent separation of the filaments. Drying of the yarn was attempted using various techniques including direct and radiant heat, forced air, and chemical drying agents. Product yarns were analyzed for ease of separation of the filaments, as well as comparison of mechanical properties. Individual fibers were evaluated on the basis of moisture content, surface morphology and fiber diameter. Results indicate that the particular drying method or agent used has a considerable impact upon all of the characteristics listed above. A methanol dry bath was found to provide optimum drying of the chitosan yarn, producing filaments with low moisture content that separated easily from one another. Methanol drying yielded chitosan fibers with smaller diameter, superior surface smoothness and superior mechanical properties to fibers dried using forced air, heat, or other tested drying agents such as acetone and isopropanol. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1435–1444, 1998

**Key words:** chitin; chitosan; chaff; fiber drying

## INTRODUCTION

Natural polymers have received considerable attention across a broad range of fields due to their "environmentally friendly" nature, generally inexpensive raw material costs, and relative abundance. The second most abundant natural polymer, chitin, is one such polymer. Studies on chitin, also known as poly (1-4)-linked 2-acetamido-2-deoxy-$\beta$-D-glucan, as well as its derivatives, have led to the development of applications ranging from absorbable sutures and wound dressings to applications in the fields of electro-optics, waste water purification, and papermaking.[1–4] In particular, the highly deacetylated product of chitin known as chitosan has been the focus of much study due to its improved solubility and processability over chitin.

The Canadian Armed Forces have recently taken an interest in developing a more environmentally friendly and biodegradable alternative to the aluminum-coated E-glass fibers currently being used as chaff, a passive radar countermeasure system. The use of chaff involves the dissemination of a cloud of metal-coated fibers that act as a myriad of individual dipoles, each reflecting incident radar signals of a given frequency and thereby presenting a radar cross-section.[5] Many nations have already banned the use of chaff in military exercises due to its negative environmental impact. Incorporating chitosan as a replacement for E-glass is predicated on the development of an efficient and economical wet spinning process. Such a process must have the ability to produce fibers with mechanical properties that are suitable for chaff fibers. E-glass in known to have a modulus between 280–320 g/denier, as well as an extremely smooth surface morphology that lends itself to a metallic coating such as aluminum. E-glass fiber used in chaff has an average fiber diameter of 19 $\mu$m, a value that serves as a target for the product chitosan filaments. Based on the above value, an acceptable target "window" of 15–25 $\mu$m may be established for chaff substrate diameter.

Wet spinning of chitosan fibers from the polymer in its bulk form, typically powder or flake, involves dissolution of the polymer in aqueous
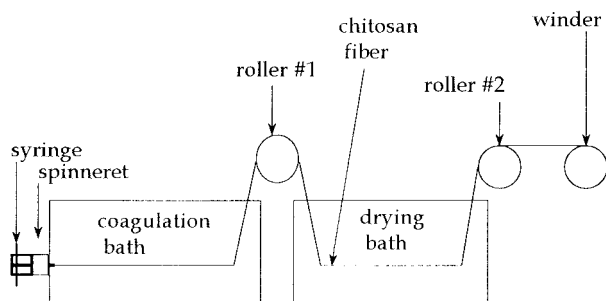
**Figure 1**   Schematic diagram of wet-spinning apparatus.

acetic acid (1–10% by volume glacial acetic acid in water) to form a 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 where the polymer is precipitated in fiber form. Following coagulation, the chitosan yarn may be washed to remove excess coagulant, dried, and subsequently wound on a bobbin. Intermediate steps such as drawing, crosslinking, and dyeing may also be incorporated into the system. Figure 1 depicts a schematic drawing of the wet spinning system used in this article. A wash step was not incorporated in this study. Instead, the wet yarn proceeded directly from the coagulation bath to a drying bath. In several experiments, a secondary drying element was used, in addition to the drying bath, to ensure sufficient water removal from the filaments prior to windup of the yarn.

The present article discusses the development of the drying system employed following the coagulation step to remove excess water from the chitosan yarn. The drying step is essential to the spinning process because it ensures that the individual filaments in the wound yarn are well separated and not stuck together. Furthermore, yarns collected following successful drying are easily handled in further processing, because they separate easily and overlapping of filaments does not present a problem. This latter factor allows one to considerably decrease the size of spool required to collect fiber, while also increasing the amount of yarn that may be wound.

Various drying methods were considered in this study, and the corresponding impact on the mechanical properties of the product chitosan fibers was analyzed. Particular emphasis is placed on the use of organic solvents for the removal of excess water from the chitosan yarn. Product fibers were evaluated both quantitatively and qualita-

tively based on water content, fiber diameter, fiber breaking strength, initial modulus (stiffness), tenacity, elongation at break, appearance (macroscopic), surface morphology (microscopic), and ease of filament separation following winding.

It was discovered over the course of experimentation that the amount of draw, just prior to windup, experienced by the chitosan yarn during spinning, also had a significant impact upon the mechanical properties of the individual filaments; hence, the effects of drawing upon the fiber characteristics are also discussed in this article.

## EXPERIMENTAL

### Materials

Chitosan was obtained from Vanson Chemical in Redmond, WA, as a 60 mesh powder that originally came from shrimp shells. The chitosan lot number was VNS-582. This product had a degree of deacetylation of 80.7% as reported by the supplier. The chitosan was further reacted in 50% by weight sodium hydroxide in water, for 1 h, at 100°C. The final degree of deacetylation was 97.3%, as determined by UV spectrometry, following the method of Muzzarelli.[6] Acetic acid, sodium hydroxide, methanol, ethanol, isopropanol, and acetone were all obtained and used as reagent grade from Fisher Scientific Inc.

### Extrusion/Coagulation

The dope consisted of 6% chitosan by weight dissolved in a 3% by volume aqueous acetic acid solution. The chitosan dope was extruded through a stainless steel 20-hole spinneret by means of a variable speed infusion pump. Mounted behind the spinneret was a 40 $\mu$m stainless steel filter. Each spinneret hole was 100 $\mu$m in diameter, with a capillary length that was twice the diameter of the hole. Solutions were degassed for 24 h in a vacuum. The linear extrusion rate of the chitosan dope was maintained at 2.47 m · min$^{-1}$ for all experimental runs. The 20-hole spinneret provided a chitosan yarn of 16–20 filaments. The exact filament count varied between experiments due to hole blockages.

The coagulation bath employed a 1$M$ NaOH solution over an immersion path of 2 meters in length. Given the extrusion rate of the dope and the length of the coagulation bath, coagulation was expected to be complete for the resulting coag-

ulation bath—residence time of 48.6 s. This latter statement is based on results of one of our previous studies concerning the coagulation rates of chitosan dopes.[5] The volume of the coagulation bath was 7 L, and the experiments were carried out at $24 \pm 1°C$. No apparatus was used to maintain the temperature in the coagulation bath. However, the temperature was monitored using a thermocouple and found to vary by only 1°C, as noted above. The takeup velocity at the end of the coagulation bath was maintained at 2.50 $m \cdot min^{-1}$ for all experiments. This was the exact velocity that gave a straight fiber line in the coagulation bath. If the takeup velocity were to be slower than 2.50 $m \cdot min^{-1}$, then the fibers would begin to kink in the coagulation bath; if the takeup velocity were to be quicker then 2.50 $m \cdot min^{-1}$, then a stretch would have been applied to the yarn. In other words, a "jet-stretch" was not applied to the yarn. Wet yarns were subjected to a variety of drying systems, grouped as either primary (chemical) or secondary (physical) elements.

## Primary Drying Elements

Following precipitation in the coagulation bath, the chitosan yarn was passed through an organic solvent bath for a period of approximately 21 s. The bath residence time was varied later in the study as a result of a drawing application in the drying bath. Acetone, methanol, ethanol, isopropanol, and mixtures of acetone/methanol and acetone/isopropanol were used as drying agents. The drying bath was maintained at room temperature and was of a depth sufficient to ensure that the yarn was completely submerged at all times. Solvent baths were not used for more than two consecutive (25-min) spin runs.

## Secondary Elements

In the event that sufficient drying of the chitosan yarn was not achieved by the primary element alone, a secondary drying element was used to ensure that the fibers were dry before they were collected. Secondary elements were also used to accelerate evaporation of solvents used as primary drying agents. Direct heat, heated chrome rollers, and forced air (not heated) were all employed independently as secondary drying elements over the course of experimentation.

## Fiber Drawing

On several occasions, yarns were subjected to drawing following the primary drying stage. The amount of draw placed on the fibers was controlled by varying the speed of the winder spool relative to the speed of the final advancing roller at the end of the drying bath. As a result, the yarn was stretched immediately following drying and prior to collection. The amount of draw induced is expressed as the draw ratio, and is a factor denoting the speed of the winder (in rpm) over the speed of the final advancing roller. Hence, a draw ratio of unity indicates that the two spools have identical speeds, while a draw ratio of 1.5 indicates that the winder is rotating at a speed 50% greater than the final advancing roller.

## Fiber Analysis

Chitosan yarns produced experimentally were analyzed using Scanning Electron Microscopy (SEM), Instron mechanical testing and Thermogravimetric Analysis (TGA), in addition to qualitative analysis of fiber properties (i.e., dryness and ease of filament separation) as noted by observation.

Chitosan filament samples were separated from the parent yarn and sputter coated with gold prior to imaging with the SEM. The SEM used was a JEOL JSM-T100. SEM photographs provided information concerning fiber surface morphology, diameter, and ease of separation of the filaments.

Mechanical testing of product fibers was performed at the facilities of DuPont (Kingston, Ontario) using the 1120 Series Instron machine. Gauge length was set at 250 mm and crosshead speed was 300 mm/min. Fibers were preconditioned for 24 h at 20°C and 65% relative humidity prior to Instron testing. Yarn counts were determined based on the weights of 9-cm lengths of yarn averaged over five such measurements, as seen in Table I. Other mechanical properties of a given chitosan yarn were also determined as the average of five Instron tests for each yarn, with mean and standard deviation values provided by the Instron computer.

Fiber moisture content at various stages of the wet-spinning process was evaluated qualitatively by fiber feel and appearance, and quantitatively by means of thermogravimetric analysis. TGA (TA Instruments TGA 2050 Thermogravimetric Analyzer and Thermal Analyst 3000) was

**Table I    Mechanical Properties and Diameters of Fibers Produced Using Various Drying Agents in the Wet Spin Process**

| Drying Agent | Filament Diameter ($\mu$m) | Yarn Count (denier) | Initial Modulus (g/denier) | Breaking Strength (g force) | Tenacity (g/denier) | Elongation at Break (%) |
|---|---|---|---|---|---|---|
| Acetone | 41.0 | 206.7 | 7.2 | 39.8 | 0.20 | 16.1 |
| Isopropanol | 33.5 | 140.5 | 14.6 | 37.4 | 0.28 | 9.0 |
| Ethanol | 28.8 | 111.6 | 26.2 | 108.6 | 1.00 | 14.5 |
| Methanol | 24.9 | 95.0 | 28.2 | 93.5 | 1.05 | 18.5 |
| Methanol with draw on yarn | 21.2 | 71.4 | 40.0 | 91.1 | 1.30 | 5.7 |

Note these results are for yarns with a filament count of $18 \pm 2$ filaments.

used to estimate the amount of moisture trapped within a given yarn on a mass % basis. The computer program used employed a 10°C/min ramp function over a 30-min period from 30 to 300°C. Yarn moisture content was thus determined for samples extracted immediately following coagulation as well as for samples tested following the various drying systems employed. Product yarn samples destined for TGA analysis were stored in airtight vials to ensure that moisture was not absorbed from the surrounding atmosphere. In all TGA data presented in this work, holding times between yarn collection and testing did not exceed 3 h.

## RESULTS AND DISCUSSION

Fiber mechanical properties and fiber diameters for chitosan yarns dried using various solvents are presented in Table I. It should be noted that diameter refers to an individual chitosan filament within a yarn, while all values for mechanical properties are those obtained for the entire yarn ($18 \pm 2$ filaments). Values presented for all fiber characteristics are based on samples obtained from a minimum of five separate spinning test runs, with quoted values being the averages obtained over all tested samples.

Given that all of the parameters of the wet spinning system were constant, with the exception of the particular drying agent used and the introduction of tensile forces in the case of the drawn fibers, one may speculate that the differences in yarn mechanical properties and filament diameters witnessed are due to interactions within the chitosan/water/drying agent system. Fiber diameters were seen to vary noticeably as

a result of the specific drying agent used; acetone-dried filaments displayed large diameters in excess of 40 $\mu$m, while methanol-dried fibers were much closer to the target diameter of 15–25 $\mu$m associated with E-glass. Propanol and ethanol-dried fibers were observed to have average diameters of 34 and 29 $\mu$m, respectively, again exceeding the desired range. Drawing of the yarn had the expected effect of decreasing product filament diameter, increasing modulus, and decreasing elongation at break, as seen in Table I.

The large fiber diameters witnessed for acetone and isopropanol-dried fibers may be explained by the size of the dehydrant molecule as well as the amount of absorbed water/drying agent trapped by the fibers themselves. Although acetone was seen to effectively dry the chitosan fibers (product fibers were dry to the touch and well separated), the yarns absorbed a considerable amount of the ketone while submerged in the drying bath. The absorbed acetone was found to remain with the yarn for a considerable period of time following winding. Figure 2(a)–(d) present scanning electron microscope (SEM) photographs of individual chitosan filaments dried using acetone, propanol, ethanol, and methanol, respectively. The difference in fiber diameters for the various chitosan filaments is quite apparent in the SEM photographs, as is the marked difference in surface morphology stemming from the use of the various drying agents.

Results of thermogravimetric analysis may provide an explanation for the difference in observed fiber diameters mentioned above. Figures 3 and 4 are thermogravimetric analysis (TGA) plots depicting the percentage weight loss of product fibers upon heating to 300°C. Figure 3 displays the TGA profiles of chitosan yarn samples tested
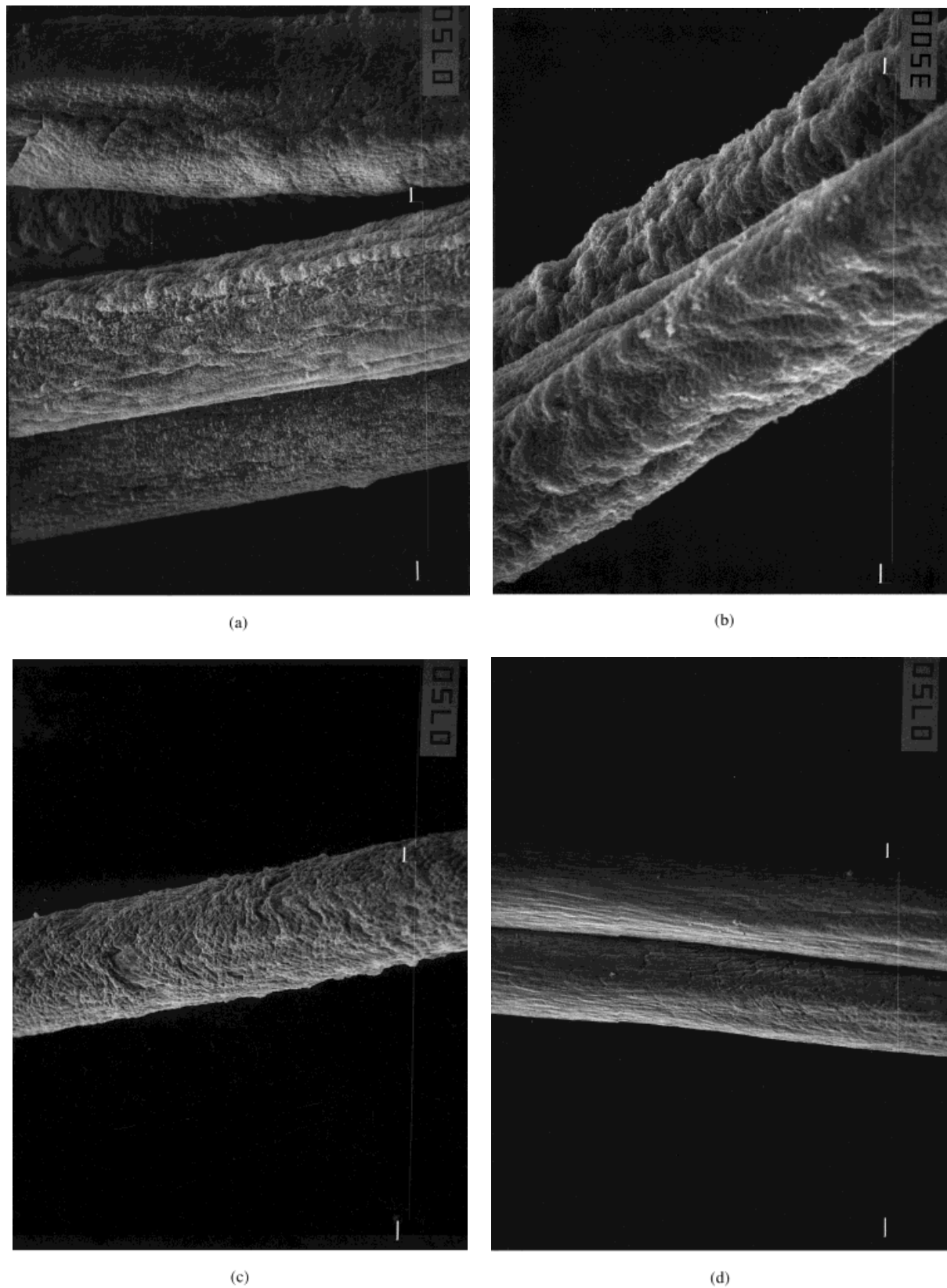
**Figure 2**  Scanning electron microscope photographs of chitosan filaments dried using (a) acetone (×660), (b) isopropanol (×880), (c) ethanol (×660), and (d) methanol (×660).
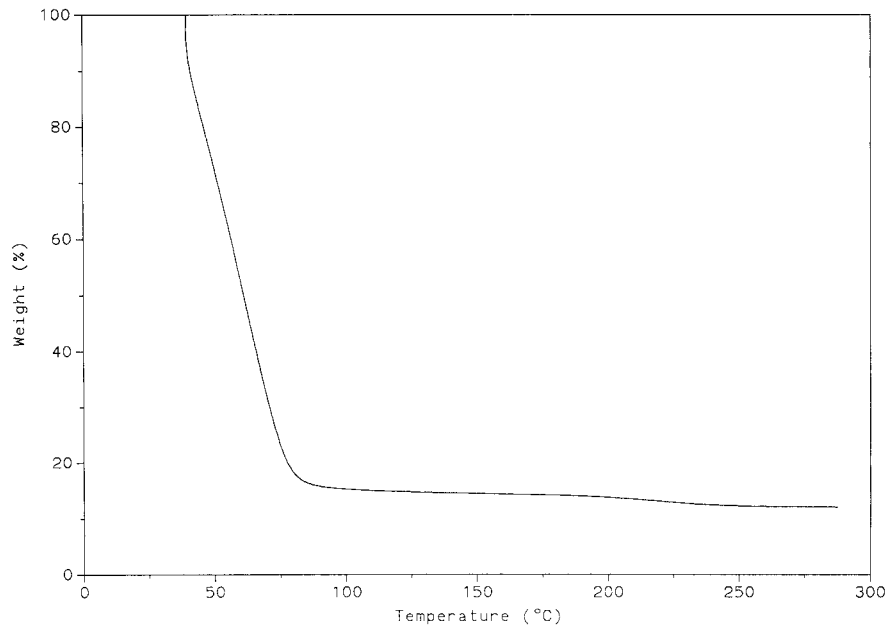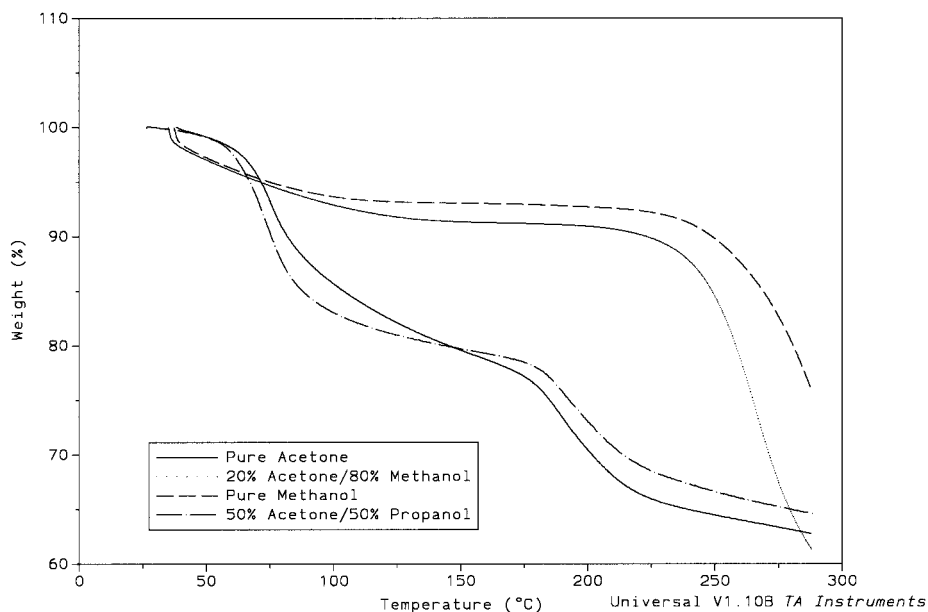
**Figure 3** TGA profile of chitosan yarn sample tested immediately following coagulation in $1M$ NaOH bath.

immediately following coagulation. The steep downwards slope and subsequent plateau visible in the plot indicate that moisture is evaporating from the sample until such time as only chitosan remains, at which point sample mass loss virtually ceases until thermal stress is sufficient to

cause chain scission along the polymer backbone. The chitosan backbone does not experience thermal degradation under normal conditions unless temperatures exceed 250°C.[6] Accordingly, the region in Figures 3 and 4(a), between 50–175°C is useful in indicating what percentage of product
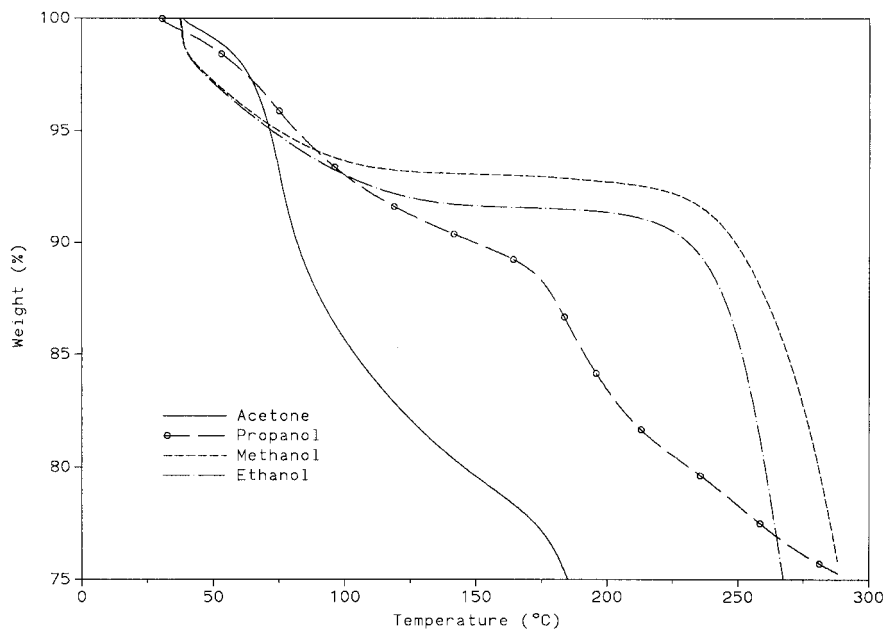


**Figure 4** (a) TGA profiles for wet-spun chitosan yarn samples tested following drying with various drying agents.

**Figure 4**    (b) TGA profiles for wet-spun chitosan yarn samples tested following drying in acetone, methanol, and mixtures thereof.

fiber is moisture or drying agent rather than chitosan. Hence, Figure 3 shows that approximately 80% of the yarn mass following coagulation is, in fact, moisture, either water from the precipitation reaction or absorbed moisture from the sodium hydroxide coagulation solution. Figure 4(a) is a TGA plot comparing the thermal degradation profiles of product chitosan fibers tested following drying with the various solvents. The TGA plot for acetone-dried fibers presented in Figure 4(a) shows a fiber weight loss exceeding 20% over the temperature range of 50–175°C, indicating that a large amount of either water or loosely bound acetone (dried chitosan yarns wound up after passing through an acetone bath retained a strong odor of acetone) is being extracted from the fiber. Acetone molecules displacing water and associating preferentially with the filament surface (i.e., hydrogen bonding to the hydroxyl groups spaced along the chitosan molecule) could thus explain the significantly larger fiber diameters observed for acetone dried fibers, as well as the extremely rough surface morphology and generally poor mechanical properties of these fibers.

In contrast to the TGA profile for fibers dried using acetone, the profiles for methanol-dried fibers showed a sample moisture content of less than 8% by mass [see Fig. 4(a)—the curve for methanol-dried fibers reaches a plateau at approximately 125°C and does not vary until thermal degradation of the polymer chain commences

near 250°C]. One may, therefore, conclude that the amount of drying agent and/or water entrained by the chitosan fibers is minimal when dried with methanol [or ethanol—the TGA profile for ethanol-dried fibers is similar to that of methanol-dried fibers, see Fig. 4(a)]. The effective dehydration of the chitosan yarn and the minimal absorption and/or entrapment of the drying agent observed when methanol or ethanol was used in the dry bath can be seen to account for the relatively small fiber diameters and the comparatively smooth surface morphology of the product fibers. The absence of surface irregularities and porous regions associated with aggressive dehydration (i.e., acetone can be seen to remove water quite rapidly, possibly leading to internal porosity upon drying of the chitosan yarn) serves to explain the superior breaking strengths observed for ethanol and methanol-dried yarns.

Although fiber densities were not measured for any of the fiber samples, it is clear from the TGA data that the density of the methanol dried fiber is about 20% higher than the acetone-dried sample. This difference and the dull appearance of the acetone fibers indicates that these fibres are probably porous. The porosity exhibited in the acetone-dried fibers may have something to do with the nature of the polymer recrystallization that takes place in the presence of acetone. It has been previously reported that marked changes in the structure and reactivity of cellulose fibers have

been observed on application of a swelling agent if the wet-swollen cellulose fibers (i.e., just emerged from the coagulation bath) are washed with solvents other than water before final drying. Vigo et al., 1970, conducted a study in which they immersed cotton yarn in various swelling agents and then examined the resulting crystallinity, moisture regain, and mechanical properties. The results of Vigo et al. demonstrated that polar, aprotic solvents such as acetone, dimethyl sulfoxide, acetonitrile, pyridine, and tetrahydrofuran all caused extensive decrystallization and lattice conversion in cellulose. The authors concluded that polar, water-soluble, nonhydroxylic solvents, such as acetone, are able to render a significant displacement of water, but solvate the complex without furnishing additional hydrogen bonds. Such an effect results in further swelling, lattice conversion, and a reduction in the crystallinity of the polysaccharide. Furthermore, it is proposed that the aprotic solvent can diffuse between certain crystallographic planes in the polymer complex. The same is likely true of chitosan fibers when immersed in acetone. On other hand, hydroxylic solvents such as propanol, ethanol, or methanol are able to engage in hydrogen bonding and thus provide for more ordered recrystallization after the fibers leave the alcohol and are finally dried and wound up.[7]

From Figure 4(a), it is clear that the fibers dried using isopropanol experienced a thermogravimetric profile quite unlike that of the fibers dried in a primary alcohol bath. The TGA curve for propanol-dried fibers displays an initial loss of moisture/alcohol that is more gradual than the loss displayed by methanol or ethanol-dried fibers. The fiber weight loss for the propanol-dried fibers continues over a greater temperature range, however, and ultimately accounts for over 11% of the fiber "dry" weight. The plateau region observed on the TGA curve for methanol and ethanol-dried fibers is also less pronounced on the propanol curve and four distinct regions of varying slopes are clearly evident prior to the 250°C mark on the propanol curve. The variation in slope for these regions may be due to different trapping mechanisms that act to hold water inside the fiber. Moisture held near the surface of the fiber would require little thermal excitation to be removed upon heating, as would any residual propanol. Thus, the initial portion of the TGA plot for propanol-dried fibers (up to ∼ 175°C) may be the result of alcohol evaporation followed by evaporation of water. In the neighbourhood of 175°C, the

slope of the curve changes drastically, indicating that the minimum temperature has been reached for the release of some new compound trapped within or bound to the fiber. The temperature is too far below the normal thermal degradation temperature of 250°C to be the result of polymer chain scission and is, thus, likely due to the release of moisture trapped within the fiber matrix. Thermal excitation of the polymer molecules may allow for the release of this water shortly before the polymer chain actually begins to degrade and break apart. The change in slope evident beyond 225°C is likely the result of polymeric degradation having finally been achieved and continues at a relatively constant rate until the end of the scanning period at 300°C. If the latter argument is accepted, one could conclude that the amount of moisture/alcohol trapped in the propanol-dried fiber is in the neighborhood of 20%.

The TGA spectrum for acetone-dried fibers displayed in Figure 4(a) may be explained in much the same manner as the spectrum for propanol-dried fibers, with the exception that acetone-dried fibers contain very little trapped water (due to the aggressive nature of the ketone towards dehydration) and a large amount of trapped acetone. This quantity of absorbed acetone accounts for the rapid drop in fiber mass over a relatively low temperature range (50–80°C). The curve assumes a more gradual slope after 100°C and maintains this slope until a temperature of nearly 185°C. At this point the curve again exhibits a change in slope, perhaps corresponding to the release of acetyl groups from the polymer chain.

The plot in Figure 4(a) does not encompass a sufficient temperature range to validate this hypothesis. However, the intersection of the methanol and acetone-dried fiber TGA curves can be seen in Figure 4(b). At the point of intersection of the two lines in question, it is clear that the methanol-dried fiber curve is descending much more rapidly than the acetone-dried fiber curve. Thus, the initial decrease in the acetone curve may be due to lightly bonded acetone molecules, while the slope change near 180°C may be indicative of the breaking of the acetyl/amine bond on the chitosan molecule.

Drawing of chitosan yarns between the dry bath and the winder was seen to improve desired fiber properties in several areas. The tension induced axially along the fiber by the draw force was seen to reduce average filament diameter to 21 $\mu$m. The draw force also acted to "stretch" the fiber surface, evening out irregularities and pro-

(a)                                              (b)
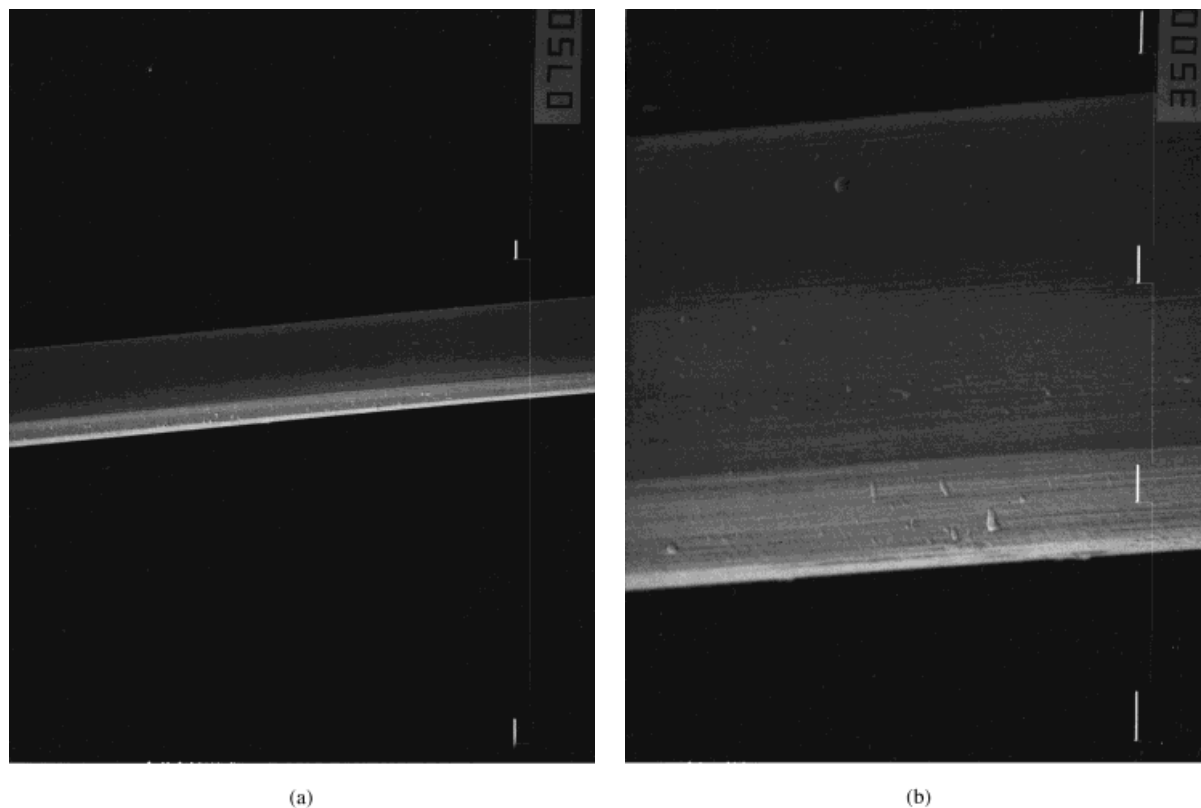
**Figure 5**  Scanning electron microscope photographs of chitosan monofilaments dried with methanol and subjected to tensile draw forces during drying. Uniform and smooth surface morphology apparent at both (a) ×660, and (b) ×3080.

viding a very smooth and uniform surface morphology, even at high magnifications (see Fig. 5). The tensile force introduced by drawing also preconditioned the fiber prior to winding, as initial modulus was seen to increase considerably at the cost of a reduction in elongation at break. These latter trends are desirable for the intended application of the product fibers; a chaff substrate should be sufficiently stiff to avoid bending, and inelastic so as to reflect incident radar in the target bandwidth.

The surface morphology of chitosan fibers was evident at the macroscopic level. An extremely smooth fiber surface (i.e., methanol-dried, drawn fibers) reflected a considerable amount of light and had a silvery sheen, while fibers with poor surface morphology (acetone, propanol-dried) were characterized by a dull white to beige color with no hint of reflectance.

Regarding secondary drying elements such as heater units and forced air tubes, it was observed that air drying on its own (even with forced air blown across the filament surface) required a relatively long period of time to achieve sufficient moisture removal and was thus not applicable to a continuous-spin process. It should be noted, however, that forced air was often employed following a solvent drying agent to accelerate evaporation of the solvent and, hence, reduce even further the amount of residual moisture entrained by the yarn upon collection. Radiant heat, such as a radiator or heated chrome rollers, was observed to damage fiber surfaces, generating cracks believed to stem from thermal stress. To dry chitosan fibers by means of radiative or convective heat required gradual application of heat over a relatively long period of time if the damage mentioned above was to be avoided.

## CONCLUSIONS

The results of the current work identified a methanol drying bath (with the possible use of a secondary forced air tube—the benefit of the forced air was noticeable but not substantial) as the optimal means of removing moisture from the chitosan yarn prior to windup. The addition, however,

of heated rollers or radiant heaters following a methanol drying bath was found to damage fiber surfaces. Methanol, on its own, was seen to dry the chitosan yarn to a sufficient degree to prevent adherence of individual filaments upon winding, thereby allowing one to collect layers of yarn one upon the other on the bobbin. Physical and mechanical properties of methanol-dried chitosan fibers were comparable or superior to the properties of fibers dried using other tested drying agents. The introduction of a tensile draw force into the wet-spinning process was seen to favorably alter both mechanical properties and surface morphology of product fibers.

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