

# The Preparation and Properties of Cellulose/Chitin Blend Filaments

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**ABSTRACT:** The focus of this article is the preparation and characterization of cellulose/chitin blend filaments obtained from cellulose/chitin xanthate blend solution over the experimental blend ratio, i.e., 2.89% and 6.46% (w/w) chitin content. The addition of chitin xanthate into cellulose xanthate leads to an increase of intermittence rate and the blend solution has good filtering property. Scanning electronic microscope photos shows that there exist grooves on the filaments surface, which are becoming coarse with increasing chitin content. The mechanical properties of the spun blend filaments is much higher than that of Crabyon® fiber, which proves that the viscose

method we adopt here is an efficient way to prepare cellulose/chitin blend filaments with satisfactory mechanical properties and processing property. Based on the data from X-ray, sonic velocity, equilibrium regain rate, and accessibility, it is concluded that the degree of crystallinity, modulus, degree of orientation, density, equilibrium regain rate, and accessibility of blend filaments decreases with increasing chitin content in the blend filaments in the experiment scope. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2777–2784, 2009

**Key words:** polysaccharides; blends; fibers

## INTRODUCTION

As a kind of regenerated cellulose fiber, viscose fiber has been the favor of people over 1 century due to its moisture absorbance, low price, easy processing, vivid color, and so on. But viscose fiber does not have the function of bacteriostatic, and under feasible condition, the viscose fabric will be an identical environment for bacteria to breed and lead to illness. As the most abundant polysaccharide sources in nature except cellulose, chitin is biocompatible, biodegradable, antibacterial, and non-noxious. The fiber made from chitin and its derivatives has not only good mechanical properties but also excellent biological activity, i.e., bacteriostatic, accelerating the growth of tissue, and so on, which has got wide use in biology, medical treatment, sanitation, and etc.<sup>1–3</sup> Therefore, how to prepare bacteriostatic cellulose fiber from chitin and cellulose seems to be of great attraction to us due to their distinguished properties. Pan and Wu<sup>4</sup> prepared blend yarn from chitin fiber, alginate fiber, and Tencel (a kind of new cellulose fiber), which had the properties of anti-inflammation, deodorization, and antibacterial. Fuji Spinning Co. in Japan has pre-

pared Chitopoly® fiber by wet spinning from cellulose viscose containing fine chitosan powders, which has antimicrobial activities and deodorant properties.<sup>5</sup> The addition of powder into solution leads to some shortcomings, i.e., special treatment of chitosan to get fine powder with small size in case of large chitosan loss during filtering process, bad dispersivity, low fiber mechanical properties, and so on. To weave different fibers into fabric leads to difficulty for further processing, fluffiness, and so on due to difference in fiber affinity.

To dissolve cellulose and chitin into blend solution is an important way to prepare fiber since there is almost no loss of raw materials, the dispersing of the blend system is stable, and the mechanical properties of the prepared fiber is high. The whole production process is simplified and the production expense is decreased. But chitin cannot dissolve in ordinary solvent system, which limits its wide uses. Bocek and coworkers<sup>6</sup> result showed that there was partial compatibility among chitin and cellulose macromolecules where dimethyl acetamide/lithium chloride(DMAc/LiCl) was used as cosolvent. Phonwong et al.<sup>7</sup> prepared chitin/cellulose blend films. Zhang and coworkers<sup>8</sup> prepared cellulose/chitin blend membrane from sodium hydroxide/thiourea aqueous solution.

A lot of efforts have been taken to use chitin derivatives as raw materials. Hirano et al.<sup>9,10</sup> prepared

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fibers from *N*-acetylchitosan xanthate/cellulose xanthate blend since the intramolecular and intermolecular hydrogen bonds of *N*-acetylchitosan are weaker than that of natural chitin, resulting in its easy solubility in 14% aqueous sodium hydroxide solution.

According to Thor<sup>11</sup> and some researchers' work, chitin viscose can be obtained by xanthating alkali chitin. Zhang et al.<sup>12</sup> discussed the rheological behavior of chitin and cellulose xanthate blend solution. However, they never referred the mass concentration of the investigated blend solution. Noguchi et al.<sup>13</sup> prepared chitin-cellulose blend fiber with low wet and dry intensity. And now Omikenshi Company (Osaka, Japan) has applied patents for Crabyon<sup>®</sup> staple in the similar way. But the mechanical property of Crabyon<sup>®</sup> is only  $0.7 \text{ cN} \times \text{dtex}^{-1}$ .<sup>14,15</sup> And there is no any report concerned with the production of filament prepared from chitin-cellulose xanthate blend solution because of more difficulty in filament production.

On the basis of our experience on chitin/cellulose staple,<sup>16</sup> we want to develop our distinguished viscose method to prepare filament with improved mechanical properties from the blend solution of cellulose and chitin xanthate to obtain a wide use in clothes, underwear, and so on. The following is a description of the production process and some physical properties of the filaments prepared.

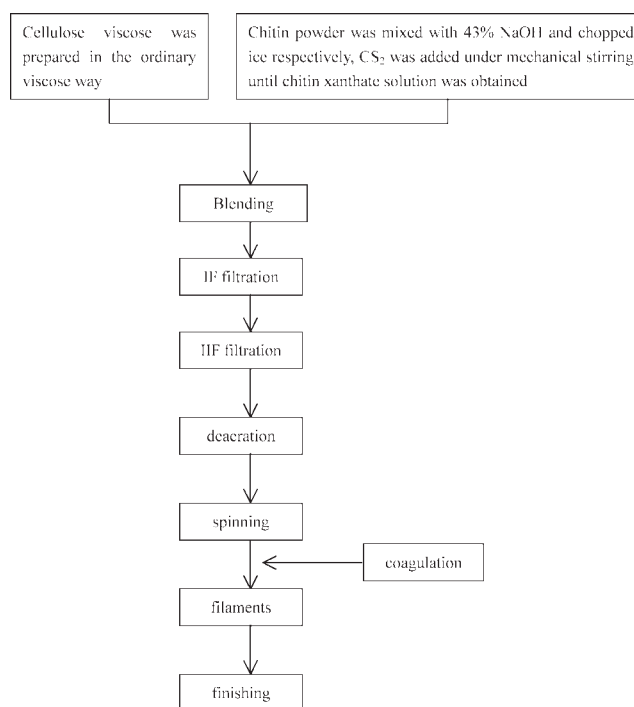
## EXPERIMENT

### Materials and reagents

The cellulose sample employed was cotton linters with a viscosity average degree of polymerization 700 obtained through cupriethylene diamine method, which was heated at 105°C until constant weight and kept over fresh phosphorus pentoxide in a desiccator before use. The viscosity average molecular mass of chitin powder was 171,000 obtained through the equation  $[\eta] = 2.1 \times 10^{-4} \times M^{0.88}$  provided by Chen and coworkers,<sup>17</sup> where dimethyl acetamide containing 5% lithium chloride (w/w) was chosen as solvent. Reagent-grade carbon disulfide, sodium hydroxide, sulfuric acid, sodium sulfate and zinc sulfate, and tetrachloromethane were supplied by Shanghai Feida Chemical Co., China.

### Preparation of blend solutions

The cellulose viscose was prepared as following: cellulose was dipped into 20 wt % sodium hydroxide solution for an hour at 20°C, crushed until its mass was three times of the original, then crumbled, and aged at 40°C for 8 h. And a certain amount of carbon disulfide [37 wt % of the original mass of



**Figure 1** Production process of cellulose/chitin filaments from cellulose/chitin xanthate blend solution.

$\alpha$ -cellulose] was added in the mixture, stirred vigorously until transparent solution was obtained.

The chitin viscose was obtained according to Thor's method as follows: chitin powder was mixed up with 43 wt % sodium hydroxide solution in a flask at room temperature for 300 min, the ratio of chitin mass to the volume of sodium hydroxide solution was 1 : 20. Then some residual sodium hydroxide solution was removed through vacuum supply until the mass ratio of the product to original chitin was 3 : 6. Then the product was mixed with chopped ice under mechanically stirring at 0°C until the whole system became transparent. A certain amount of carbon disulfide was added under stirring until orange-like stable solution was obtained.

After both cellulose and chitin viscose were filtered, they were blended under strong mechanically stirring in postdissolving machine according to different mass ratio until homogenous solution was obtained. The dissolving temperature was 14–25°C and alkali content was controlled around 4–12 wt %.

The former rheological work has provided theoretical data for further fiber spinning [unpublished data]. Here for the first time, blend filament was prepared with excellent mechanical properties.

### Spinning condition

The spinning routine is described in Figure 1. The blend solution was filtered for the first time which was defined as IF filtration, deaerated under

0.08 Mpa vacuum for 15 h, and aging at 15–26°C for 10 h until a certain aging extent was reached. Then the spinning solution was filtered for the second time, which was defined as IIF filtration. And the spinning solution was spun through spinneret into coagulation bath at 40–55°C. The coagulation bath had the following composition, i.e., sulfuric acid 100–135 g/L, zinc sulfate 6–25 g/L, and sodium sulfate 200–330 g/L, respectively. The adopted spinneret diameter was 0.08 mm. The spinning velocity was 70 m/min. Jet stretch ratio (the ratio of taking-up speed to spinning speed) was 3%, stressed draw ratio was 2.69%, and draw ratio between drawing godget and coagulation roller was 20%, respectively.

### Finishing

Finishing procedure of cellulose/chitin fiber includes washing by water at 35–55°C, desulfurization, bleaching, washing by acid, and oiling, respectively. The concentration of aqueous sodium hydroxide solution for desulfurization was 3–9 g/L, operated at 50–90°C. The concentration of hydrogen peroxide for bleaching was 1–5 g/L, operated at 20–40°C and the pH value was controlled at 7–10. The acid washing temperature was 25–45°C. The concentration of oil bath was 1–2 g/L, operated at 25–45°C.

### Equipment and testing conditions

#### SEM photos

A JOEL JSM-5000LV scanning electron microscope (Tokyo, Japan) was used to study the surface morphology of the filaments. The filaments were extracted with ether at 35°C for 4 h; then, the filament surface was coated with gold and used for observation.

#### X-ray diffraction

X-ray diffraction patterns were recorded on a flat-plate camera using nickel-filtered Cu K $\alpha$  radiation from a Philips generator (Dutch) operated at 40 kV and 20 mA.

#### Degree of orientation

The degree of orientation of the filament is measured on sonic velocity instrument prepared by Donghua University (Shanghai, China).

#### Mechanical properties

Measurement of the mechanical properties is carried out according to China Standard GB/T14337-93 as following: the tensile strength was measured on a tensile testing machine provided by Chang-Zhou

Textile Machine Co., China (Changzhou, China). The breaking intensity  $\delta_b$  is calculated as following:

$$\delta_b = F/A$$

where,  $F$  is the breaking force the machine shows and  $A$  is the original cross section area of the fiber.

The breaking extension rate  $\varepsilon_b$  was calculated as following:

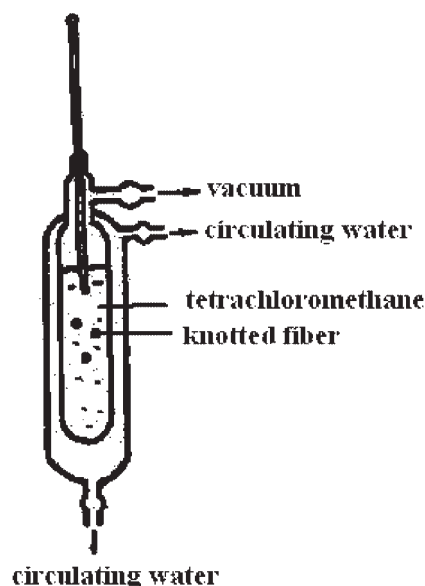
$$\varepsilon_b = (L - L_0)/L_0 \times 100\%$$

where,  $L_0$  is the original length of the fiber and  $L$  is the length of the fiber at breakage.

About 20 replicates were performed to obtain an average value of  $\delta_b$  and  $\varepsilon_b$ , and standard deviations were reported.

#### Density

The density of filaments was measured as shown before<sup>16</sup>: The knotted filaments were sunk in the centrifugal test tube filled with hot tetrachloromethane, kept running for 5 min at 2000 rad/min to remove the air in the knotted filaments. Then, the filaments were moved into the apparatus, as shown in Figure 2, where the suspending solvent was tetrachloromethane. The apparatus was originally kept at 50°C and heated until knotted filaments suspended in the middle of tetrachloromethane. The temperature of tetrachloromethane was recorded at the accuracy of 0.1°C. The density of tetrachloromethane at this temperature was just the density of the filaments.



**Figure 2** Sketch map of apparatus for fiber density measurement.

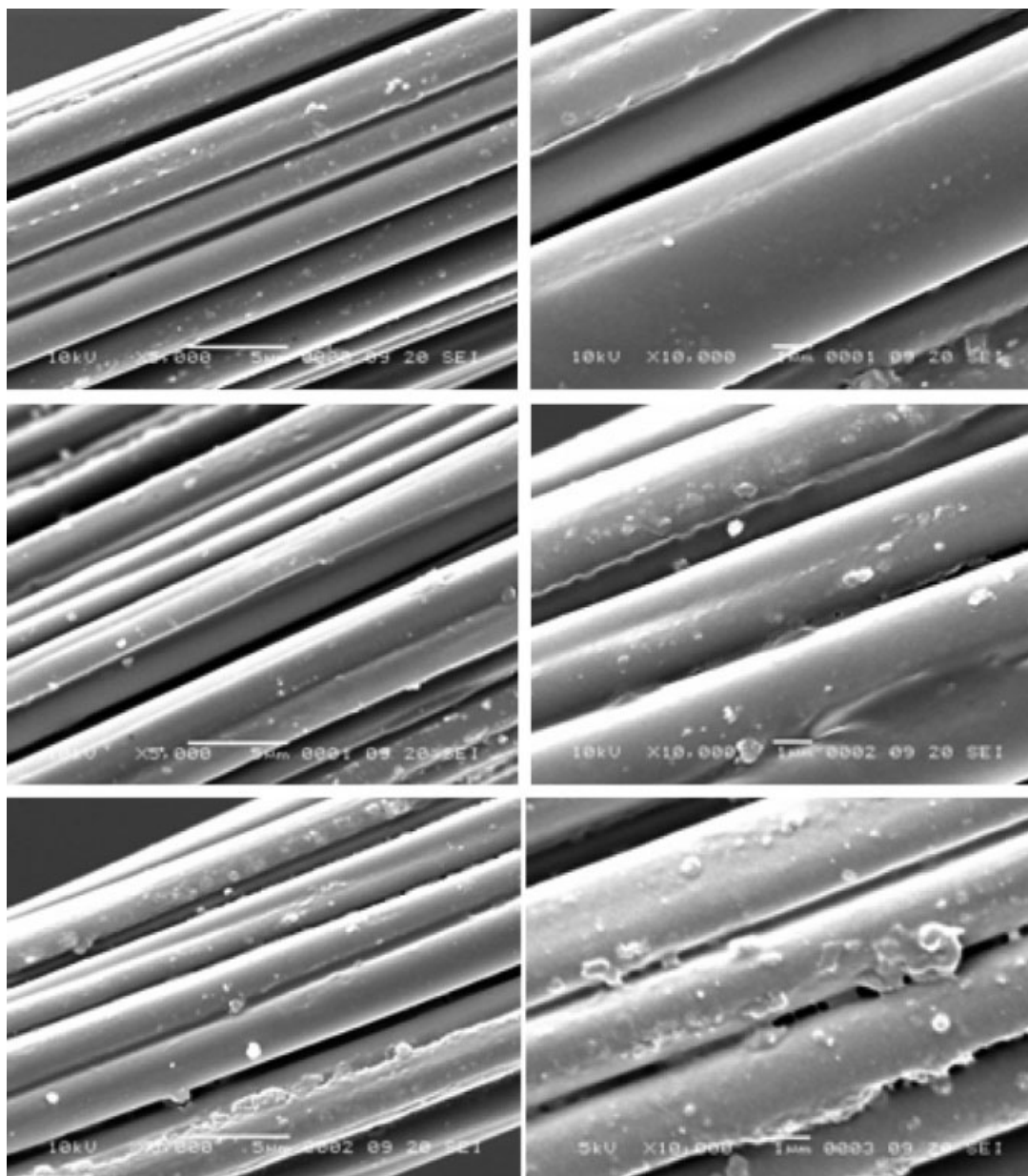
**TABLE I**  
**Spinnability of Cellulose/Chitin Blend Solution for Filament Preparation**

Chitin content (%)	Nonplanning intermittence rate (%)	Foreside intermittence rate (%)	Rear end intermittence rate (%)	Total intermittence rate (%)
0	2.3	4.1	5.6	9.7
2.89	3.0	2.9	9.4	12.3
6.46	3.1	0.8	11.1	11.9

### Hygroscopicity

The filaments with different blend ratio were kept in a desiccator where 35 wt % sulfuric acid was kept at the bottom, which kept the relative humid-

ity in the desiccator 65% at 20°C. After being kept in the desiccator for 48 h until constant weight, the filaments were weighed  $w_1$ , and then the filaments were heated at 102°C until constant weight  $w_2$ . The



**Figure 3** SEM photos of the filaments surface pure viscose 2 sample (2.89% chitin content) 3 sample (6.46% chitin content).

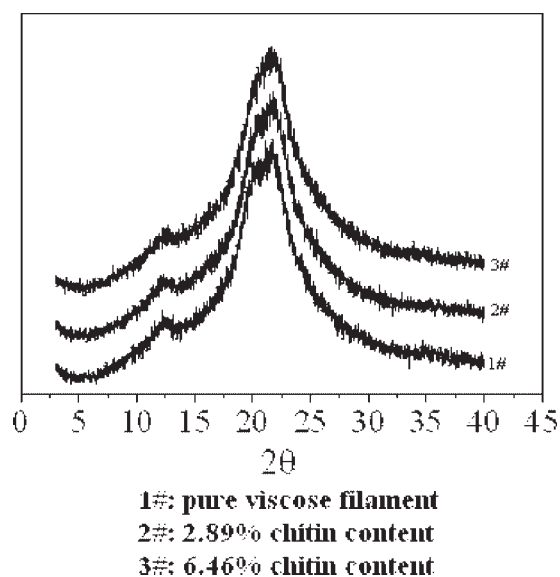


Figure 4 The X-ray diffraction curves of the filaments.

equilibrium regain rate  $W$  was calculated as following:

$$W = (w_1 - w_2)/w_2$$

The rate of water content  $W'$  was calculated as following:

$$W' = (w_1 - w_2)/w_1$$

Accessibility

Fiber accessibility  $A$  was calculated according to the ratio of equilibrium regain rate between the sample and cotton as following:

$$A = W/W_{\text{absorbent cotton}} \times 0.44$$

where, the equilibrium regain rate of absorbent cotton  $W_{\text{absorbent cotton}}$  is 6.81%, and its accessibility is 0.44.<sup>18</sup>

Chitin content in the blend filaments was determined through Kjeldahl method: 300 mg predried blend fiber sample was blended with 300 mg potassium sulfate/copper sulfate hydrate (mass ratio 3 : 1) mixture, then 2 mL sulfuric acid was added, and heated until the medium had become clear and colorless (initially very dark). The solution was then distilled with 10 mL 30 wt % sodium hydroxide which converted the ammonium salt to ammonia. The amount of ammonia present (hence the amount of nitrogen present in the sample) was determined by back titration with 2 wt % boric acid, 0.1N hydrochloric acid, and methyl orange pH indicator.

## RESULTS AND DISCUSSIONS

### Spinnability of the spinning solution

Spinnability of the spinning solution is an important data to indicate the filtering property of spinning solution, reasonability of acid bath composition, and stretching assignation. Excellent spinnability means excellent filtering property, reasonable acid bath composition, and elongation assignation. In industrial production, spinnability is expressed by daily intermittence rate. Low daily intermittence rate means excellent spinnability. (Table I) As shown in Table I, the addition of 2.89% (here 2.89% means that chitin mass percentage in the mass sum of cellulose and chitin is 2.89%, so does 6.46%) and 6.46% chitin into cellulose viscose leads to an increase of rear end intermittence rate, but the increasing extent is still acceptable. And the addition of chitin does not influence nonplaning intermittence rate a lot. Therefore, the investigated blend cellulose/chitin blend solutions still have excellent filtering property, which fit for further filament spinning process.

### SEM photos

The SEM photos of filaments show that there exist grooves on the filaments' surface, which is getting wider with increasing chitin content (Fig. 3). Filament surface is becoming coarse with increasing chitin content. More chitin phase is observed on the surface of the blend fiber with increasing chitin content, which indicates phase separation occurs after precipitation from coagulation bath. And we had expected that chitin could disperse on the filament surface as much as possible to make full use of the biostatic property of chitin and SEM photos showed that this reached our goal. Sample 3 could not endure 10 kV during the SEM observation, whereas sample 1 and 2 could and sample 1 could endure longer time, which may suggest that the thermal stability of the invested samples decreases with chitin content.

We also find that there exists more deflection on the surface of pure viscose filament than that of the blend filaments during the measurement procedure. There is still much dust on the surface of the pure viscose filament after being treated by ether, and the

TABLE II  
Dependence of Degree of Crystallinity on  
Chitin Content

Sample	Chitin content (%)	Degree of crystallinity
1	0	0.33
2	2.89	0.32
3	6.46	0.28

**TABLE III**  
Dependence of Degree of Orientation and Modulus on Chitin Content

Sample	Chitin content (%)	Velocity of sonic (km/s)	Modulus (cNf/dtex)	Degree of orientation
1	0	4.124	172.9 ± 8	0.76 ± 0.3
2	2.89	3.738	142.1 ± 5	0.71 ± 0.2
3	6.46	3.704	139.4 ± 6	0.69 ± 0.2

surface of the blend filaments is relative cleaner, which shows that the blend filaments are easy to be cleaned and may have an excellent application in clothing.

### X-ray diffraction and degree of crystallinity

The X-ray diffraction curves of fibers are shown in Figure 4. The diffraction peaks of pure cellulose fiber appears at  $2\theta$  12.3°, 20.3°, and 21.6°, which is in accordance with Ref. 19. The diffraction peak of cellulose at  $2\theta$  20.3° decreases with increasing chitin content, and the diffraction peak at  $2\theta$  19.8° increases with increasing chitin content, which shows that the addition of chitin destroys the crystal structure of cellulose. As seen in Table II, degree of crystallinity of fibers measured through paper weighing method decreases with increasing chitin content, which shows that the addition of chitin deteriorates the crystallinity of cellulose.

### Degree of orientation and mechanical properties

The degree of orientation is an important parameter to characterize the supermolecular structure of the filaments. Flow of polymer solution or melt during spinning leads to the elongation and orientation of macromolecules along the axis of filament, which have striking influence over the physical properties, i.e., tensile strength, breaking elongation ratio, modulus, and dying property of the filaments. On the other hand, orientation affects polymer crystallization, kinetics of solidification, dynamics of deformation, and etc., and thus plays a very important role in fiber formation process.

The orientation in polymeric system is reflected in marked anisotropy, which provides useful information about the orientation in fiber structure. Here, the degree of orientation is measured through the method of sonic velocity on the principle of spread-

ing anisotropy of sonic wave due to the orientation of macromolecules, which provides information about the combined orientation of amorphous and crystalline regions. The velocity of sonic wave is the largest when sonic wave spreads in the direction of fiber axial in ideal orientation condition. The velocity of sonic wave is the least when sonic wave spreads in the vertical direction of fiber axial. So the value of velocity of sonic wave in fiber increases with increasing orientation degree. Modulus of fiber is an important parameter to represent the mechanical properties of fiber. Sonic modulus is in a close relation with the degree of orientation.

According to the theory of Moseley et al.,<sup>20,21</sup>

$$f_s = 1 - C_u^2 - C^2$$

$$E = \rho C^2$$

where,  $f_s$  is the degree of orientation,  $C_u$  is the sonic velocity of an unoriented sample,  $C$  is the sonic velocity of the test filament,  $E$  is sonic modulus, and  $\rho$  is the density of the test filament.

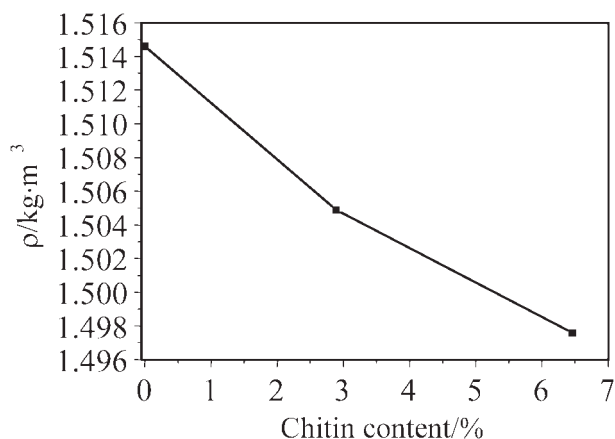
The degree of orientation and modulus of the filaments decreases with increasing chitin content, and the decreasing rate decreases with increasing chitin content (Tables III and IV). Chitin addition [2.89% (w/w)] leads to an apparent decrease. The dry and wet intensity decreases with increasing chitin content in the experimental scope. The addition of small amount of chitin interferes with the orientation of cellulose macromolecules, which is in close relevance with the orientation of macromolecules. So, the mechanical properties of blend filaments decrease with increasing chitin content. But the mechanical properties of blend filaments still reach the national criteria and fit the need for further process. The dry intensity of the blend filaments containing 2.89% and 6.46% (w/w) chitin content is 1.98 and 1.92 cN × dtex<sup>-1</sup>, respectively, which is much higher than that of Crabyon, i.e., 0.7 cN × dtex<sup>-1</sup>.<sup>15</sup> Therefore, the cellulose/chitin filament we prepared has improved intensity.

### The measurement of density

Density is an important physical parameter for fiber, which is a characterization of fiber inner structure.

**TABLE IV**  
Physical Properties of Filaments

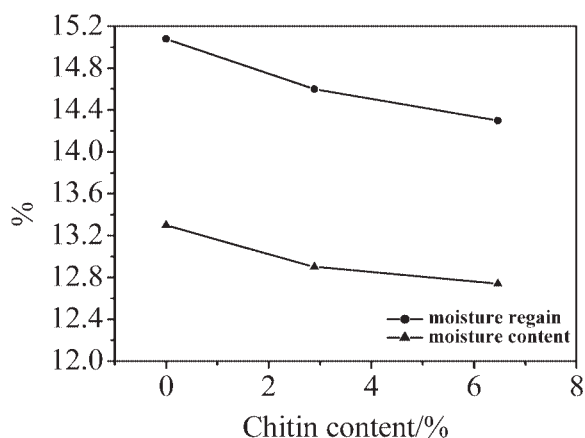
Sample ID	Chitin content (%)	dry intensity (cN × dtex <sup>-1</sup> )	wet intensity, (cN × dtex <sup>-1</sup> )	Ratio of wet to dry intensity (%)	Dry elongation (%)	Uniformity of dying (%)	Oil content (%)
1	0	2.24 ± 0.2	1.13 ± 0.2	50.5 ± 5	19.2 ± 2	3.5	0.58
2	2.89	1.98 ± 0.5	1.02 ± 0.4	51.5 ± 6	16.9 ± 1	3.5	0.58
3	6.46	1.92 ± 0.3	0.94 ± 0.1	49.0 ± 2	15.4 ± 5	3.5	0.62



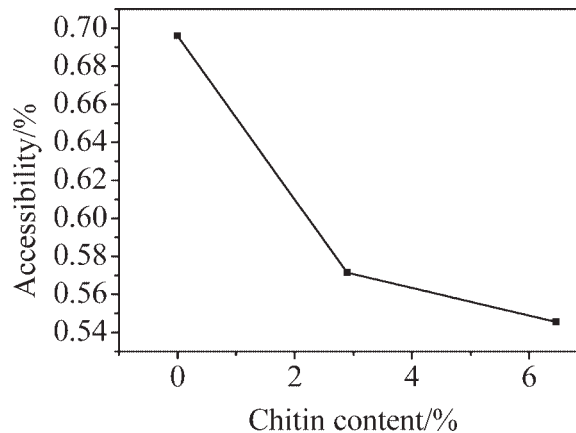
**Figure 5** Dependence of filament density on chitin content.

We can know not only the fiber's basic physical properties but also some supermolecular structure according to the measurement of fiber density. Therefore, the research on fiber density is of great theoretical and practical meaning.

As seen in Figure 5, the density of blend filament decreases with increasing chitin content, which is in accordance with the changing tendency of degree of crystallinity. The addition of small amount of chitin interfere the extent of impaction among cellulose macromolecules when it regenerate from the coagulation bath and the decreasing extent of impaction among cellulose macromolecules interferes the crystallization of cellulose macromolecules, which leads to a decrease of the degrees of crystallinity. Since cellulose consists of crystal phase and amorphous phase and the density of crystal phase is higher than that of amorphous phase, the density of the blend filaments is lower than that of pure cellulose filament.



**Figure 6** Dependence of equilibrium regain rate and rate of water content on chitin content.



**Figure 7** Dependence of accessibility on chitin content.

**Hygroscopicity and accessibility**

Hygroscopicity is the ability of fiber to absorb steam, which characterizes the comfort of woven made from fibers in the form of regain rate and rate of water content. Regain rate is calculated through the mass ratio of water content in the fiber to dry fiber mass, whereas rate of water content is mass ratio of water content in the fiber to wet fiber mass. Equilibrium regain rate is the regain rate of fiber at certain temperature and relative humidity, which is normally 20°C and 65%, respectively (Fig. 6). The equilibrium regain rate and rate of water content decrease with increasing chitin content and the decreasing extent is not so much, which shows the blend filaments have good sweat absorbing ability as cellulose fiber (Fig. 7). The accessibility also decreases with increasing chitin content.

As seen from the above results, the blend filaments has got certain physical properties that fit further processing need, the handle and color of the woven material is satisfying. Since the blend filaments and woven prepared do no harm to human body on the basis of acute toxicity test and skin stimulation hyper susceptibility tests, the blend filaments are suggested to be widely used for the preparation of advanced clothes, underwear, and so on. The viscose method we adopted here is a satisfying way to prepare cellulose and chitin blend filaments, which has never been reported before.

**CONCLUSIONS**

1. The SEM photos show that there exist grooves on the surface of filaments, which is becoming coarse with increasing chitin content.
2. X-diffraction curve shows that degree of crystallinity of blend filaments decreases with increasing chitin content, which shows that the addition of chitin deteriorates the crystal structure of cellulose.

3. The modulus, degree of orientation, and dry and wet intensity of blend filaments decrease with increasing chitin content. The addition of chitin interferes with the orientation of cellulose macromolecules.
4. The density of blend filament decreases with increasing chitin content, which is in accordance with the changing tendency of crystallinity degree on chitin content.
5. The equilibrium-regain rate decreases with increasing chitin content, which shows good sweat absorbing ability as pure cellulose fiber. The accessibility shows the same tendency.

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