Preparation and Properties of Cellulose/Chitin Blend Fiber

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ABSTRACT: The blend solution of cellulose xanthate with chitin xanthate has excellent filtering property as an ordinary cellulose viscose. The SEM photos show that the fiber surface becomes coarse with increasing chitin content. The X-ray diffraction shows that the addition of chitin interferes with the crystallization of cellulose. The dry and wet strength and density of blend fibers decrease with increasing chitin content. The hygroscopicity of the blend staples decreases with increasing chitin content, and there exists a minimum at 3.85% chitin mass percent, while the accessibility shows the same tendency. The fiber prepared has effective bacteriostatic effects on *Staphylococcus aureus*, *Escherchia coli*, etc., and the bacteriostastic rate increases with increasing chitin content. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3430–3436, 2003

Key words: fibers; blending; polysaccharides

INTRODUCTION

Chitin is the most abundant polysaccharide sources found in nature except cellulose, whose annual bioproduction amount exceeds 10,000 million tons. Chitin is an excellent polymer abstracted from shrimp, crab, and some micro-organisms, and is biocompatible, biodegradable, antibacteria, and nonnoxious. It can be degraded by bacteriolysis enzymes in the body and absorbed absolutely, and the body has little immune antigen to it.[1] Fiber made from chitin has not only good mechanical property but also excellent biological activity, and thus has wide use in biology, medical treatment, sanitation, etc.

Cellulose fabric is not only moisture absorbent, comfortable, and cheap, but handling of viscose fabrics is excellent. But viscose fiber does not have the function of being bacteriostatic; if bacteria exists on the surface of the viscose fabric and the environment is feasible, the fabric is an identical environment for bacteria to breed. When bacteria makes contact with secretions of the body, an odorous smell is emitted, and even a series of illnesses. Because chitin fiber has the function of bacteriostatic, inflammation diminishing, odor resistance, and itch restraining, the blend of cellulose and chitin seems to be of great attraction to us. But chitin cannot dissolve in ordinary solution, which limits its wide use. Hirano et al.[2–5] have discussed N-acylchitosan xanthate and some xanthate ester derivatives deeply, and have prepared fibers from N-acetylchitosan xanthate, its derivatives, or their blend with cellulose xanthate. But they mainly use N-acetylchitosan (a regenerated chitin) prepared by chemical N-acetylation of chitosan as material because the intramolecular and intermolecular hydrogen bonds of N-acetylchitosan are weaker than that of a natural chitin, resulting in easy solubilization into 14% aqueous sodium hydroxide solution. According to some researchers'[6–9] work, chitin viscose can be obtained by xanthating alkali chitin. Noguchi et al.[10] prepared a chitin–cellulose blend fiber by spinning an aqueous alkali solution of sodium cellulose xanthate blend with sodium chitin xanthate into a coagulation bath. The cellulose–chitin blend fiber has been commercialized, with the commercial name of "Crabyon" by Omikenshi Company Ltd. in Japan, who have applied patents.[11,12]

As the production of cellulose xanthate has had a history over one century, we want to develop the advantages of the two components through the blending of cellulose and chitin xanthate to obtain a wide use in clothes, underwear, and so on, and thus provide experimental data for later industrial production. The following is a description of the method adopted for fiber preparation and the properties of the fibers prepared.

EXPERIMENTAL

Materials and reagents

The cellulose sample employed was cotton linters with a degree of polymerization 700, heated at 105°C

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TABLE I
The Statistical Result of Disassembling Frequency of Filtering Machine

Sequence number	Spinning solution	Disassembling frequency of filtering machine
1	ordinary cellulose xanthate solution	5–6 batch
2	blend solution	5–6 batch

until a constant weight is reached and kept over fresh phosphorus pentoxide in a desiccator before use. The chitin sample was made from shrimp with a viscosity average molecular mass of 171,000 and 0.3% ash content. The chitin sample was ground into powders, which could pass a #60 mesh. Reagent-grade carbon disulfide, sodium hydroxide, sulfuric acid, sodium sulfate, zinc sulfate, and tetrachloromethane were supplied by Shanghai Feida Chemical Co., China.

Preparation of blend solutions

The cellulose viscose was prepared as follows: the mixture of cellulose, a certain amount of 280 g/L sodium hydroxide solution was mechanically stirred for about half an hour, then a certain amount of carbon disulfide was put into the mixture, and stirred continually until a transparent solution was obtained. The chitin viscose was obtained according to ref. 9: a certain amount of chitin powder was mixed up with 43% (wt) sodium hydroxide solution in a flask at room temperature for 300 min, and the ratio of chitin mass to the volume of sodium hydroxide solution was 1 : 20. Then the sodium hydroxide solution was removed through a vacuum supply; the weight of product obtained was three to six times the weight of the original chitin powder, which was mixed with chopped ice under violent 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 of chitin xanthate was obtained. After both were filtered, cellulose xanthate solution was blended with chitin xanthate solution according to a different mass ratio. The homogeneous orange-like solutions were obtained, and kept at 1–4°C in a fridge until used. The blend solutions had excellent filtering properties like the ordinary cellulose xanthate solution. Table I gave the statistical result of disassembling frequency of a filtering machine, which showed that the frequency did not change much, and meant that the addition of chitin did not greatly vary the filtering properties of the solutions.

The former rheological work has provided theoretical data for further fiber spinning. The blend fiber was prepared through the ordinary viscose routine, adopting the wet spinning method.

Spinning condition

The spinning routine is described as followed:

$$\text{Blend solution} \rightarrow \text{IF filtration} \rightarrow \text{IIF filtration} \rightarrow \text{deaceration} \rightarrow \text{wet spinning} \rightarrow \text{finishing}$$
$$\uparrow$$
$$\text{coagulation bath}$$

Coagulation bath had the following constitution, i.e., the concentration of sulfuric acid was 110–130 g/L, the concentration of zinc sulfate was 10–25 g/L, and the concentration of sodium sulfate was 200–380 g/L. The bath temperature was 40–55°C.

The diameter of the spinnert adopted was 0.06 mm. The spinning velocity was 45 m/min.

Spinneret draw ratio was 40–50%, first draw ratio was 25–40%, and the plasticizing stretch ratio was 12–20%.

Finishing procedure

The finishing procedure includeed desulfuration, washing by water, washing by acid, bleach, oiling, and so on. The washing temperature was 60–70°C. The bath concentration for desulfation was 3–5 g/L, and the temperature was 80–90°C. The concentration of the hydrogen peroxide for bleach was 1–3 g/L at room temperature. The concentration of the oil bath was 3–7 g/L, operated at room temperature.

Equipment and testing conditions

X-ray diffraction patterns were recorded on a flat-plate camera using nickel-filtered CuKα radiation from a Philips generator operated at 40 kV and 20 mA.

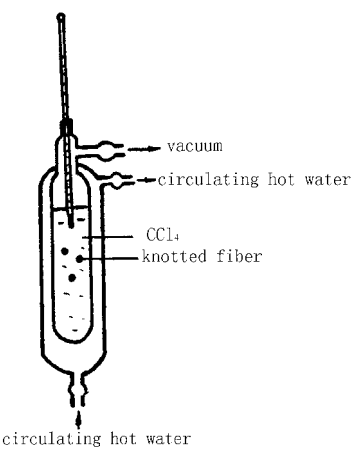

Figure 1 Diagramof apparatus for fiber density measurement.

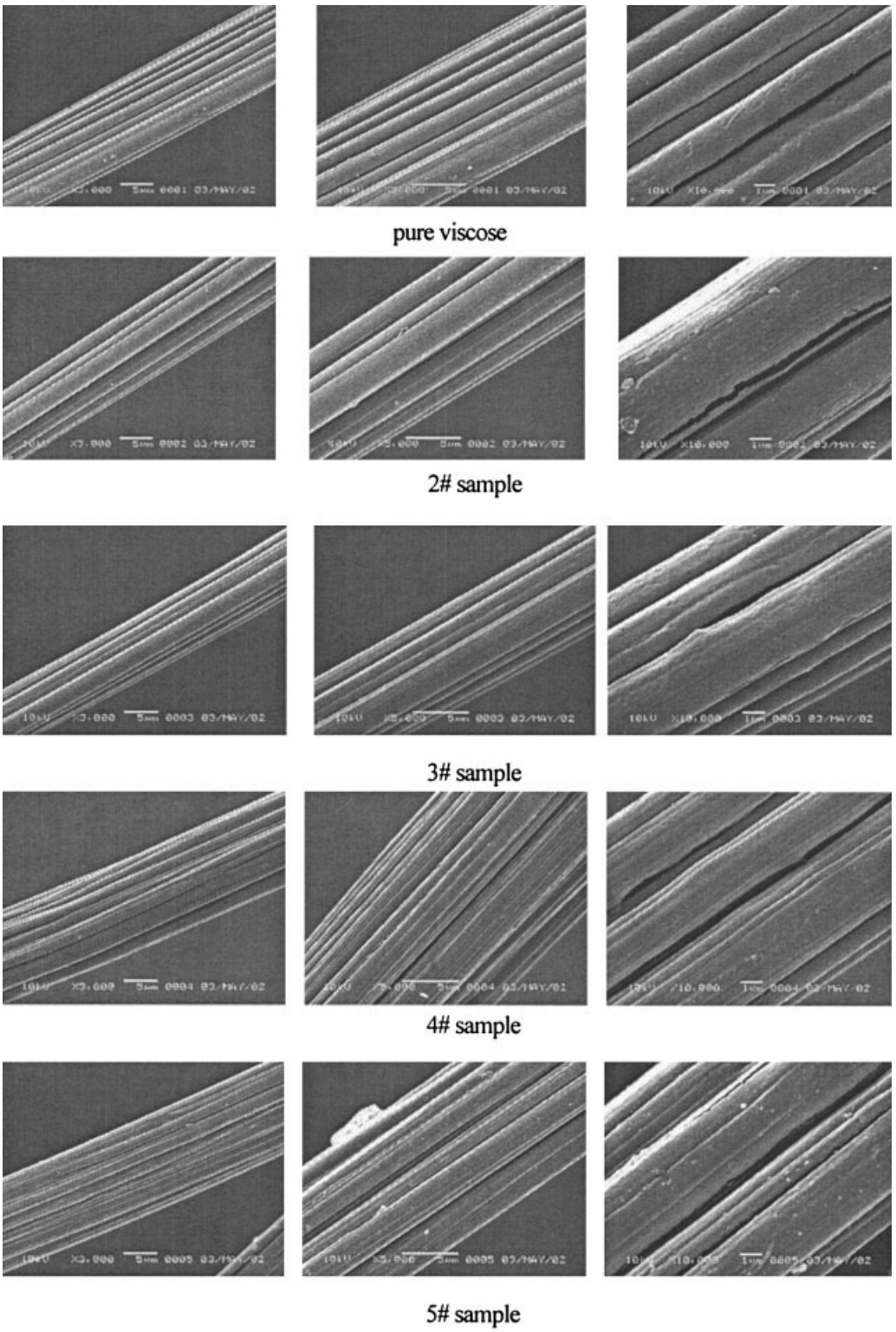

Figure 2 SEM pictures of the surface of the blend staple.

A JOEL JSM-5000LV scanning electron microscope was used to study the surface morphology of the fibers. The fibers were deoiled by ether at 35°C, then coated with gold for testing.

Measurement of mechanical properties

Tensile strength was measured on a testing tensile machine provided by Chang-Zhou Textile Machine

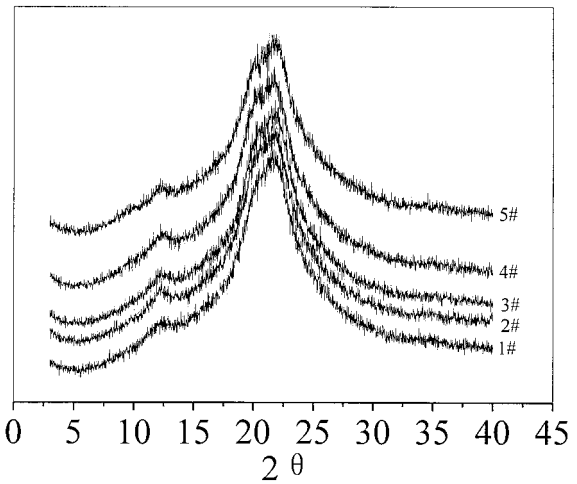

Figure 3 The X–ray diffraction curves of blend fibers with different blend ratios.

Co. The tensile stress δ_b and elongation ratio at break ϵ_b was calculated as follows: (1) $\delta_b = F/A$, where F is the tensile force that the machine shows, and A is the cross-section area of fiber; (2) $\epsilon_b = (L-L_0)/L_0 \times 100\%$, where L_0 is the original length of fiber and L is the length of the fiber at break.

The density of the fiber was measured as follows: the knotted fibers were kept in the centrifugal test tube where the dipping fluid was hot tetrachloromethane to ensure that the knotted fibers sank in the tube, and kept running for 5 min at 2000 rad/min to remove the air in the knotted fiber. Then the fibers were moved into the apparatus shown in Figure 1, where the dipping solvent was tetrachloromethane, kept at 50°C, and elevated little by little until knotted fibers were suspended in the middle of the apparatus when the temperature of the tetrachloromethane was recorded accurately. The density of tetrachloromethane at this temperature was just the density of the fiber.[13,14]

Moisture regain of staples

The fibers with different blend ratios were kept in a desiccator, and the room temperature was kept at 20°C, where 35% (wt %) sulfuric acid was kept at the bottom, which kept the relative humidity in the desiccator at 65%. After being kept for 48 h until the fibers reached a constant weight, the fibers were weighed (w_1), then the fibers were heated at 102°C until constant weight (w_2), The regain rate W was calculated as follows:

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

The rate of water content $W \cdot$ was calculated as follows:

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

The measurement of fiber accessibility $= W/W_{\text{absorbent cotton}} \times 0.44$. (The room temperature is 20°C, the relative humidity in the desiccatoris 65%, the regain rate and accessibility of absorbent cotton is 6.81% and 0.44,[14] relatively.)

Bacteriostatic test

The testing condition is that the fiber was surged at37°C for 120 min, and the testing procedure is according to the Pasteurization Technical Standard issued by the Department of Health, P.R. China.

Bacteriostastic rate was calculated as follows: bacteriostastic rate $= (N_2-N_1)/N_2 \times 100\%$, where N_2 means the colony number where the contrast sample is added, and N_1 means the colony number where the trial sample was added.

RESULTS AND DISSCUSSIONS

SEM photos

The SEM photos of fibers in Figure 2 show that there exist grooves on the surface of all fibers, which widens with increasing chitin content. For samples #4 and #5, a larger groove is divided into several smaller grooves. The surface of the fiber becomes coarse with increasing chitin content.

We also observe that there exists more defection on the surface of the pure viscose fiber in the measurement process, which is improved in the blend fibers. There is still much dust on the surface of the pure viscose fiber after being treated by ether, while the surfaces of the blend fibers are clean, which shows that the blend fibers are easily cleaned and may have an excellent application in clothing.

X-ray diffraction

The X-ray diffraction curves of fibers are shown in Figure 3. The diffraction apex of pure cellulose fiber appears at 2θ 12.3°, 20.3°, 21.6°, which is in accordance with the reference. Only blend fiber #5 has a diffraction apex at $2\theta = 9.6°$. The diffraction apex at 2θ 19.8° increases with increasing chitin content, the diffraction

TABLE II
Degree of Crystallinity on Chitin Content

Sample	Chitin content (%)	Degree of crystallinity
1#	0	0.505
2#	0.92	0.502
3#	3.54	0.462
4#	6.46	0.389
5#	8.62	0.388

TABLE III
The Physical Property of Staples with 3.54% Chitin Content

Sample	Chitin content (%)	Dry strength ($cN \cdot dtex^{-1}$)	Dry elongation (%)	Wet strength ($cN \cdot dtex^{-1}$)	Wet elongation (%)
1#	0	2.43	18.0	1.75	29.1
2#	0.92	2.38	17.0	1.70	28.8
3#	3.54	2.32	19.5	1.69	31.6
4#	6.46	2.32	18.8	1.65	28.8
5#	8.62	2.30	19.2	1.68	29.5

apex of cellulose at 2θ 20.3° increases with increasing chitin content, which shows that the crystal structure of cellulose changes after blending; the addition of chitin destroys the crystal structure of cellulose. As seen in Table II, the degree of crystallinity of fibers decreases with increasing chitin content, which shows that the addition of chitin destroys the crystallinity of cellulose.

Mechanical property

The mechanical property of the blend staples prepared is shown in Table III. The dry and wet strength decreases with increasing chitin content in the experimental scope, but the extent of decrease is very low. The dry strength, wet strength, dry and wet elongation of all blend fibers fit the National criterion, and they are an eligible product for further processing.

Even a small additional amount of chitin can interfere with the orientation of cellulose macromolecules, and the mechanical property of the fiber is relevant close to the orientation of macromolecules. So the mechanical property of the blend staple decreases with chitin content.

The measurement of density

Figure 4 shows the dependence of tetrachloromethane density on its absolute temperature, which shows a linear tendency.[15] So tetrachloromethane is chosen as a dipping solvent here. As seen in Figure 5, the density of the blend fiber decreases with increasing chitin content, which is in accordance with the changing tendency of crystallinity on the chitin content. The decreasing rate relaxes at a small amount (chitin content $<1.54\%$) or a higher amount (chitin content $>6.15\%$).

Hygroscopicity

Hygroscopicity is the ability of the fiber to absorb steam, which characterizes the comfort of woven made from fibers. Regain rate is calculated through the weight ratio of the water content in the fiber to dry fiber; while the rate of the water content is the weight ratio of the water content in the fiber to the wet fiber. Equilibrium regain rate is the regain rate of fiber in the air with a certain temperature and relative humidity, which are normally 20°C and 65%, relatively.

Figure 6 shows that the regain rate and rate of water content decreases with increasing chitin content, and the extent of decrease is not much, which shows that the blend fibers have as good a sweat-absorbing ability as the cellulose fiber. There exists a minimum at 3.85% chitin content in the invested blend ratio.

The accessibility shows the same tendency as regain rate and rate of water content, as shown in Figure 7.

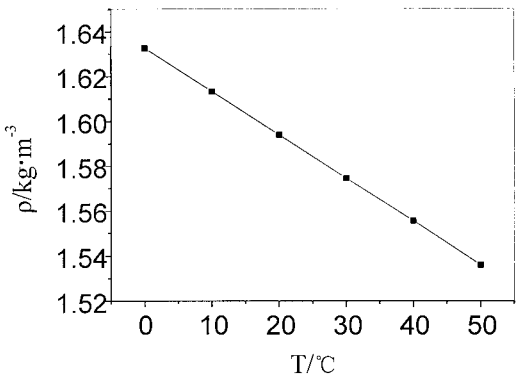

Figure 4 The dependence of density of the tetrachloromethaneon temperature.

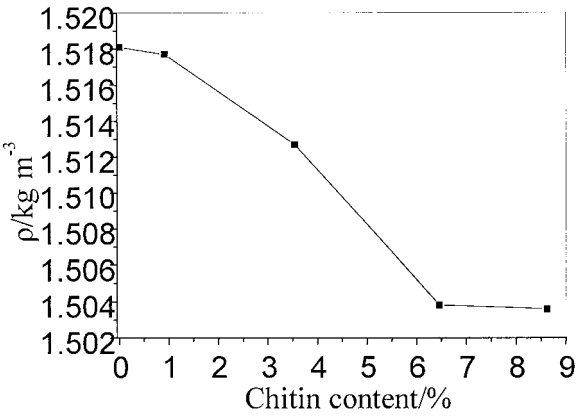

Figure 5 The dependence of staple density on the blend ratio.

TABLE IV
The Bacteriostastic Results of Blend Fibers

	Staphylococcus Aureus			*Corinebacterium Michiganence*			*Escherchia coli*		
	Colony number $\times 10^2$ cfu/mL			Colony number $\times 10^2$ cfu/mL			Colony number $\times 10^2$ cfu/mL		
Sample	Before surging	After surging	Bacteriostastic rate (%)	Before surging	After surging	Bacteriostastic rate (%)	Before surging	After surging	Bacteriostastic rate (%)
1#	116	111	4.31	110	107	2.73	121	108	10.74
3#	88	37	57.95	93	45	51.61	107	56	47.66
4#	86	30	65.12	94	28	70.21	104	46	55.76

TABLE V
The Bacteriostatic Results of Fabric Prepared

Bacterium kind	Bacteriostatic rate of the contrast (%)	Bacteriostatic rate of the fabric (%)	Balance of bacteriostatic rate (%)
Staphylococcus aureus (ATCC6538)	1.09	60.23	62.18
Escherchia coli (8099)	8.77	58.34	47.04
Corinebaterium michiganence (ATCC10231)	1.63	47.32	46.33

Bacteriostatic results

The product is considered as eligible if the bacteriostatic effect is over 26%, according to the National Standard. The bacteriostatic results provided by the China Defending Iatrical Academy of Science are shown in Table IV. The testing method is according to GB15981-1995 I Pasteurization and Supervision Technical Standard of Pasteurization Product. Table IV shows that the bacteriostatic effect is over 26%. So the blend fibers prepared have effective bacteriostatic results to *Staphylococcus aureus*, *Escherchia coli*, etc.

To test the bacteriostatic effect of fiber when it is dyed and processed, a certain amount of woven made from blend fiber is also prepared and tested. Table V shows that the woven made from the blend fibers still has bacteriostatic results after processing and several times of machine washing. Fibric made of blend fiber with 3.54% chitin content is prepared to test its bacteriostatic effect. The fibric has effective bacteriostatic results on *Staphylococcus aureus*, *Escherchia coli* and *Corinebaterium michiganence*, which are all higher than 26%. So the blend fibers and the woven made from them have an effective bacteriostatic effect on *Staphylococcus aureus*, *Escherchia coli*, and *Corinebaterium michiganence*, and they are eligible bacteriostatic product.

Because the blend fibers and woven prepared from cellulose/chitin blend fibers do no harm the human body on the basis of an acute toxicity test and skin stimulation hypersusceptibility tests, the blend fibers are suggested to be used in many fields, i.e., the preparation of underwear, sanitation things for women, bacteriostatic diminished inflammation in socks, work

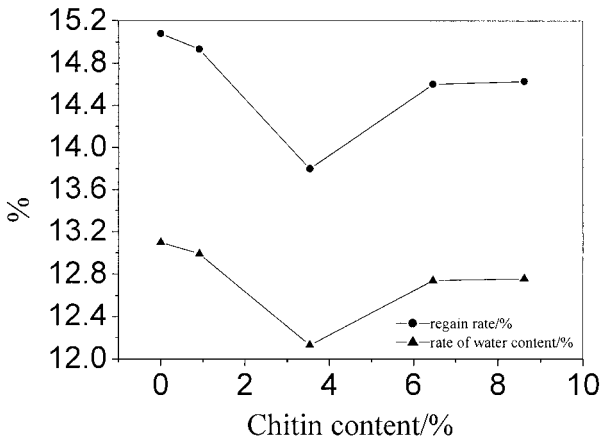

Figure 6 The dependence of regain rate and rate of water content on the blend ratio (relative humidity is 65% and the surrounding temperature is 20°C).

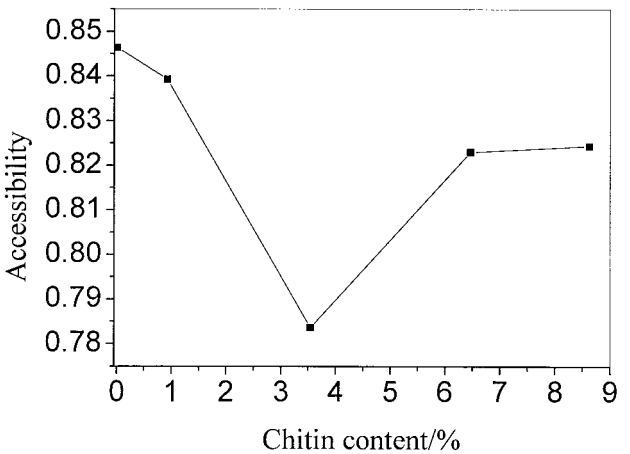

Figure 7 The dependence of accessibility of the staple on the blend ratio.

cloth used in food industry, medicine industry, hospital, and infant's school, underwear, and cloth for people field working, or soldiers.

CONCLUSIONS

1. The blend solution of cellulose xanthate with chitin xanthate has an excellent filtering property as ordinary cellulose viscose; the addition of chitin xanthate does not change the filtering property, and the ordinary equipment for the preparation of cellulose viscose fiber can also be used for the invested blend fibers.
2. The SEM photos show that there exist grooves on the surface of fibers, which is widened with increasing chitin content. The surface of the fiber becomes coarse with increasing chitin content.
3. The mechanical property decreases with increasing chitin content in the experimental scope.
4. The density of the blend fiber decreases with increasing chitin content. The decreasing rate relaxes at a small amount (chitin content $<1.54\%$) or higher amount (chitin content $>6.15\%$).
5. The regain rate decreases with increasing chitin content, and there exists a minimum at 3.85% chitin content, which shows good sweat-absorbing ability. The accessibility shows the same tendency.
6. The fiber prepared and woven made from the blend fibers has an effective bacteriostatic result to *Staphylococcus aureus*, *Escherchia coli*, etc.

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