The Influence of Chitosan and Some of its Depolymerized Grades on Natural Color Printing

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ABSTRACT: Chitosan samples with different molecular weights were prepared using sodium nitrite in acidic medium. These samples were practically confirmed by measuring nitrogen content and average molecular weight. The chitosan samples were applied to cotton fabric by the pad dry method. The pretreated cotton fabric was printed with natural coloring matter, curcumin. The color yield of the prints increased by increasing the molecular weight of chitosan. Both wet and dry rubbing fastness of the prints was good. The stiffness results of the printed cotton fabric pretreated with low molecular weight chitosan showed better performance. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 559–563, 2005

Key words: chitosan; depolymerized grades; natural color printing

INTRODUCTION

In recent years biopolymers have attracted a great deal of scientific and industrial interest as possible substitutes for scientific polymers. One of the most promising is the polysaccharide biopolymer chitosan, owing to its unusual combination of properties, such as biocompatibility, biodegradability, and water-binding capacity.[1,2]

Chitosan[3] is a cationic polyelectrolyte obtained after *N*-deacetylation of chitin by treatment of alkali. The molecular structure of chitosan is similar to cellulose and chitin, except that the secondary hydroxyl ion on the α-carbon atom of the cellulose molecule is replaced with an amino group (Fig. 1). The affinity of chitosan to cotton and wool has been employed as surface coating to alter characteristics such as friction, moisture adsorption, and dye affinity.[4–6] Almost all properties of chitin and chitosan depend on two fundamental parameters, the degree of acetylation and molecular weight distribution (average molecular weight). The influence of the molecular mass of chitosan on dyeing properties of chitosan-treated wool was studied; the dyeing behavior depends only on the presence of chitosan on wool fibers.[7] The use of chitosan as a combined thickener and binder for pigment printing has been examined. The drawbacks in using chitosan in this way were a reduced color yield and a much higher fabric stiffness.[8]

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Natural dyes are not 100% ecofriendly due to the use of synthetic mordants. The printing of cotton with natural dye using conventional mordants is relatively well known. In the present work the cotton fabric has been pretreated with biopolymer chitosan and some of its depolymerized grades. The pretreated samples were printed with natural color, Curcumin without using mordants, in an attempt to increase the print uptake of natural color in an ecofriendly manner.

EXPERIMENTAL

Material

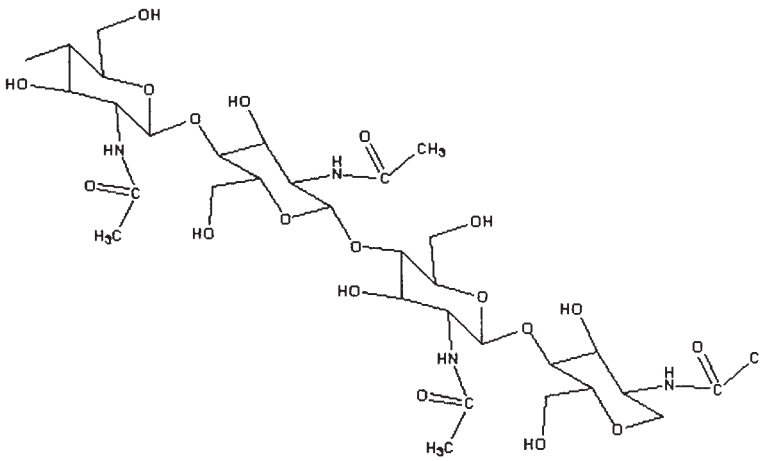
The material used was desized scoured and bleached cotton fabric (140 g/m^2). Chitosan was kindly supplied by Sigma (USA). Curcumin was kindly supplied by Sigma (USA), [C.I. 75 300; natural yellow 3; 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione] from Curcuma longa (Turmeric). Carboxymethyl cellulose (CMC) was supplied by Hoechst under the commercial name Tylose C 600. Acetic acid, Sodium nitrite, Sodium hydroxide, Methanol, and Ethanol used in this study were of laboratory grade.

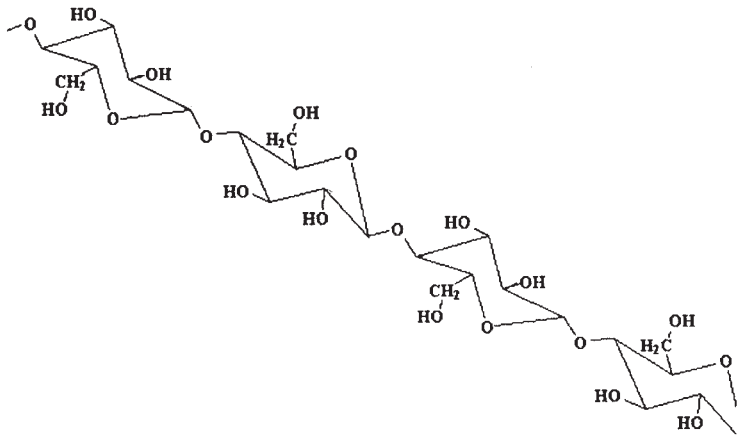
Methods

Preparation of chitosan samples having different average molecular weights

This could be established through depolymerization of chitosan using $NaNO_2$ in acid medium.

A solution of chitosan (I) was prepared by adding 6g of chitosan to 300 mL of a 2% (W/W) aqueous acetic acid solution. An aqueous solution containing





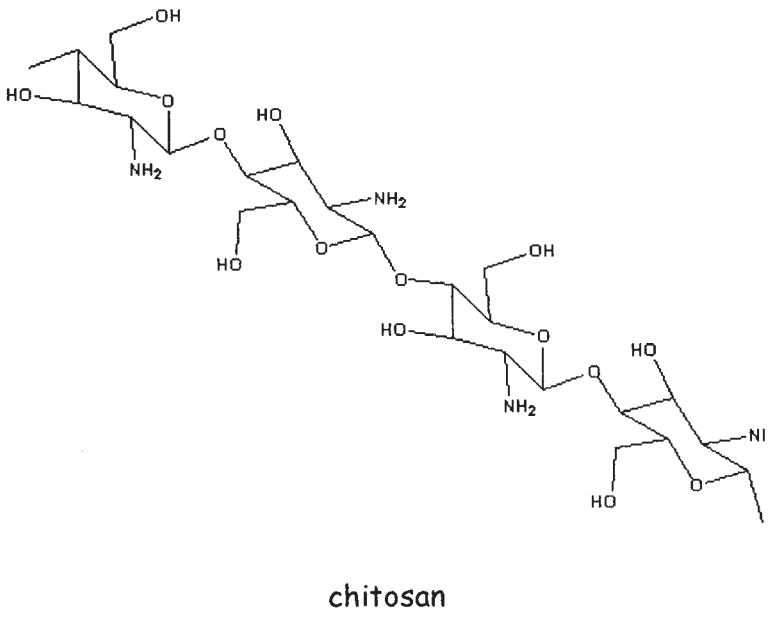


Figure 1 Structure of chitin, cellulose, and chitosan.

0.0895, 0.179, or 0.543 g of sodium nitrite corresponding to chitosan samples (II, III, or IV respectively) was slowly stirred into the chitosan solution over a half-hour period. The reaction mixture was stirred an additional 2.5 h at 30°C, then neutralized with dilute NaOH solution. Excess water was evaporated by rotary evaporator at 50–60°C while applying a vacuum to make a concentrated solution of 20% of the total volume. To extract chitosan samples, the concentrated solutions were poured into excess methanol. The precipitates were collected by filtration and washed several times with acetone, dried at room temperature overnight, and kept in a refrigerator.

Nitrogen content

Nitrogen content of the chitosan samples was measured according to the Kjeldhal method.[9]

Average molecular weight calculation

The average molecular weight was determined viscosimetrically using the Mark–Houwink–Sakurada equation.[10,11]

Fabric treatment

The cotton fabric was immersed in a solution containing different concentrations of chitosan samples in 2% acetic acid. The fabric was padded with 80% pick-up using a laboratory padder for one run, then dried at 80°C for 3 min. The dried samples were then treated in a solution containing 1*N* sodium hydroxide to precipitate chitosan onto the fabric, squeezed, dried at 80°C for 3 min, rinsed with tap water, and finally air dried.

Printing

The printing pastes were prepared according to the following recipe: Dye (Curcumin): 3 g
Carboxymethyl cellulose (CMC): 80 g
Glycerin: 30 g
Water: 887 g
Total: 1000 g

The printing paste was prepared by adding CMC stepwise to water with stirring, then the required amount of Curcumin was added, followed by addition of glycerin with stirring to ensure homogeneity. Finally, water was added to complete the weight of the printing paste to 1Kg.

The printing pastes were applied to the untreated and pretreated cotton fabrics according to the conventional screen-printing method. After drying, the printed samples were fixed by steaming at 125°C for 45 min. Finally, the samples were rinsed with cold water, soaped for 45 min at 45°C, washed with hot water followed by rinsing with cold water, and then air dried.

TABLE I
Nitrogen Content (N%) and Average Molecular Weight of Chitosan Samples

Sample	N%	Average molecular weight
I	6.79	5.9854×10^4
II	6.17	7.7×10^3
III	6.0	2.521×10^3
IV	5.92	592

Analysis and measurements

Color of chitosan samples

The measurements were made of the UV-VIS absorption using a 6405 UV/VIS spectrophotometer, England. Measurements were made in 1 cm path length cells using acetic acid (10 mL/L) in the reference cell.

Fabric whiteness

The treated and untreated cotton samples were examined on a Hunter Lab DP 9000, USA, to obtain a measure of the whiteness index using the CIE 1982 equation.[12]

Color strength (K/S)

The printed samples were evaluated for color strength (K/S), which was calculated from the reflectance measurements using the Perkin–Elmer (Lambda 3 B) visible spectrophotometer and the Kubelka–Munk equation.[13]

Fastness properties

The fastness to washing and rubbing was assessed according to the standard methods.[14]

Fabric stiffness test

The stiffness of the printed samples was measured using a Gurely Stiffness Tester (Toyoseiki-Japan); the samples were tested for warp direction.

RESULTS AND DISCUSSION

Characterization of chitosan samples

The depolymerization of chitosan is practically confirmed by the results of Table I.

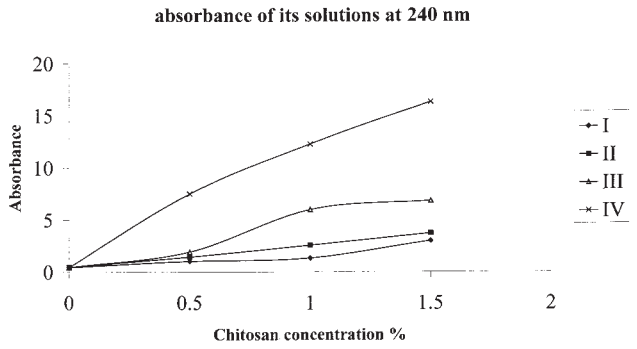


Figure 2 Effect of chitosan sample concentration on the absorbance of its solutions at 240 nm.

Color of chitosan

In Figure 2, the absorbance data for solutions of chitosan samples (I–IV) at 240 nm are plotted as a function of concentration. The results show an increase in absorbance with increasing concentration irrespective of the chitosan sample used. It is clear that the absorbance increases by decreasing the average molecular weight of chitosan at definite concentration in the range studied. This was confirmed by the highest absorbance of the IV sample. The increase in absorbance with decreasing the average molecular weight of chitosan may be attributed to the increase of the amount of terminal aldehyde groups.

Figure 3 also shows how the concentration of the chitosan sample affects the color of treated fabrics. The whiteness index decreases with increasing concentration of chitosan regardless of the chitosan sample used. It is also clear that the yellowing increases with decreasing the average molecular weight of chitosan, for example, at 1.5% concentration, the chitosan samples exhibit the order of whiteness index values: I > II > III > IV. The higher decrease in whiteness with respect to IV may be attributed to the ability of low molecular weight to penetrate inside the fabric structure so the reaction between chitosan and the cotton fabric will take place inside the fabric structure and, in so doing, will cause a drastic effect on the whiteness index.

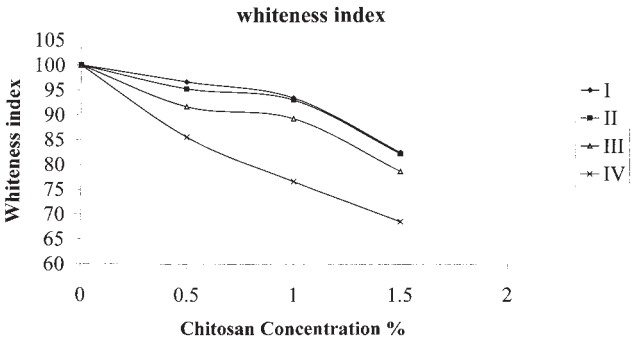


Figure 3 Effect of chitosan concentration on the whiteness index.

TABLE II
The Effect of Chitosan Concentration on the Color Strength (K/S) of the Printed Cotton Samples

Chti. concn. % (owf)	K/S			
	I	II	III	IV
0	2.1	2.1	2.1	2.1
0.5	3.21	3.12	2.6	2.6
1.0	3.26	3.16	2.9	2.7
1.5	3.28	3.29	3.26	2.9

Color strength

The color strength as expressed as K/S for the printed cotton fabrics treated with chitosan is given in Table II. It is clear that the printed samples exhibit K/S of higher values in the presence of chitosan than in its absence regardless of the molecular weight of chitosan. This observation may be attributed to the structure features of curcumin which is possibly function as a direct dye. The interaction between the dye (curcumin) and the fabric and/or amino groups of chitosan is affected by means of hydrogen bonds. Another possibility is the formation of salt side linkage between the protonated amino groups of chitosan and the dye. Nevertheless, K/S follows in order depending on the molecular weight of chitosan, I > II > III > IV.

The reason of this order is that depolymerization of chitosan during the preparation of II, III, and IV leads to the decrease in the number of amino groups, which are the site for the dye used.

Color fastness

Fastness properties of the treated sample prints are given in Table III. Comparative results using untreated samples are also given; the wash fastness of chitosan treated samples are comparable to the untreated samples. The abrasion resistance of the prints can also be seen from the results of rubbing fastness properties of the prints in wet and dry state.

TABLE III
Wash and Rub Fastness of the Printed Samples

Sample	Wash Fastness		Rub fastness	
	Change of color	Staining	Dry	Wet
untreated	2–3	3	3–4	3
I	3	4	4–5	3
II	3	3	4–5	3
III	3	3	4	2–3
IV	3	3	4–5	3

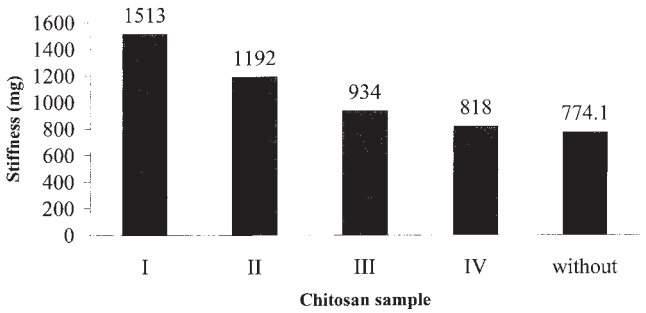


Figure 4 Effect of molecular weight of chitosan on the stiffness of the printed fabric.

Stiffness

Figure 4 shows the effect of the molecular weight of chitosan on the stiffness of the printed samples. It is clear that the treatment of the samples with chitosan prior to printing leads to increase in the stiffness of the printed samples. This increase in the stiffness depends on the molecular weight of chitosan. The value of stiffness reaches its minimum value by decreasing the molecular weight of chitosan, which is comparable with the untreated samples (774.1 for the untreated, 818 for the treated by the lowest molecular weight of chitosan, sample IV).

CONCLUSIONS

From the observations observed in the present study, it may be concluded that:

a. Color yield of printed samples accepts a higher value in the presence of chitosan than in its absence.
b. The color yield increases with increasing the molecular weight of chitosan.
c. The value of stiffness reaches its minimum value by decreasing the molecular weight of chitosan.

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