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Antibacterial Properties of Cotton Fabrics Treated with Chitosan

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ABSTRACT

Chitosan is used to treat cotton fabrics to impart antibacterial activities. The effect of concentration, molecular weight, and degree of deacetylation of chitosan on antibacterial activity to *Escherichia coli* and the Hay bacillus is investigated. Bacteria reduction is evaluated using the modified Quinn method. *Escherichia coli* is effectively inhibited at 0.3 g/l chitosan solution and the Hay bacillus at 0.5 g/l. To bond chitosan to fabric chemically, glutaric dialdehyde is chosen as the crosslinking agent. Cotton fabrics treated with glutaric dialdehyde and chitosan show a good ability to inhibit bacteria reproduction. IR spectra of the surface of cotton fabrics and SEM pictures of fibers are presented.

Chitosan applied to textiles has been widely studied for effects such as shrink resistance, improved dye uptake, and as auxiliary or anti-static agents, etc., because of the low toxicity and good biocompatibility of this natural polymer. There are two important structural parameters, degree of deacetylation (DD) and molecular weight (MW). Its performance in physics and chemistry is determined by the influence of these two parameters on such things as solubility, enrichment ions, the mechanics of the chitosan membrane, flocculation, etc. In acidic solvents, the NH_2 group in chitosan becomes a quaternary amino group and allows the chitosan to inhibit the growth of many bacteria, including gram-negative and gram-positive ones. Shin studied the effect on antibacterial activity of the molecular weight of various chitosans with similar degrees of deacetylation [6]. Lee found that cotton fabrics treated with chitosan and fluoropolymers exhibit durable antimicrobial activity after repeated launderings [4]. Several other studies confirmed [1, 3, 5, 7] the effect of chitosan as an antibacterial finishing agent.

In this study, we use two series of chitosans, one with the same DD but different MW, and the other with the same MW but different DD. We investigate the antibacterial behaviors of chitosan to *Escherichia coli* and the Hay bacillus. We then determine the best concentration of chitosan for effective antibacterial activity for each. In order to enhance chitosan bonding to cotton fabrics, we use glutaric dialdehyde as the crosslinking agent.

Experimental

Cotton fabrics were pretreated by singeing, destarching, scouring, and bleaching. Chitosan was modified to obtain two series, one with different molecular weights of 9210, 58,200, 90,800, 113,600, and 158,600 but the same DD of 69%, and the other with different DD of 69, 74.82, 84.19 and 92.48% but the same MW of 500,000.

Chitosans were dissolved in an acetic acid solution (mass concentration of 1%). Cotton fabrics were padded twice with chitosan solutions of various concentrations to a wet pickup of 110%. The padded fabrics were then dried at 80°C for 5 minutes and cured at 140°C for 3 minutes.

For the crosslinking, a glutaric dialdehyde solution was mixed with the chitosan solution at a 1:1 ratio of CHO groups in glutaric dialdehyde to NH_2 of chitosan. The chitosan and glutaric dialdehyde reacted with each other for an hour, then the fabrics were padded in this solution to a wet pick-up of 110%. The padded fabrics were dried at 80°C for 5 minutes and cured at 140°C for 3 minutes.

Bacteria reduction was evaluated according to the modified Quinn method [2]:

$$R(\%) = \frac{C_0 - C}{C_0} \times 100\% \quad ,$$

where R = rate reduction, C_0 = number of bacteria colonies on the cotton fabrics treated without chitosan as control samples, and C = number of bacteria colonies on the cotton fabrics treated with chitosan.

Results and Discussion

EFFECT OF CHITOSAN CONCENTRATION ON ANTIBACTERIAL ACTIVITY

Figure 1 shows that the reduction rate depends on the strain of bacteria. The growth of *Escherichia coli* is effectively inhibited at 0.3 g/l chitosan solution and the Hay bacillus at 0.5 g/l. With increased concentration, the

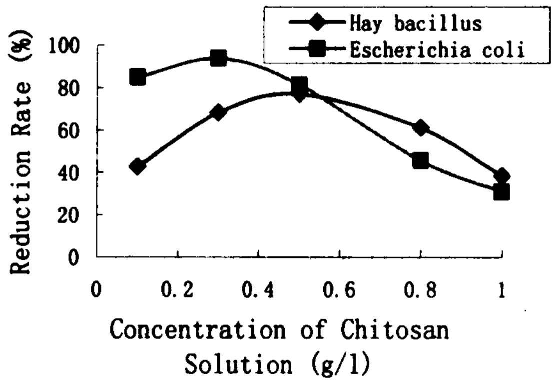

FIGURE 1. Change of antibacterial activity with concentration of chitosan solution.

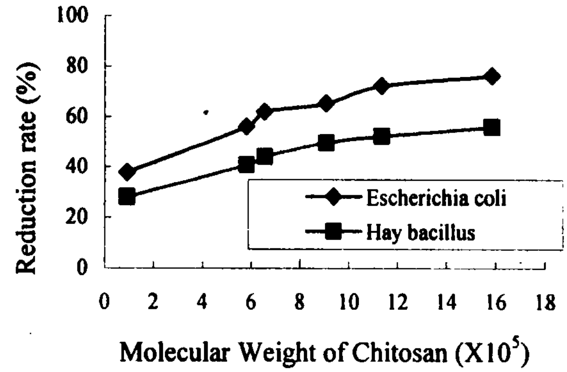

FIGURE 2. Change of antibacterial activity with MW of chitosan (*Escherichia coli* 0.3 g/l solution, Hay bacillus 0.5 g/l solution).

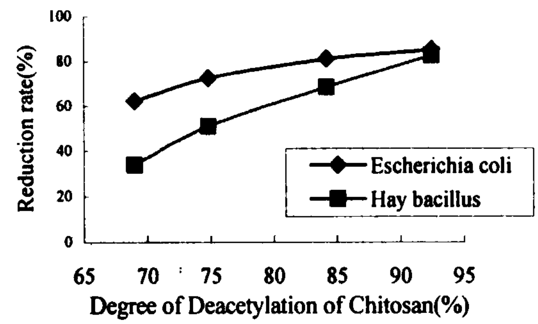

FIGURE 3. Effect of degree of deacetylation on antibacterial activity (*Escherichia coli* 0.3 g/l solution, Hay bacillus 0.5 g/l solution).

reduction is first enhanced, then it weakens after the highest value. There are two proposed mechanisms of antibacterial activity by chitosan. In one mechanism, the polycationic nature of chitosan interferes with the bacterial metabolism by stacking at the cell surface [2]. The other mechanism is the binding of chitosan with DNA to inhibit mRNA synthesis. In the latter mechanism, chitosan must be hydrolyzed to a molecular weight less than 5000, which can easily penetrate the cells [8]. In our research, the molecular weight of chitosan is higher than 5000, so the former mechanism should be considered to be closer to the real situation. When the chitosan concentration is small, its viscosity is low. When the concentration reaches a higher value, its viscosity becomes larger, and chitosan that would ordinarily be absorbed by the cotton fabrics will barely penetrate or just stay on the surface. Thus, the amount of quaternary-amino groups will decrease when the concentration of the chitosan solution reaches a higher level, and the reduction also decreases.

EFFECT OF MW ON ANTIBACTERIAL ACTIVITY

Figure 2 shows that with increasing MW, the reduction rate increases proportionally. When the MW increases from 9210 to 158,600, the reduction rate of *Escherichia coli* increases from 37% to 76% and the Hay bacillus from 28% to 56%. Chitosan and cellulose have a similar chemical structure. Therefore, with the accretion of molecules, the Van Der Waals force between chitosan and cellulose molecules becomes stronger. As a result, the increased chitosan absorbed on the fabrics will reduce the rate of bacteria increase.

EFFECT OF DD OF CHITOSAN ON ANTIBACTERIAL ACTIVITY

Figure 3 shows that the reduction rate of *Escherichia coli* increases from 62.14% to 84.98% with DD from 69.10% to 92.52%, and that of the Hay bacillus from 33.96% to 82.53%. It is obvious that the DD of chitosan has affected the reduction rate, especially for the Hay bacillus. The number of quaternary-amino groups in high DD would be greater than that of low DD, so the probability that a quaternary-amino group meets the bioplasm of bacteria would increase, resulting in a larger reduction rate.

EFFECT OF CROSSLINKING BY GLUTARIC DIALDEHYDE ON ANTIBACTERIAL ACTIVITY

Table I shows that crosslinking by glutaric dialdehyde enhances the reduction of bacteria. With the glutaric dialdehyde treatment, the number of *Escherichia coli* on fabrics is only 17, whereas the number without glutaric dialdehyde is 32. The situation is similar for the Hay bacillus, being 23 and 28, respectively. Comparing the colony numbers before washing and after washing, crosslinking by glutaric dialdehyde improves the fastness of antibacterial activity to washing. Glutaric dialdehyde is a binary aldehyde compound: no doubt one aldehyde group reacts with chitosan and the other with cellulose.

TABLE I. Effect of glutaric dialdehyde on antibacterial activity.

	1#[a]		2#[b]	
	Before washing	After washing	Before washing	After washing
Escherichia coli	32	64	17	27
Hay bacillus	28	92	23	37

[a] 1#: treated only with chitosan, no glutaric dialdehyde. [b] 2#: treated with glutaric dialdehyde and chitosan (DD 92.48%, MW 500,000) 0.5 g/L

Figure 4 shows the IR spectra of cotton fabrics treated by glutaric dialdehyde—with (2#) and without (1#)—reflected on the surface. The difference between 1# and 2# is not large. The bond in —CHO of glutaric dialdehyde is located at 1733.15 cm^{-1}. From the intensity of the —C=N— band at 1682.57 cm^{-1}, the reaction between glutaric dialdehyde and chitosan can be directly proved. Contrasted to 1#, the intensity of 2# of the amide bands at 1652.07 and 1645.12 cm^{-1} increases, indicating that the amount of chitosan bonded on cotton fabrics increases. The intensity at 1557.19 and 1505.09 cm^{-1} reveals the quaternary-amino band.

Figure 5 shows the SEM pictures of the fiber surface. The surface of 2# cotton has a few white particles compared with 1#. The white particles might be the chitosan absorbed on the surface of fiber. The 3# fiber surface is very rough, indicating that the reaction has taken place on the surface.

Conclusions

The concentration, MW, and DD of chitosan and the bacterial strain are the main factors that affect the antibacterial behavior of chitosan. *Escherichia coli* is effectively inhibited at 0.3 g/l of chitosan solution, whereas the Hay bacillus is 0.5 g/l. With increased MW and DD, the reduction rate of bacteria will increase.

As a crosslinking agent, glutaric dialdehyde enhances chitosan uptake on the surface of cotton fabrics, with good durability of antibacterial properties to washing.

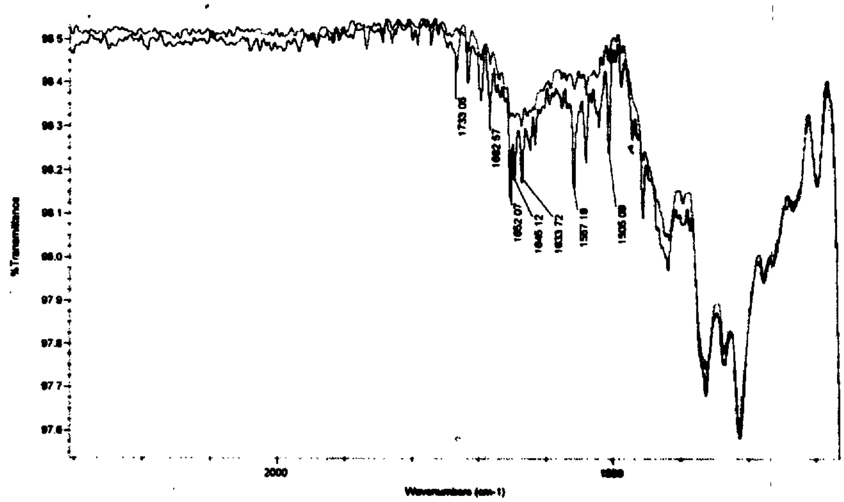

FIGURE 4. IR spectra of cotton fabric. The top is 1# treated with chitosan, the bottom is 2# treated with glutaric dialdehyde and chitosan (DD 92.48%, MW 500,000) 0.5 g/l.

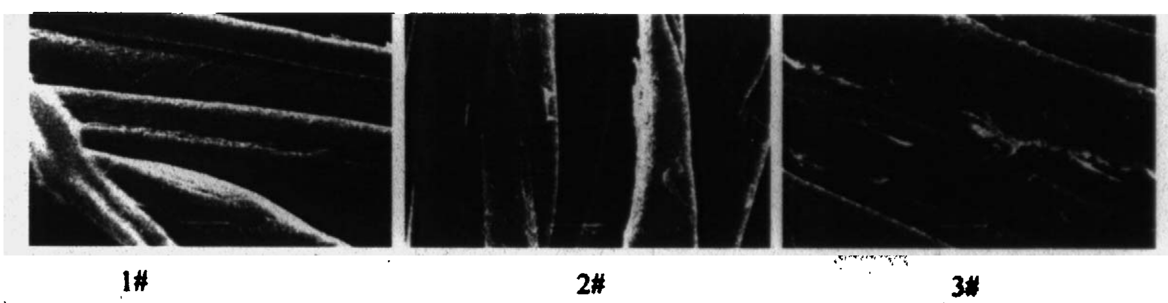

FIGURE 5. SEM pictures (×2000 times): 1# control, 2# treated only with chitosan, 3# treated with glutaric dialdehyde and chitosan, chitosan (DD 92.48%, MW 500,000) 0.5 g/l.

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