

# Wet Spinning of Chitosan and the Acetylation of Chitosan Fibers

GEORGE C. EAST\* and YIMIN QIN†

Department of Textile Industries, University of Leeds, Leeds LS2 9JT, England

## SYNOPSIS

Chitosan fibers were made by wet spinning of its solution in 2% aqueous acetic acid. The fiber properties were affected by processing conditions, such as spin stretch ratio, coagulation bath composition, and drying conditions. The chitosan fibers were acetylated with acetic anhydride in methanol, producing regenerated chitin fibers. The acetylation process was affected by the reaction temperature, the treatment time, and the molar ratio of anhydride to amine groups. The properties of the acetylated chitosan fibers were studied in terms of thermal stability, solubility, and mechanical properties. It was found that, after acetylation, the fibers had an improved thermal stability and tensile strength. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Chitin, poly(1,4-2-acetamido-2-deoxy- $\beta$ -D-glucose), is the second most abundant natural polymer. Chitosan is the deacetylated product of chitin. Both polymers have attracted much attention, due to their unique properties and the renewed interest in natural polymers. Van Luyen and Rossbach<sup>1</sup> have reviewed the sources, extraction methods, and properties and applications of chitin and chitosan. Biodegradability, biocompatibility, and wound healing are among many properties widely appreciated in the medical field, where fibers made of chitin and chitosan have been useful as absorbable sutures and wound-dressing materials.<sup>2-6</sup> The chitin sutures resist attack in bile, urine, and pancreatic juice, which are problem areas with other absorbable sutures.<sup>6</sup> It has been claimed that wound dressings, made of chitin and chitosan fibers, accelerate the healing of wounds by up to 75%.<sup>3</sup>

Apart from their applications in the medical field, chitin and chitosan fibers have potential applications in waste water treatment, where the removal of heavy metal ions by chitosan through chelation

has received much attention.<sup>2,7-10</sup> Their use in the apparel industry, with a much larger scope, could be a long-term possibility.

There have been many attempts to produce chitin and chitosan fibers.<sup>3,4,11-17</sup> With chitin, the major problem has been to find a suitable solvent. Although a number of solvents, such as formic acid,<sup>15</sup> concentrated mineral acid,<sup>11</sup> trichloroacetic acid,<sup>16</sup> dimethylacetamide-lithium chloride,<sup>4,17</sup> and a 40/40/20 mixture of trichloroacetic acid, chloral hydrate, and dichloromethane,<sup>14</sup> can dissolve chitin, the solvents are not convenient and, in some cases, degradation of the polymer is unavoidable. Nonetheless, chitin fibers with a tenacity of up to 0.44 N/tex (4.5 g/dtex) have been reported.<sup>14</sup>

Chitosan is readily soluble in most aqueous acid solutions, because of the basicity of the primary amine groups, and several groups have produced chitosan fibers by wet spinning solutions in aqueous acidic solutions into aqueous alkaline coagulating baths.<sup>18-22</sup> As chitosan is the deacetylated product of chitin, it should be possible to obtain chitin fibers by acetylating chitosan fibers. This indirect route of producing chitin fibers may be advantageous in three respects. First, chitosan is readily available from the deacetylation of chitin with concentrated alkali solution. Second, the production of chitosan fibers may be much simpler than chitin fibers, since the process will use only aqueous acid solutions as solvent and

\* To whom correspondence should be addressed.

† Present address: Innovative Technologies LTD, Road 3, Winsford Industrial Estate, Winsford, Cheshire. CW7 3PD, U.K.  
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dilute aqueous alkali solutions as coagulant. Third, the acetylation of amine groups is, chemically speaking, a relatively simple process, although its efficiency with the chitosan in fiber form remains to be discovered.

This article describes the results of a study of the production of chitin fibers via the indirect route. Chitosan fibers were first produced by a wet spinning process and the fibers were then acetylated to produce chitin fibers. A preliminary report of this work has been presented elsewhere.<sup>23</sup>

## EXPERIMENTAL

### Materials

The chitosan used was supplied by Protan Laboratories as a "medium grade." It was claimed that the material had a degree of deacetylation of 84% and produced a solution viscosity of 750 cp when dissolved to give a 1% solution in 1% acetic acid. It also contained 1.2% insoluble material. The nitrogen/carbon (N/C) content (see below) was consistent with a degree of deacetylation of 82%. Glacial acetic acid (Aldrich) and sodium hydroxide (Wharfedale Laboratories) were used as supplied. Analytical grade acetic anhydride (Koch-Light) and analytical grade methanol (BDH) were also used as supplied.

### Wet-Spinning Procedure

A typical dope was prepared by dissolving 50 g chitosan in 950 mL of 2% (v/v) aqueous acetic acid solution. The solution was filtered through a candle filter system before adding it to the reservoir of the spinning system, where it was degassed under vacuum. A laboratory scale extrusion unit was used, comprised of a reservoir, a metering pump (1 cm<sup>3</sup> rev<sup>-1</sup>), and a spinneret (20 holes, 80 μm diameter). The filaments were coagulated in a dilute NaOH bath, with an immersion length of *ca.* 100 cm. The take-up rollers, drawing system, drying rollers, and the winding up procedure were as described previously.<sup>24</sup> Drawing was carried out in hot water at 80–85°C and the filaments were washed and dried by radiant heat on chrome rollers. On occasion, different drying procedures were used.

### Acetylation of Chitosan Fibers

Acetylation was performed using a variety of procedures, most of them using a 5% v/v acetic anhydride solution in methanol. Typically, 2 meters

(12.9 mg) of chitosan fibers were treated with 10 mL of anhydride solution. The reaction time and temperature varied (see Results and Discussion). In studying the effect of the molar ratio of anhydride to amine, 50 meters (0.32 g) of chitosan yarn were treated with 50 mL of methanol, containing 0.04 to 10 mL of acetic anhydride. The reaction was allowed to proceed for two days with occasional stirring. In most cases, the acetylated chitosan fibers were treated with 10 mL 1 M aqueous NaOH solution overnight, to remove O-acetylation. The fibers were finally washed with distilled water and were dried. The degree of acetylation [DA] was obtained from the N/C ratio, as obtained by elemental analysis.

### Viscosity Measurement

Solution viscosities were measured on a Haake Rotovisko cylinder-type viscometer, with a type SV1 cup and a type M1500 measuring head. The measurement was carried out at room temperature.

### Tensile Testing

Tensile properties of the chitosan yarn samples were measured on an Instron tensile tester, model 1122, with load cell-type 1105. The gauge length was 20 mm and the extension rate was 20 mm min<sup>-1</sup>. The test was performed at 20°C, 65% R.H. The figures quoted are the averages of 10 tests, the standard deviation being generally less than 5%. When required, tests were also performed on yarns, previously immersed in water at room temperature, to obtain wet strength values.

### Thermal Analysis

DSC and TGA were carried out on a DuPont 910 Differential Scanning Calorimeter and a DuPont 950 Thermal Gravimetric Analyzer, respectively, with a monitoring unit model 2000. The heating rate was 10°C min<sup>-1</sup> and the nitrogen flow rate was 50 mL min<sup>-1</sup>.

### Elemental Analysis

Carbon and nitrogen contents of the acetylated chitosan fibers were measured by elemental analysis, carried out on a Carlo Erba Instrumenzione elemental analyzer, model 1106, in the Department of Chemistry.

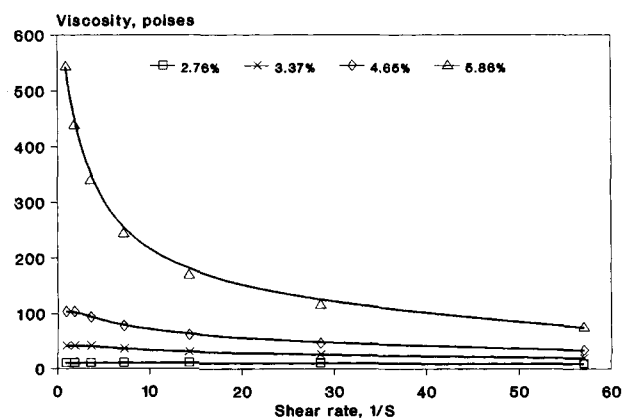
## RESULTS AND DISCUSSION

### Wet Spinning of Chitosan

The choice of chitosan concentration to be used for the first spinning trials was decided upon by measuring solution viscosities. Figure 1 shows the flow curves of the chitosan solutions of various concentrations. As the concentration increased, the shape of the curve changed gradually from a near Newtonian behavior, at a solution concentration of 2.76%, to non-Newtonian shear thinning at higher concentrations. The solution viscosity was low when the chitosan content was below 3%. Dramatic increases in solution viscosity occurred at higher chitosan concentrations, with the 5.86% solution showing a viscosity of more than 500 poises. The 4.65% solution showed a solution viscosity of about 100 poises, which is typical of a wet spinning solution. A 5% chitosan solution was, therefore, used as the spinning dope.

Table I shows the effect of spin stretch ratio (ratio of take-up speed to extrusion rate) on the maximum draw ratio and it shows the properties of the resultant fibers. It can be seen that the extent to which the newly formed filaments can be drawn is largely dependent on the extent of the applied spin stretching. Interestingly, despite the variations in draw ratios and spin stretch ratios, the variation in the tensile properties of the fibers was small. In fact, the fiber tenacity fell within the range of 0.167 to 0.189 N/tex (1.7–1.9 g/dtex); the strongest sample was obtained at a spin stretch ratio of 0.41.

Table II shows the tensile properties of chitosan fibers, created using different coagulation bath concentrations. The minimum NaOH concentration was 2%, below which spinning was not possible be-



**Figure 1** Flow curves of chitosan solutions in 2% aqueous acetic acid solution.

**Table I** Effect of Spin Stretch Ratio on Maximum Draw Ratio and Yarn Properties

Spin Stretch Ratio	0.20	0.32	0.41	0.46	0.67
Maximum draw ratio	1.60	1.40	1.37	1.23	1.13
Yarn count (tex)	14.72	10.59	8.50	8.50	6.37
Tenacity (N/tex)	0.170	0.176	0.189	0.177	0.167
Elongation (%)	4.9	5.6	5.4	5.6	8.7

Dope: 5% chitosan in 2% acetic acid; extrusion rate: 15 m min<sup>-1</sup>; coagulant: 5% NaOH. Yarn dried with radiant heat.

cause of too slow a rate of precipitation. As can be seen from Table II, the fiber tenacity showed a slight improvement with the reduction in NaOH concentration. In general, fiber tenacities of about 0.2 N/tex were again obtained.

In the wet spinning of viscose rayon and polyvinyl alcohol fibers, the coagulation bath usually contained concentrated inorganic salts as dehydrating agents. With chitosan fibers, the addition of 15% Na<sub>2</sub>SO<sub>4</sub> to the coagulating bath improved the spinning process and the fiber properties. Using this concentration of sodium sulfate allowed the NaOH concentration to be lowered to 1% and the filaments were capable of the relatively high draw ratio of 1.76. The resultant fibers had a tenacity of 0.243 N/tex and an elongation at break of 5.7%, when spun under the conditions described for the samples in Table II.

The method of drying the fibers had a strong influence on the fiber properties. Of the three methods used, that is, by passing the fibers over chrome rollers, heated with a radiant heater (heat dried), by passing the fibers through an acetone bath to extract water (acetone dried), and by collecting the wet fibers and allowing them to dry naturally in air (air

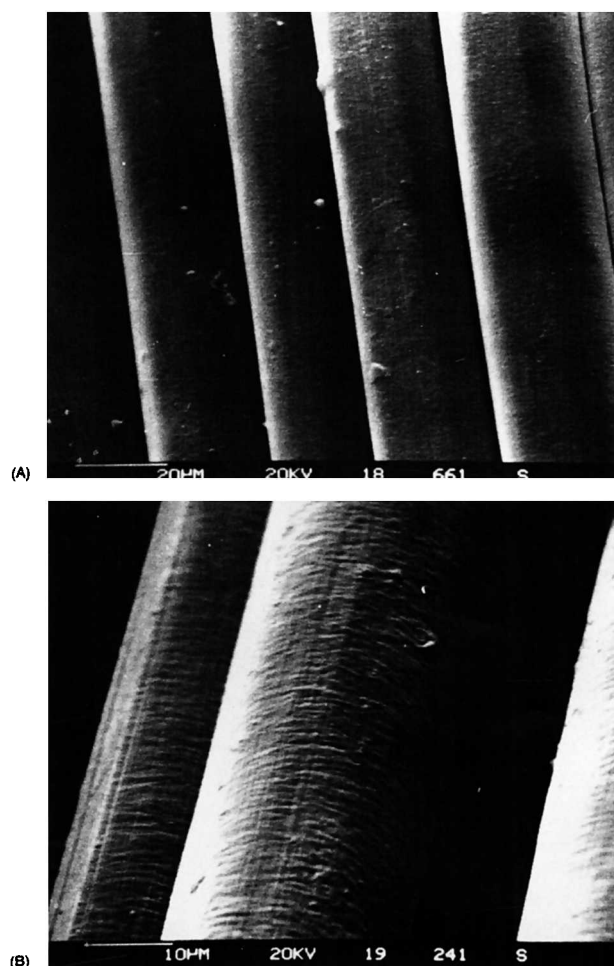
**Table II** Effect of Coagulation Bath Concentration on Maximum Draw Ratio and Yarn Properties

NaOH Concentration (%)	2	3	4	5
Maximum draw ratio	1.74	1.70	1.78	1.57
Yarn count (tex)	7.74	7.66	7.19	7.80
Tenacity (N/tex)	0.198	0.189	0.194	0.177
Elongation (%)	7.8	7.0	7.5	10.4

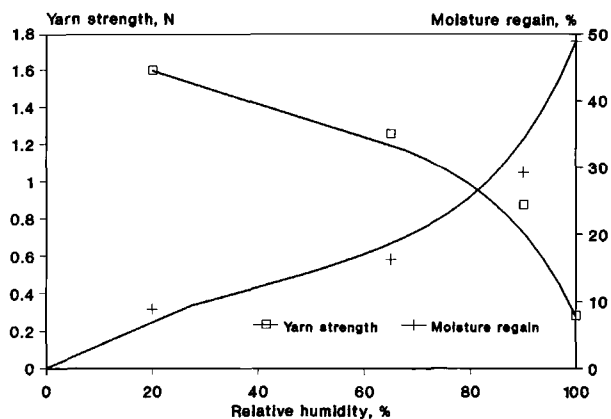
Dope: 5% chitosan in 2% acetic acid; extrusion rate: 13.6 m min<sup>-1</sup>; jet stretch ratio: 0.4. Yarn dried with radiant heat.

dried), the heat dried sample has a tenacity of 0.193 N/tex and an elongation at break of 7.9%, as compared with a slightly lower fiber tenacity of 0.180 N/tex, but a much higher elongation at break of 19.3% for the air dried sample. Both the heat dried and the air dried yarns contained individual filaments that adhered to each other, while in the acetone dried yarn, the individual filaments were well separated. Figure 2 shows the SEM micrographs of heat dried and acetone dried samples. It is clear that, while the heat dried sample has a smooth surface structure [Fig. 2(a)], the acetone dried fiber has a slightly ridged fiber surface [Fig. 2(b)]. In all cases, fibers with round cross-sections were obtained.

It is difficult to compare the results obtained here with the results of other workers, since only a few studies have been made on the preparation of fibers from chitosan. The work by Mitsubishi Rayon<sup>18</sup> used a 3% chitosan solution in 0.5% aqueous acetic acid,



**Figure 2** SEM micrographs of the chitosan fibers: (A) dried by radiant heating, (B) dried by acetone extraction.



**Figure 3** Moisture regain and yarn breaking load vs. relative humidity (conditioned for one week).

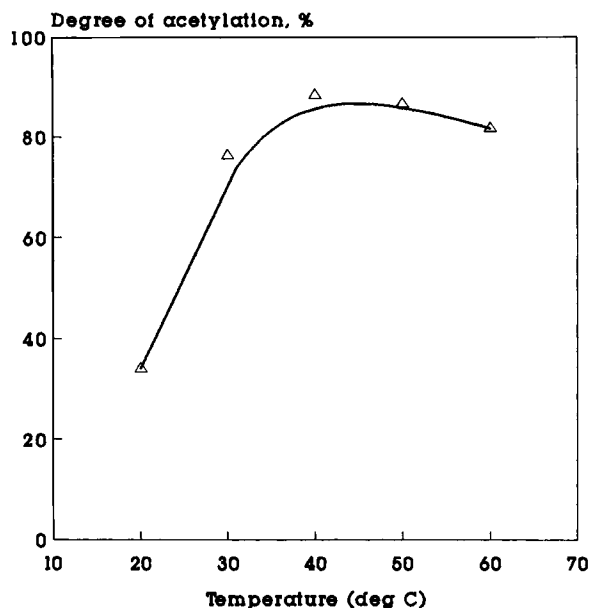
spun into a 5% aqueous NaOH bath. They obtained a fiber tenacity of 0.239 N/tex, with an elongation at break of 10.8%. In similar studies on chitosan fibers, involving the use of a 2% aqueous Na lauryl sulfate as a coagulating bath,<sup>19</sup> aqueous solutions of dichloroacetic acid,<sup>20</sup> and urea-acetic acid<sup>21</sup> as spinning solvents have been reported. A recent study by Tokura et al.<sup>22</sup> used coagulating baths containing  $\text{CuSO}_4\text{-NH}_4\text{OH}$  or  $\text{CuSO}_4\text{-H}_2\text{SO}_4$ ; the fibers obtained were a complex of chitosan and copper ions.

#### Moisture Regain of the Chitosan Fibers

Figure 3 shows the moisture regain and the breaking load of one chitosan yarn sample, conditioned under different levels of relative humidity, for one week. At 20°C and 65% R.H., the moisture regain is 16.2%. As is evident from Figure 3, the fiber strength decreases sharply with the increase in relative humidity; the wet strength is only 22% of the strength at 65% R.H.

#### Acetylation of Chitosan Fibers

The chitosan sample used in this study had a degree of acetylation (DA) of 16.0% and the acetylation studies used yarns with an individual filament of about 9 dtex (ca 30  $\mu\text{m}$  diameter). Figure 4 shows the DA of chitosan fibers, acetylated at temperatures between 20 and 60°C for  $\frac{1}{2}$  h, using 5% acetic anhydride in methanol, followed by the de-O-acetylation treatment. It is evident that a relatively low degree of acetylation was obtained at 20°C. As the temperature was increased, a significant increase in DA was obtained, with the highest DA value being obtained at 40°C. Further increases in temperature showed little effect, with the values obtained at 50



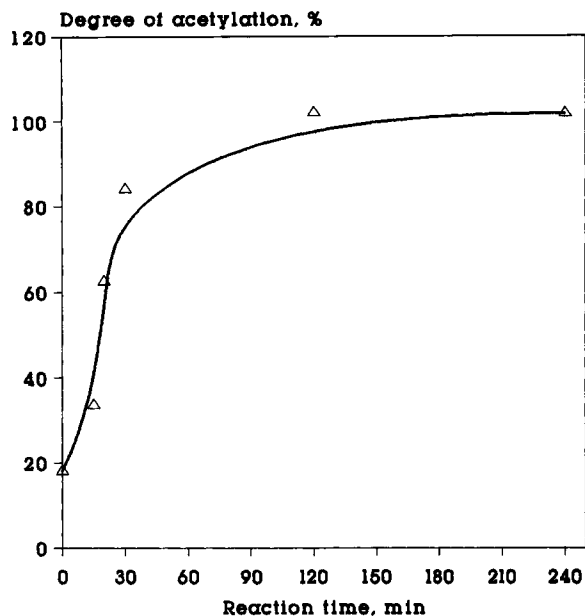
**Figure 4** Degree of acetylation vs. reaction temperature. The reaction was allowed to proceed for 30 min, using 10 mL 5% acetic anhydride in methanol and 12.9 mg fiber.

and 60°C being slightly lower than that at 40°C. The increased reaction speed, with an increase in temperature, could be the result of many effects, such as an increased rate of diffusion of the anhydride, an increased reactivity, and an increased fiber swelling. The slight decrease in the degree of acetylation beyond 40°C may be explained by an increased rate of side reactions, which result in the more extensive consumption of acetic anhydride.

Figure 5 shows the effect of time on the acetylation of the chitosan fibers at 40°C under the same reaction conditions. It can be seen that the acetylation is a fairly rapid process, in that 84% of the amine groups were acetylated within 30 min. Further treatment led to a degree of acetylation exceeding 100%, which was considered to be the result of the acetylation of the hydroxyl groups. This was confirmed by redetermining the DA after dilute NaOH treatment.

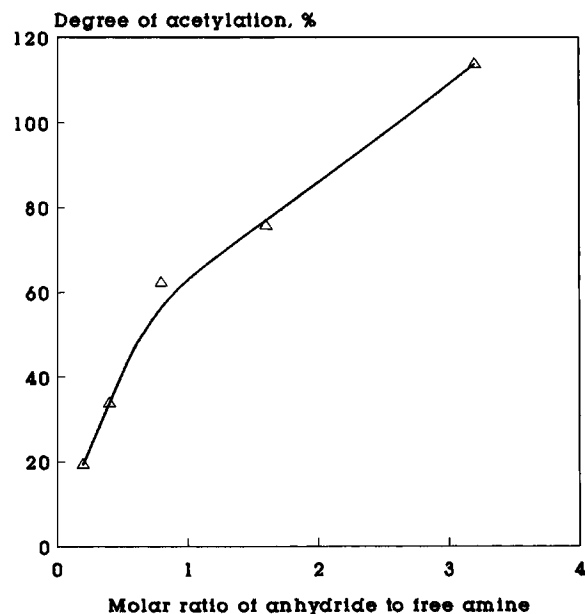
Figure 6 shows the effect of varying the molar ratio of acetic anhydride to amine on the acetylation of chitosan fibers at room temperature for 48 h. Only a low degree of acetylation was achieved when the ratio was lower than 1.6. The degree of acetylation reached 75% when the ratio was 1.6; this DA is similar to the values reported for natural chitin. *O*-acetylation was produced when the ratio exceeded 3.2.

These results confirm the earlier studies on the acetylation of chitosan film and chitosan in solution, which demonstrated the importance of the choice



**Figure 5** Degree of acetylation vs. treatment time. The acetylation treatment was carried out at 40°C, using 10 mL 5% acetic anhydride in methanol and 12.9 mg fiber.

of solvent and the ratio of anhydride to amine in obtaining an efficient reaction.<sup>25-27</sup> Thus, there appears to be no difficulty in converting chitosan fibers to chitin by the acetylation procedure.



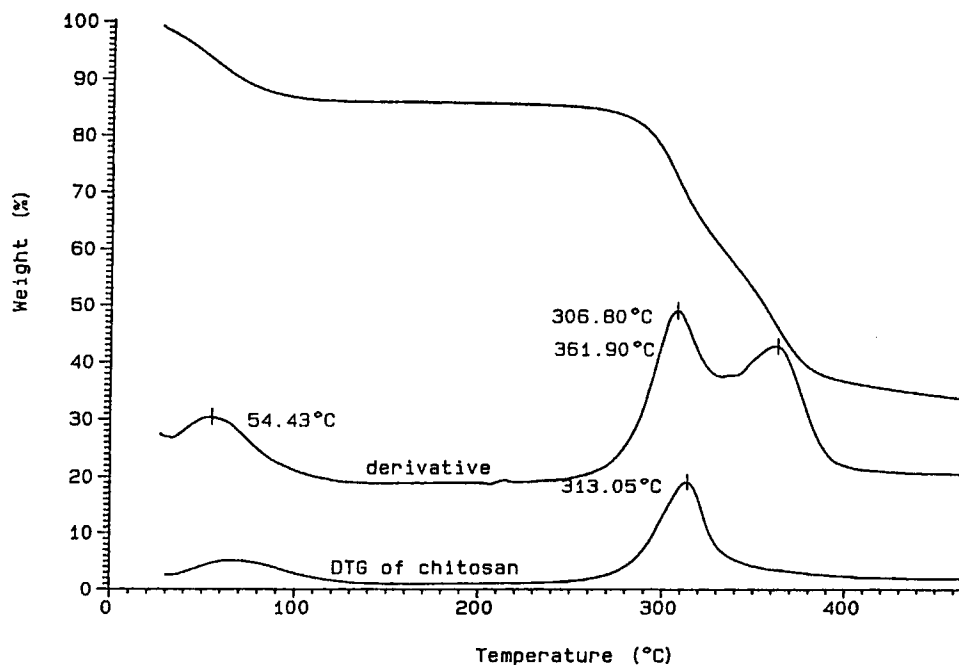
**Figure 6** Degree of acetylation vs. molar ratio of anhydride to primary amine groups in chitosan. The acetylation process was carried out at room temperature for two days, followed by de-*O*-acetylation.

### Properties of the Acetylated Chitosan Fibers

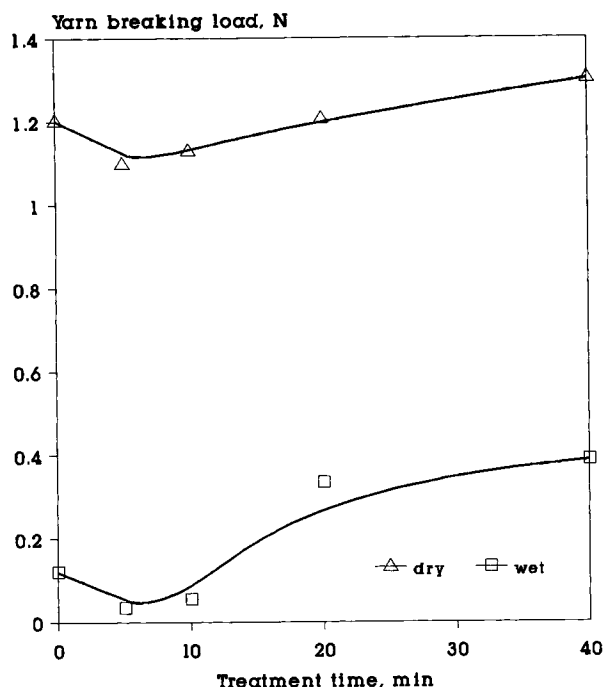
Confirmation that the reaction occurred efficiently followed from infrared and X-ray diffraction measurements, as well as from elemental analysis.<sup>23,28</sup> In addition, it was found that the acetylated chitosan fibers (> 70% DA) became insoluble in acidic media. Interestingly, selected samples, with full acetylation, were found to be soluble in a chitin solvent, DMA-LiCl. Thermal gravimetric analysis showed that, as the degree of acetylation increased, the sample became thermally more stable. The initial chitosan sample showed a maximum rate of decomposition at 313°C, while the fully acetylated sample showed the equivalent DTG peak at 357°C. The increased thermal stability, after acetylation, must be attributed to the chemical stability of the amide groups over the primary amine groups. Figure 7 shows the TGA curve of a partially acetylated chitosan fiber (DA = 62%) and the DTG curves for the acetylated and the original chitosan fibers. It is evident that the decomposition occurs in two distinctive chitosan and chitin peaks. It is not clear whether these two peaks represent the behavior of a homogeneously acetylated chitosan fiber or, perhaps more likely, a bicomponent fiber, consisting of a chitosan core and an acetylated sheath.

One sample of chitosan fibers was boiled in 5% v/v acetic anhydride in methanol to prepare samples

of different levels of acetylation. The boiling method was used in order to prevent the fibers from adhering to one another. As is evident from Figure 8, the breaking load first decreased with treatment time and then showed an increase of about 10% after 40 min treatment. The wet breaking load showed a more dramatic change with time of treatment. After 5 min, the wet value was reduced to a third of the original, while after a 40 min treatment, the wet breaking load was three times that of the original fiber. The changes in the fiber dry and wet breaking loads with treatment time must be a reflection of the structural changes occurring during the acetylation process. Though individual DA values were not determined, the increase in the degree of acetylation of chitosan with treatment time is followed first by a destruction of the chitosan structural regularity. This structural change is reflected in the fall in fiber wet strength, which showed a near zero value after the 5 min treatment. This phenomenon is possibly related to the findings of Sannan et al.,<sup>29</sup> where after a partial deacetylation of chitin, a water soluble product can be produced. As the degree of acetylation increased further, the fiber structure became predominantly a chitin structure. As chitin is reported to be more crystalline than chitosan<sup>30</sup> and is less sensitive to water, the dry and wet strength increased upon further acetylation.



**Figure 7** TGA curves of a partially acetylated chitosan fiber (DA = 62.2%) and of original chitosan fiber.



**Figure 8** Yarn breaking load vs. time of acetylation treatment. The chitosan fibers were boiled in a 5% acetic anhydride solution in methanol for different lengths of time.

## CONCLUSIONS

1. Chitosan fibers can be created by the wet spinning of its solution in dilute aqueous acetic acid. The fiber properties were affected by the spinning conditions, such as spin stretch ratio, coagulation bath concentration, and drying conditions. Fiber tenacities of up to 0.24 N/tex can be obtained.
2. The chitosan fibers can be converted into chitin fibers by acetylation with acetic anhydride. The acetylation process was affected by reaction time, temperature, as well as molar ratio of anhydride to primary amine groups in chitosan. Elevated reaction temperature and the use of an excess of anhydride are essential if a substantial degree of acetylation is required.
3. The acetylated chitosan fibers, or regenerated chitin fibers, showed good thermal stability and improved wet and dry strengths. With the conversion of primary amine groups to acetamide groups, the chitosan fibers became insoluble in acidic media.

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