

# The Chelating Properties of Chitosan Fibers

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## SYNOPSIS

Chitosan fibers were treated with aqueous solutions of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  for different periods of time to prepare samples containing different levels of metal-ion contents. The effect of metal ions on the tensile properties of chitosan fibers was studied. It was found that after chelation of metal ions the chitosan fibers gained substantial increases in both dry and wet strengths. The metal ions were readily removed from the chitosan fibers by treatment with an aqueous EDTA solution. The effect of the degree of acetylation on the chelating ability of the chitosan fibers was also studied. It was found that after acetylation the chitosan fibers lost the chelating ability due to the conversion of primary amine groups to acetamide groups. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Chitin, 1,4-2-acetamido-2-deoxy- $\beta$ -D-glucan, is the second most abundant natural polymer. Chitosan is the deacetylated product of chitin. Both polymers have attracted much attention in recent years due to their unique properties.<sup>1-3</sup> One of the most important properties of chitin and chitosan is their ability to chelate heavy metal ions.<sup>4</sup> Chitin, chitosan, and their derivatives are now widely used in wastewater treatment where many hazardous heavy metal ions such as Cu(II), Cd(II), Ag(I), Zn(II), Pb(II), Fe(III), and Mn(II) can be removed through chelation.<sup>5-8</sup> In fact, the majority of chitinaceous products are currently consumed in this application. At present, commercial scale waste-water treatment using chitosan is carried out with chitosan dissolved in aqueous acidic solutions. With regard to recycling of chitosan and ease of the treatment, it would be preferable if the treatment is carried out using chitosan fabrics. It is therefore necessary to study the chelating properties of chitosan fibers.

This paper describes the results of a study on the chelating properties of chitosan fibers. It is among the objectives to study the kinetics of the chelation

process and the effect of the metal ions on the tensile properties of the resultant fibers. The effect of the degree of acetylation on the chelating properties of chitosan fibers is also studied.

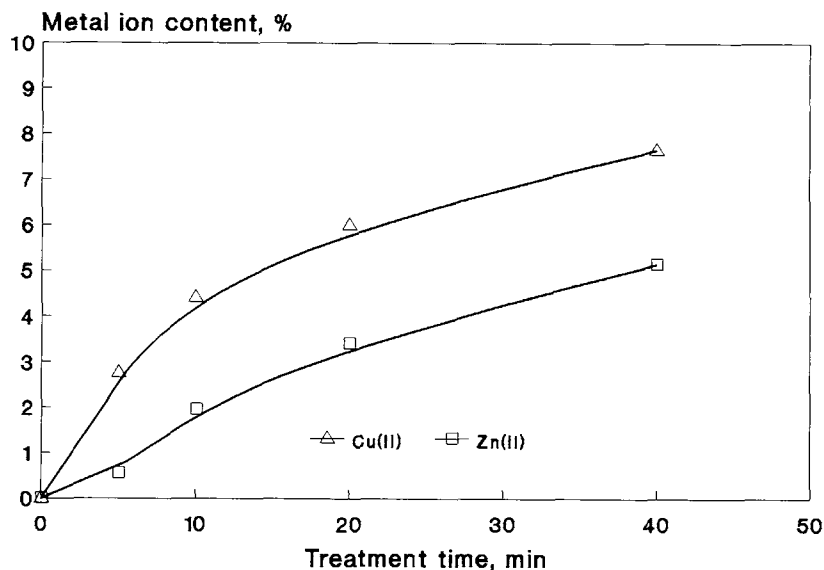
## EXPERIMENTAL

Chitosan fibers were prepared by wet-spinning of a 5% wt/wt chitosan (medium grade, Protan Laboratory) solution in 2% aqueous acetic acid solution, spun into a coagulation bath of 5% aqueous NaOH solution. The extrusion rate was  $13 \text{ m min}^{-1}$  and the spin stretch ratio was 0.4. The as-spun fibers were stretched in a hot water bath ( $80\text{--}85^\circ\text{C}$ ) before they were washed and dried. The yarn of 20 individual filaments (spinneret plate: 20 holes,  $D = 80 \mu\text{m}$ ) has a linear density of 6.45 tex.

The chitosan fibers were treated with aqueous solutions of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$ . Typically, 4 m of chitosan yarn (25.8 mg) were treated with 20 mL of a 0.01 M salt solution for different periods of time. After the treatment, the salt solution was filtered off and the fibers were washed with deionized water before they were dried in vacuum at room temperature.

Acetylation of the chitosan fibers was carried out using acetic anhydride in methanol. One gram of chitosan fibers was treated with 50 mL methanol containing 0, 0.3, 0.6, and 1.2 mL acetic anhydride, respectively, for 2 days at room temperature before

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**Figure 1** Cu(II) and Zn(II) contents of chitosan fibers as a function of the time of treatment with aqueous  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  solutions.

they were treated with 10 mL aqueous NaOH solution (1*N*) at room temperature overnight to remove O-acetylation. The degree of acetylation was calculated from the ratio of nitrogen to carbon contents of the sample. The fibers with various degrees of acetylation were treated with an excessive amount of 0.01*M* aqueous  $\text{CuSO}_4$  solution overnight to study the effect of the degree of acetylation on the chelating ability of chitosan fibers.

Tensile properties were measured on an Instron tensile tester, Model 1122. The gauge length was 20 mm and the extension rate was 20 mm  $\text{min}^{-1}$ . The dry strength was measured at 20°C, 65% RH, and the wet strength was measured with the sample holder immersed in water. Figures quoted are the

average of 10 tests, the standard deviation being generally less than 5%. The Cu(II) and Zn(II) contents were measured by atomic absorption after the samples were digested in sulfuric acid to remove the organic material.

## RESULTS AND DISCUSSION

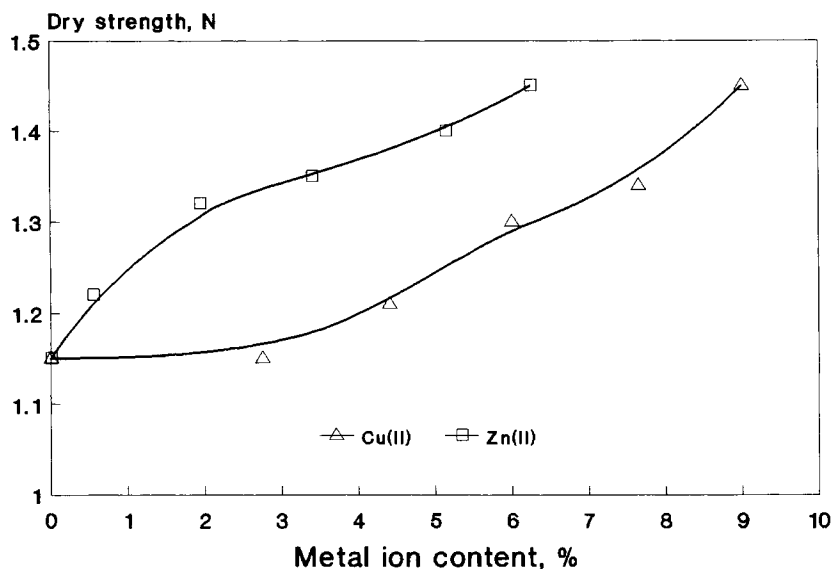
Figure 1 shows the Cu(II) and Zn(II) contents of chitosan fibers as a function of the time of treatment with aqueous  $\text{CuSO}_4$  and  $\text{ZnSO}_4$ . The fibers absorbed 7.6% Cu(II) and 5.2% Zn(II), respectively, after 40 min treatment. The Cu(II) and Zn(II) contents were 9.0% and 6.2%, respectively, after 24 h treat-

**Table I** Effect of Cu(II) Content on Tensile Properties of Chitosan Fibers

	Cu(II) Content (%)					
	0	2.8	4.4	6.0	7.6	9.0
Dry strength (N)	1.15	1.15	1.21	1.30	1.34	1.45
Elongation (%)	6.3	12.8	14.0	15.0	14.6	14.8
Wet strength (N)	0.28	0.42	0.52	0.65	0.72	0.77
Elongation (%)	11.5	16.6	19.4	20.8	22.1	19.8

**Table II** Effect of Zn(II) Content on Tensile Properties of Chitosan Fibers

	Zn(II) Content (%)					
	0	0.6	2.0	3.4	5.2	6.2
Dry strength (N)	1.15	1.22	1.32	1.35	1.40	1.45
Elongation (%)	6.3	11.7	12.4	11.1	11.6	11.5
Wet strength (N)	0.28	0.29	0.31	0.34	0.38	0.46
Elongation (%)	11.5	12.8	14.4	17.8	18.6	16.0



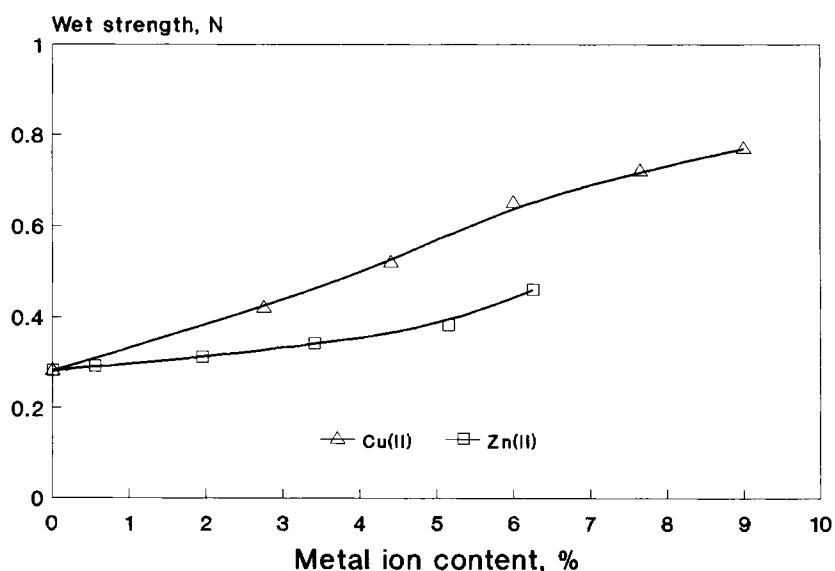
**Figure 2** Effect of Cu(II) and Zn(II) contents on the dry strength of chitosan fibers.

ment. The metal-ion contents after 40 min treatment were equivalent to 84.4 and 83.9% of the metal-ion contents after 24 h treatment for Cu(II) and Zn(II), respectively, which indicated that the chelation of metal ions by chitosan fibers is a fairly rapid process. The molar ratio of primary amine groups in chitosan to Cu(II) ions is approximately 3 after 24 h treatment.

It is interesting to note that after chelation of Cu(II) the chitosan fibers showed a dark blue shade characteristic of Cu(II) ions. It has been reported in the literature that the interaction of the first-row

transition metal ions with chitin and chitosan is accompanied by the appearance of color in almost all instances, namely, red with titanium, orange with metavanadate, green with trivalent chromium, and orange with hexavalent chromium, yellowish brown with divalent iron, yellowish green with trivalent iron, pink with cobalt, and green with nickel.<sup>1</sup>

The effect of Cu(II) and Zn(II) ions on the tensile properties of chitosan fibers are shown in Tables I and II. In both systems, the fibers gained strength after the absorption of metal ions. Both the dry and wet strengths of the chitosan fibers increased with



**Figure 3** Effect of Cu(II) and Zn(II) contents on the wet strength of chitosan fibers.

the increase in metal-ion contents. In the Cu(II) system, the dry strength increased by 25.7% when the fiber absorbed 9.0% Cu(II) ions, whereas with the same fiber, the wet strength was 2.7 times that of the original chitosan fiber. In the Zn(II) system, although the metal-ion contents were generally lower than those in the Cu(II) system, the dry strength showed a more remarkable increase even at low metal-ion contents (Fig. 2). However, the wet strength is much lower in the Zn(II) system than in the Cu(II) system, as can be seen in Figure 3.

Tables I and II show that the chitosan fibers are capable of absorbing a substantial amount of heavy metal ions through chelation. It would be preferable that the metal ions be collected and the chitosan fibers be recycled for further application. Table III shows the results of a treatment with an aqueous ethylene diamine tetraacetic acid (EDTA) solution for a sample of chitosan fibers containing 7.3% Cu(II) ions ( $\text{CuSO}_4$ ). The EDTA treatment was carried out by treating 4 m of chitosan fibers with 20 mL of a 0.1 M EDTA solution containing 0.4 M  $\text{Na}_2\text{CO}_3$  for different periods of time. It can be seen from Table III that the desorption of Cu(II) ions from chitosan fibers by EDTA is a fairly rapid process. No traces of Cu(II) ions can be detected from chitosan fibers after 5 min treatment. Interestingly, the fiber strength decreased with the decrease in Cu(II) content. This is contrary to the phenomenon observed earlier in Table I where the fiber strength increased with the increase in Cu(II) content. In addition, after the removal of Cu(II) ions by EDTA, the chitosan fibers became much more extensible than was the original fiber. The elongation-at-break of 19.2% for the sample free of Cu(II) ions is more

**Table III Desorption of Cu(II) Ions by EDTA and the Tensile Properties of the Resultant Fibers**

	Treatment <sup>a</sup> Time (min)				
	0	1	2	5	10
Carbon content (%)	28.0	35.0	36.4	38.2	37.6
Cu(II) content (%)	7.3	3.7	1.9	Nil	Nil
Fiber strength (N)	1.47	1.35	1.27	1.24	1.22
Elongation (%)	14.6	17.1	16.5	18.4	19.2

<sup>a</sup> Chitosan fibers containing 7.3% Cu(II) were treated with 20 mL of a 0.1 M EDTA solution containing 0.4 M  $\text{Na}_2\text{CO}_3$ .

**Table IV Effect of the Degree of Acetylation on the Chelating Properties of Chitosan Fibers**

	Degree of Acetylation (%)			
	0.86	36.6	60.8	97.2
Cu(II) content <sup>a</sup> (%)	8.2	5.4	3.6	0.6
Molar ratio of $\text{NH}_2$ to Cu(II)	2.9	2.9	2.8	1.2

<sup>a</sup> The fibers were treated with an excessive amount of  $\text{CuSO}_4$  solution (0.01 M) overnight.

than three times that of the original chitosan fiber. It is reasonable to suggest that during chelation the molecular chains of chitosan would contract in order to fit into the Cu(II)-chitosan complex. After the removal of Cu(II) ions, the polymer chains would remain in a relaxed structure and become more extensible.

Both chitin and chitosan are well known as natural chelating polymers.<sup>4</sup> Practically, it is difficult to obtain chitin with 100% acetylation or chitosan with 100% primary amine groups and, therefore, chitin is defined as the polymer where the majority of amine groups are acetylated, whereas chitosan is the polymer where the majority of the amine groups are free. It is possible to convert chitin into chitosan by deacetylation<sup>1</sup> and, reversely, chitin can be produced from chitosan by acetylation.<sup>9-11</sup> In Table IV, the chitosan fibers were treated with acetic anhydride in methanol to prepare samples with different levels of acetylation. It can be seen from the table that the chelating ability is strongly affected by the degree of acetylation, with the fully acetylated sample showing very little chelating ability. The molar ratio of primary amine groups to Cu(II) ions showed a general trend of 3.

## CONCLUSIONS

This study has shown that chitosan fibers are capable of chelating up to 9.0% Cu(II) and 6.2% Zn(II) ions. The chelation process is a fairly rapid process. The metal ions have a significant reinforcing effect on the chitosan fibers, especially with the wet strength for the Cu(II)-chitosan complex and the dry strength for the Zn(II)-chitosan complex. The metal ions can be easily removed from the chitosan fibers by treatment with an aqueous EDTA solution, thereby making it possible to collect the metal ions and recycle the chitosan fibers. The study on the effect of the degree of acetylation on the che-

lating ability showed that the absorption of metal ions by chitosan is due mainly to the primary amine groups.

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