

# Spinnability of Chitosan Butyrate/Cellulose Acetate for Obtaining a Blend Fiber

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**ABSTRACT:** The production of chitosan fibers has remained of interest over the last decade. However, the copolymer structure of partially deacetylated chitosan generally lowers the dry/wet strength properties of chitosan fibers. There are numerous methods available for improving the mechanical properties of chitosan fibers, that is, the strain and stress to failure. In this work, the blending of chitosan with cellulose acetate is described. The chitosan is in

the form of the butyrate ester, which, like cellulose acetate, is easily transesterified to regenerate the polysaccharide. The fibers obtained from codissolving cellulose acetate with chitosan butyrate are described. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2801–2805, 2007

**Key words:** biofibers; biopolymers; composites; esterification; microstructure

## INTRODUCTION

Chitin is the second most abundant naturally occurring polysaccharide next to cellulose. Chitosan is the deacetylated product of the alkali hydrolysis treatment of chitin and is a crystalline polymer with a structure similar to that of cellulose.<sup>1</sup> Chitosan is biodegradable, relatively nontoxic, nonimmunogenic, and biocompatible; much research has been directed toward its use in medical applications such as drug delivery, artificial skin, and blood anticoagulants.<sup>2–4</sup>

The intractability of chitin is due mainly to its rigid crystal structure, which is a result of the close packing of the molecular chains and four different types of hydrogen bonds. Chitosan does not have the same degree of hydrogen bonding; although it has an abundance of hydroxyl groups, it remains insoluble in water and organic solvents.

The production of chitosan fibers continues to attract interest as the availability of chitosan has increased and new uses are found for the fibers.<sup>5–7</sup> However, the copolymer structure of partially deacetylated chitosan generally lowers the dry/wet strength properties of chitosan fibers by limiting the recrystallization of the deacetylated units of chitosan.<sup>8</sup> There are numerous methods available for improving

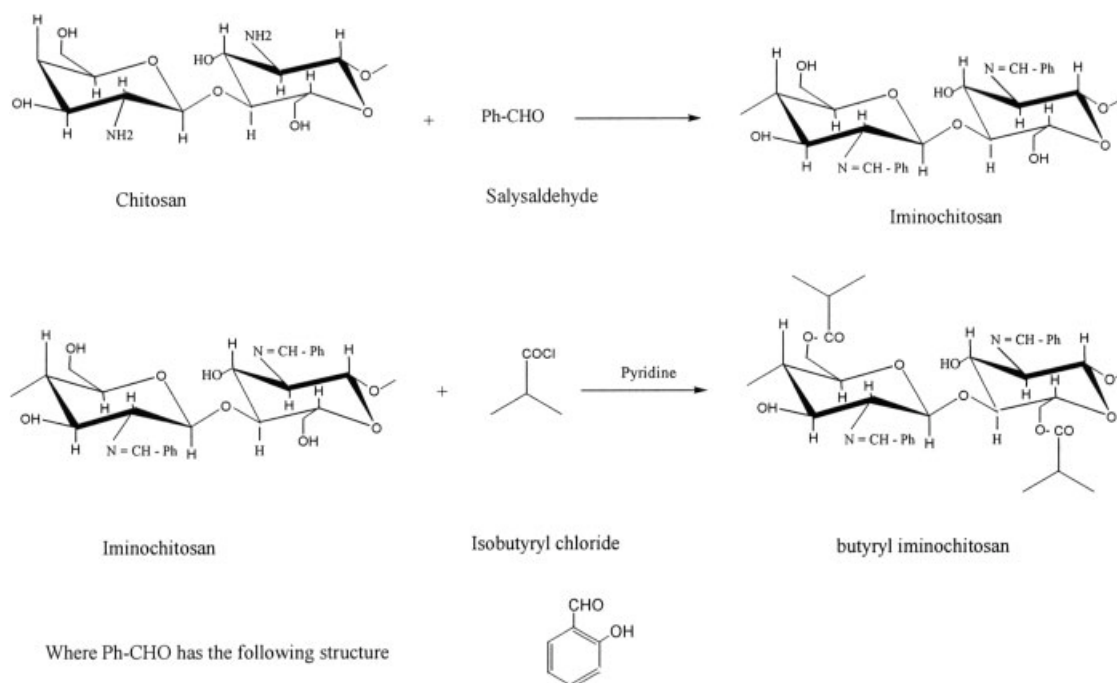
the mechanical properties of chitosan fibers, particularly the tenacity and toughness, which have been reviewed.<sup>3,9,10</sup> These methods can follow one of two approaches: physical or chemical processing of the fibers. With a physical approach, improvements to a fiber's mechanical properties can be rendered by the application of stretching to the yarn in the coagulation step of wet spinning, by the application of stretching to the yarn after coagulation but while it is still wet and swollen with water, or by the application of stretching to the yarn after it is dried and just before it is wound up. With a chemical approach, the mechanical properties of the fibers can be altered by a reaction with another compound; usually this involves cross-linking the polymer chains.

The spinning of dibutyl chitin has been reported in the literature. Szosland and East<sup>11</sup> described the preparation of a chitin fiber using acetone as a solvent. Dibutyl chitin was synthesized by the reaction of krill chitin with butyric anhydride in the presence of perchloric acid as a catalyst at 25°C. Dibutyl chitin is easily dissolved in several organic solvents, such as acetone, alcohols, methylene chloride, and dimethylformamide (DMF). Also, the preparation of dibutyl chitin using methanesulfonic acid as both the catalyst and solvent has been described.<sup>12</sup>

In this work, butyryl iminichitosan (CB) was prepared by the reaction of iminichitosan with an equimolar ratio of butyryl chloride and pyridine and with DMF as a solvent. Iminichitosan is the amino-protected form of chitosan obtained by its reaction with salicyl aldehyde.<sup>13</sup> This allows the esterification of chitosan's hydroxyl groups and the subsequent deprotec-

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**Scheme 1** Reaction scheme for the preparation of CB.

tion of the amino group. Previous work has identified CB as an easily prepared ester compatible with cellulose acetate (CA).<sup>14</sup> CB/CA blend solutions with different CB percentages (15, 30, and 45%) were prepared in *N*-methyl pyrrolidone (NMP). The spinnability of these solutions was determined with a single-hole spinneret. Sulfuric acid (aqueous) was used as a coagulant. The spun fibers were evaluated through the determination of the tenacity, elongation at break, and fiber density. Also, scanning electron microscopy (SEM) was used for the surface analysis for the untreated, sodium methylate (SM)/methanol treated, and HCl-treated blend fibers.

## EXPERIMENTAL

### Materials

Commercial crab-shell chitosan was kindly supplied by Vanson [Redmond, WA; medium viscosity (30 cps), lot 01-ASCC-0279]. The degree of deacetylation (DD) of the chitosan was reported to be 85%. Pyridine, *n*-butyryl chloride, NMP, and DMF were purchased from Aldrich Chemicals (Milwaukee, WI). Fisher Scientific (Waltham, MA) supplied all other chemicals.

### Characterization of chitosan

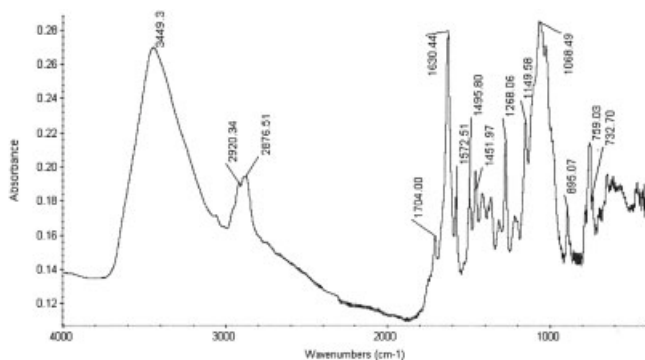
Chitosans having four different molecular weights were prepared by the acid hydrolysis of commercial chitosan with a 1N HCl/isopropyl alcohol binary mixture at 85°C for 2 h with different ratios of HCl to isopropyl alcohol.

The DD of chitosan was calculated from elemental analysis data. The elemental analyses of the carbon, hydrogen, and nitrogen percentages (CHN) of CA and their blends with chitosan butyrate were determined with a Leco (St. Joseph, MI) CNS 2000 automated, bench-top CHN analyzer. The DD was calculated from the C/N ratio, which ranged from 5.14 for 100% deacetylated chitosan to 6.86 for completely acetylated chitosan (chitin). The DDs for the chitosan samples were calculated to be 82.4, 81.4, 80.7, and 78.7%, respectively. The viscosity-average molecular weights of hydrolyzed chitosan were determined from the intrinsic viscosity, which was measured in an Ubbelohde viscometer with 0.1M acetic acid/0.2M sodium chloride as the solvent, and they were calculated to be 127, 75, 50, and 26 kDa.

### Chitosan modification

The reactions for the preparation of CB are illustrated in Scheme 1. Hydrolyzed chitosan (3 g; molecular weight = 26 kDa) was reacted with an equimolar amount of salicyl aldehyde (9.9 mL) in 50 mL of water at room temperature for 6 h to protect the amine groups of chitosan.<sup>13</sup> Iminochitosan was filtered off, purified through washing with distilled water and then purified by methanol Soxhlet extraction for 6 h, and dried at room temperature for 24 h. The CHN values of the iminochitosan were determined to be 55, 7.15, and 5.4, respectively.

CB was prepared by the reaction of iminochitosan with butyryl chloride in the presence of pyridine as a



**Figure 1** FTIR spectrum of the butyrylated iminochitosan reaction product.

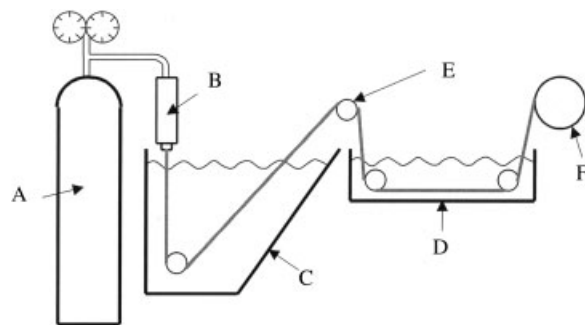
catalyst.<sup>14</sup> In a dry-ice bath, 3 g of iminochitosan was slurried in 50 mL of DMF. A known concentration of pyridine (2.96 mL) was added in one portion and stirred for 15 min. A definite amount of acid chloride (3.8 mL) in 25 mL of DMF was then added dropwise over a period of 1 h, and stirring was continued for 3 h at 0°C. The reaction solution was poured onto crushed ice and then washed with cold/hot distilled water several times to remove the pyridinium salts. The product was finally purified by Soxhlet extraction with methanol for 24 h. The chitosan butyrate derivative was dried at 60°C for 24 h. The CHN values of chitosan butyrate were determined to be 57.45, 6.65, and 3.51, respectively. The Fourier transform infrared (FTIR) spectrum of the iminobutyryl chitosan is shown in Figure 1. The FTIR spectra for acylated derivatives of iminochitosan show a carbonyl peak at 1736 cm<sup>-1</sup>, indicating the formation of a carbonyl ester derivative of chitosan, at the expense of the OH stretching of chitosan at 3420–3250 cm<sup>-1</sup>.

### Fiber spinning

CB/CA blend solutions were prepared by the dissolution of the blend ingredients in NMP under continuous stirring overnight. The solution was filtered and put in an ultrasonic bath to remove the air bubbles. The polymer cell was charged with 50 mL of the solution and pressurized. The volumetric flow rate (mL/s) was determined by the collection of the solution in a beaker below the capillary for 30 s and weighing. The capillary dimensions of the diameter and length along with the volumetric flow rate were used to calculate the apparent solution viscosity ( $P$ ) via Poiseuille's law. The spinning apparatus is shown in Figure 2.

### Fiber regeneration

The spun fiber was treated with a 0.5 SM/methanol solution for 6 h at room temperature. This regenerated the chitosan and cellulose from their respective esters



**Figure 2** Schematic of a bench-top scale apparatus for 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.

via transesterification and increased the hydrophilicity of the spun fiber. To deprotect the amino group in the chitosan, the imino derivative was washed in 0.1N HCl at room temperature for 15 min.

### Testing and analysis

The spun and SM-treated fibers were evaluated with an Instron model 5544 with a 5N load cell. The denier was determined from the weights of lengths of the fibers. The fiber density was determined with a neutral buoyancy method using mixtures of acetone and perchloroethylene and the rule of mixtures for calculating the density. The as-spun and SM-treated CA/chitosan butyrate derivative fibers were evaluated by SEM with a Hitachi S-3200N scanning electron microscope and by FTIR spectra. FTIR spectra were obtained with a Nicolet 510P FTIR spectrometer. Sixty four repeated scans from 4000 to 400 cm<sup>-1</sup> were averaged.

## RESULTS AND DISCUSSION

### Preparation and spinning of the blend solutions

CA and CA blend solutions having different amounts of CB (15, 30, and 45 wt/wt %) were prepared with NMP as a solvent. With a mechanical stirrer, the solu-

**TABLE I**  
Elemental Analysis of the CA/CB Blend Fibers

CA/ CB ratio (%)	Elemental analysis of the CA/ CB blend fibers					
	Spun fiber			SM-treated fiber		
	C	H	N	C	H	N
100/00	35.6	6.5	0.79	35.4	6.19	0.36
85/15	51.87	6.13	1.02	47.8	6.01	1.21
70/30	53.98	6.4	1.51	49.1	6.21	1.72
55/45	54.01	6.6	2.81	49.6	6.0	3.01

**TABLE II**  
Physical Properties of Iminochitosan/Cellulose Fibers

CA/CB ratio (%)	Treated fiber	Tenacity (g force/d)	Elongation at break (%)	Denier	Fiber density	Viscosity (P)
100/00	Spun fiber	0.886	8.66	54	1.31	0.641
85/15		0.899	4.64	34.6	1.27	0.98
70/30		0.795	7.32	39.8	1.27	0.876
55/45		0.492	6.87	49.4	1.29	0.512
100/00	SM-treated fiber	0.66	4.07	50	1.42	
85/15		0.761	4.62	36.5	1.48	
70/30		0.74	11.27	41.5	1.46	
55/45		0.762	11.26	51.4	1.44	

tion was allowed to stir for 24 h at room temperature. The solution was then filtered through a stainless steel screening filter under pressure to get the air bubbles out of the solution. The spinning solutions were spun in the pressure range of 25–50 psi according to the viscosity of each solution. The coagulant was 0.5N sulfuric acid. The spun fibers were washed several times with water before any further examinations. The compositions and elemental analysis of the fibers are indicated in Table I.

The tensile properties of the fibers are summarized in Table II. Increasing the amount of CB in the fiber decreased the as-spun fiber properties. This was expected because there was a considerable difference in the shapes of these two polymers leading to poor packing of the chains and most likely some micro-phase separation of the polymers at the molecular level. However, upon the regeneration of the cellulose and chitosan, better packing and the establishment of hydrogen bonds between the polymers were expected to result in improved compatibility and crystallization. This was reflected in the improved tensile prop-

erties and increased densities of the regenerated fibers, which are also shown in Table II.

#### SEM examination of the fibers

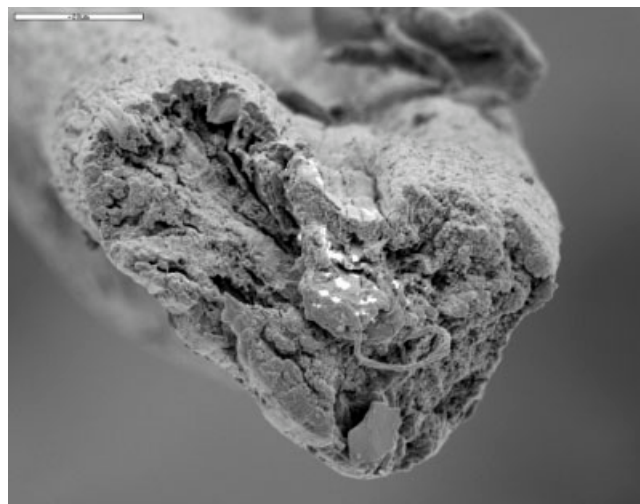
The fibers that had a 55/45 ratio of CA to butyryl iminochitosan were selected for examination by SEM to reveal morphological changes during the regeneration of the cellulose/chitosan fibers. The fiber surface and the fractured ends of the fibers were examined.

Figures 3 and 4 present the as-spun fiber and the regenerated fiber, respectively. In Figure 3, on the upper half of the fiber cross section, fluted voids, typical of viscous fingering, appear. This occurs because of the heat of mixing between the solvent (NMP) and the coagulant, sulfuric acid. Figure 4 shows that these voids coalesced as the fibers density increased from 1.29 to 1.44 g/mL. Fibrillar fragments are also present in both images.

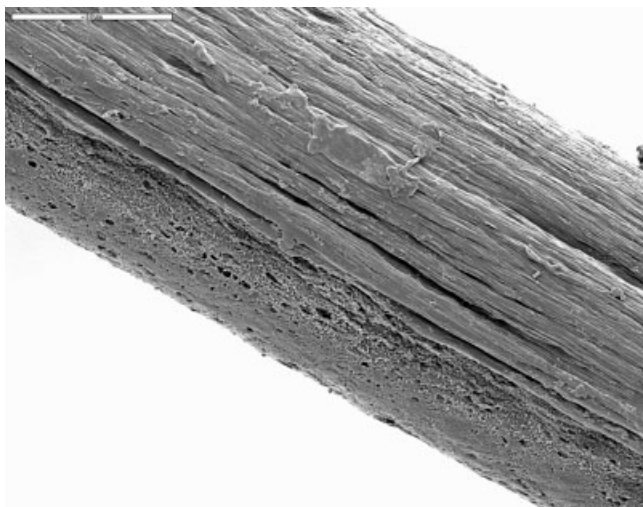
Figures 5 and 6 indicate the rearrangement of the fiber surface after regeneration. Again, in Figure 5, the fluted void structure extending down into the fiber



**Figure 3** SEM for a CA/CB (55/45%) as-spun fiber blend. The scale bar represents 50  $\mu\text{m}$ .



**Figure 4** SEM for a CA/CB (55/45%) fiber blend treated with 0.5N SM/methanol. The scale bar represents 20  $\mu\text{m}$ .



**Figure 5** SEM for a CA/CB (55/45%) as-spun fiber blend. The scale bar represents 50  $\mu\text{m}$ .

structure can be observed. Upon the regeneration of the cellulose and chitosan after transesterification, the surface is smoother, and the voids have coalesced. There is also a substantial reduction (up to 50  $\mu\text{m}$ ) in the cross-sectional diameter, as indicated by a comparison of Figures 5 and 6.

### CONCLUSIONS

Blend fibers of cellulose and chitosan were obtained. They were prepared by the blending of CB and CA in a common solvent, NMP. These solutions, with CB ratios ranging from 15 to 45 wt/wt %, were spun into a coagulant bath of sulfuric acid. The sulfuric acid solidified the fibers and hydrolyzed the iminichitosan, freeing the amino group on the chitosan. A solution of SM in methanol was used to transesterify the esters of the chitosan and cellulose to regenerate the respective polysaccharides. As the weight percentage of chitosan increased in the fibers, the tensile strength and density of the regenerated fibers generally increased. The tensile strengths for the blend fibers were comparable to those of conventionally prepared fibers.<sup>8,10</sup> SEM observations revealed that the fibers became more consolidated upon regeneration and that fluted voids



**Figure 6** SEM for a CA/CB (55/45%) blend fiber treated with 0.5N SM/methanol. The scale bar represents 50  $\mu\text{m}$ .

that formed during coagulation coalesced. The regeneration of the cellulose/chitosan fibers from the esters led to stronger fibers.

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