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Properties Evaluation of Sodium Nitrite Treated Chitosan-Cotton Fabric

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Abstract

In this study, chitosan coated-cotton fabric was prepared and then treated with sodium nitrite under mild condition, aiming at the partial removal of surface-chitosan in order to solve the problems of surface dyeing and fabric stiffness. The results showed that sodium nitrite treated chitosan-fabric exhibited an improvement of dyeability (higher dye exhaustion and color strength) when compared to untreated fabric. The improvement in dyeability was due to the availability of chitosan amino groups which had an affinity to anionic dyes including reactive dyes. Other fabric properties were evaluated. The results showed that color fastness properties (crocking fastness and light fastness) and fabric stiffness were found comparable to those of dyed untreated fabric (commercial dyeing). These findings led to the conclusion that problems of poorer fastness properties and stiffness arising from chitosan coating onto cotton fabric were minimized by sodium nitrite treatment under mild condition which resulted in the partial removal of chitosan coated film present on the fabric surface. The remaining chitosan on the fabric surface showed its ability of enhancing reactive dyeability without causing interference to fabric’s fastness properties.

Key words: Chitosan-coated cotton fabric, sodium nitrite, in-situ depolymerization, dyeing properties

Introduction

Cellulose can be dyed with various classes of dyes. Most importantly, reactive dyes are widely employed because of excellent fastness properties. However, dyeing of cellulose fibers with reactive dyes still suffers from two major disadvantages; one is poor dye uptake and another is unsatisfactory dye fixation. Poor dye uptake is related to the existence of the charge barrier effect between the negatively charged fiber surface and anionic reactive dyes. In practice, an increase in dye uptake is promoted by the addition of salts such as sodium sulphate and sodium chloride to the dye bath in order to suppress the negative charge on the fiber surface. Researche papers on the chemical modification of cellulose have received much attenttion in order to improve the reactive dye uptake as well as to reduce the high consumption of electrolytes. The results showed that cationic or aminated cellulose exhibited an improved dye uptake. Unfortunately, the problem of surface dyeing (ring dyeing) is clearly evident and as a result color fastness properties is decreased.[(1)] Chitosan, a natural polymer, has been studied to improve dyeability of cotton with reactive dyes. The application of chitosan onto cotton fabrics is usually carried out by pad-dry method. After drying process, chitosan by itself exhibits strong adhesion on cellulose substrate due to their structural similarity. The reason is that the chitosan amino groups play a key role in improving dye affinity of the treated fabric.[(2-3)] However, drawbacks arising from coating of fabrics with large molecular weight chitosan include the problems of fabric stiffness and ring dyeing which is derived from an ease of film formation of chitosan on the fabric surface. These disadvantages discourage promising applications of chitosan in textile industry. Fortunately, these problems could be overcome in some extent by the usage of low molecular weight chitosan. Chitosan is easily depolymerized into a series of low molecular weights. Sodium nitrite is a common depolymerizing agent which easily depolymerizes chitosan under mild conditions. However, care must be taken during handling of liquid chitosan due to the susceptibility to further degradation. In this study, an alternative approach to treatment of cotton fabric with low molecular weight chitosan was proposed. Firstly, cotton fabric was coated with a high Mw chitosan. Then in-situ depolymerization of coated chitosan using sodium nitrite under mild condition was carried out to control the degradation of the coated film. Treated fabrics was tested for dyeability. The fastness properties of dye fabrics such as washing fastness, rubbing fastness and light fastness were evaluated.

Materials and Experimental Procedures

Bleached woven cotton fabric (12.027 g/m^2) was purchased from a local dyeing factory. Commercial grade-chitosan flake (approx. 85% degree of deacetylation with the molecular weight of about 10^6) was bought from Ebase Co., Ltd (Thailand). Drimarene Red HF-2B (containing difluorochloropyrimidine and vinyl sulphone reactive groups), a commercial reactive dye was kindly supplied from Clariant (Thailand), Ltd. Acetic acid, sodium nitrite, sodium sulfate and sodium carbonate used in this study were of analytical grade.

Coating of Chitosan onto Cotton Fabric

The cotton fabrics (7.5 g, size 21 x 30 cm.) were padded in chitosan solutions containing various concentrations from 1%, 1.5% and 2% (w/v). The application was carried out using pad-dry-cure process as follows: padding nip pressure was set to obtain 80% wet pick up. Then drying followed by curing in the mini-istenter at 100°C, for 10 mins. and 150°C for 3 mins., respectively, were carried out.

In-Situ Depolymerization of Coated Chitosan and Dyeing

The in-situ depolymerization of coated chitosan on the fabric was carried out as follows: The chitosan coated fabric was put into a dye pot containing a solution of sodium nitrite. The treatment was performed in a laboratory dyeing machine at the liquor ratio of 1:25. An effect of sodium nitrite concentration ranging from 5, 10 and 15 g/L was investigated. Treatment was carried out at room temperature (30°C) for 30 mins. Finally, treated fabric was rinsed in tap water, and subsequently air dried. Chitosan coated fabrics including depolymerized chitosan-fabrics were dyed with various dye concentrations of 0.5, 1, 1.5 and 2% o.w.f (on weight of fabric) plus sodium sulphate (50, 60, 65 and 70 g/L) and sodium carbonate (6, 7, 8 and 9 g/L). Dyeing was done in a laboratory dyeing machine, Labtec. The temperature of dyebath was raised to 60°C and kept at this temperature for 40 mins. to obtain the maximum dye fixation.

Measuremens of Dye Exhaustion and Fixation

For all dyeings, the percentage of dye exhaustion was measured on the UV-VIS spectrophotometer SPECORD S 100 at λ_{max}. The percentage of dye exhaustion (%E) was calculated using the following equation.

$$\%E = 100 \times [1-(C/C_0)]$$

Where C_0 and C are the absorbance of the dye solution before and after dyeing, respectively.

Color measurement of the dyed fabrics before and after soaping were measured using a spectrophotometer, Macbeth color-EYE® 7000. The measurement parameters were as follows: 10° observer; D65 illuminant; specular reflectance included; and UV reflectance included. Color strength (*K/S*) values were instrumentally determined. The *K/S* value was proportional to the dye concentration on the fiber.

Fastness Testing

The light and the wash fastness of samples were evaluated according to ISO 105-B02:1994(E) and ISO 105-C01:1989(E), respectively. The bending stiffness was evaluated according to BS

3356:1990. Crocking fastness was evaluated according to AATCC Test Method 8-2004.

Results and Discussion:

Effect of Sodium Nitrite Ttreatment on Dye Uptake and Color Strength.

Chitosan fabrics treated with various concentrations of sodium nitrite ranging from 5, 10 and 15 g/L were dyed with 2 wt% Drimarene Red HF-2B. The percentage of dye exhaustion and color yield values of resultant dyed fabrics are shown in Table 1. The control fabric exhibits relatively low dye uptake (82%), yielding the lowest value of percent dye exhaustion and color strength due to the repulsive interaction between anionic dye and negatively charged fiber surface. After being coated with chitosan, the percent dye exhaustion (%E) and color strength are higher when compared to control fabric. An increase in the dyeability of the chitosan coated fabrics was attributed to the presence of chitosan NH_2 groups which typically attract anionic dyes including reactive dyes. In case of chitosan fabrics aftertreated with sodium nitrite, %E values (also see Figure 1) in comparison with chitosan-fabric are relatively lower with increasing concentration of sodium nitrite. The decreasing trend is a clear consequence of depolymerization of coated chitosan, resulting in a reduction of chitosan NH_2 groups. In contrast, those corresponding K/S values are found higher, indicating that most of the absorbed dyes were covalently bonded onto both cellulose hydroxyl groups and chitosan amino groups.

Table 1. Effect of sodium nitrite concentration on percent dye exhaustion (%E) and color yield (K/S)

$NaNO_2$ conc (g/l)	%E	K/S Before treatment	K/S After treatment
Control (normal fabric)	82.98	9.19	9.01
Chitosan Fabric	84.04	9.99	9.64
5	83.33	10.06	9.64
10	83.13	10.13	9.40
15	82.14	9.87	9.59

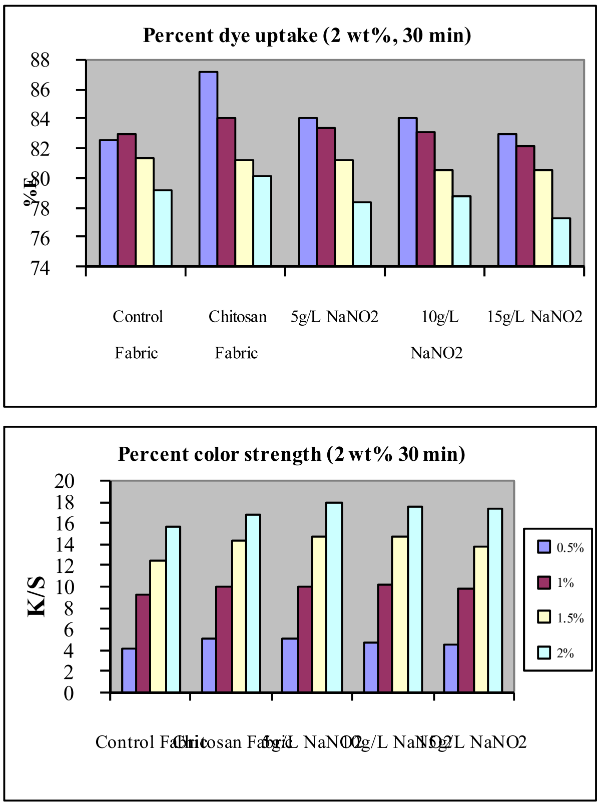


Figure 1. Plots of dye concentration(0.5, 1, 1.5 and 2 owf%) and sodium nitrite concentration against percent dye uptake and percent color strength (2 wt% chitosan , sodium nitrite treatment time of 30 mins.)

Properties Evaluation

Fabric Stiffness

Fabric stiffness was assessed by bending stiffness tester. A measured bending length is indicative of fabric stiffness; the higher the bending length the higher the fabric stiffness. The results presented in Figure 2 show that the average bending length of chitosan fabric is found to be 6.1 cm in warp direction and 4.4 cm in weft direction. In comparison, the bending length of chitosan fabric treated with sodium nitrite decreases with an increase in sodium nitrite concentration. The results indicate that parts of chitosan were removed from the fabric surface due to the depolymerization by sodium nitrite, resulting in loss of film characteristic.

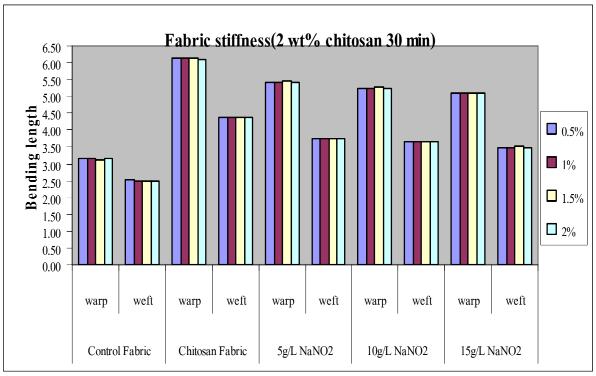


Figure 2. Fabric stiffness of chitosan-fabrics aftertreated against concentration of sodium nitrite (2 wt% chitosan , treatment time of 30 min)

Color Fastness

Coated chitosan on cotton fabric commonly produces surface dyeing due to poor dye penetration, leading to poor fastness properties such as crocking fastness and light fastness. In this study, chitosan-fabrics were aftertreated with sodium nitrite under mild condition. The results of fastness testing are presented on Tables 2, 3 and in Figure 3. It is found that the crock fastness rating (on grey scale) and light fastness (percent color fade) are poorer in case of chitosan-fabric than those fabrics without chitosan coating, resulting from the characteristic of surface dyeing. For chitosan-fabrics treated with sodium nitrite, color loss due to crocking and light is reduced and comparable to that of fabric without chitosan coating, indicating that chitosan film on the fiber surface was partially removed. As a result, better dye penetration into the interior of the fiber was achieved.

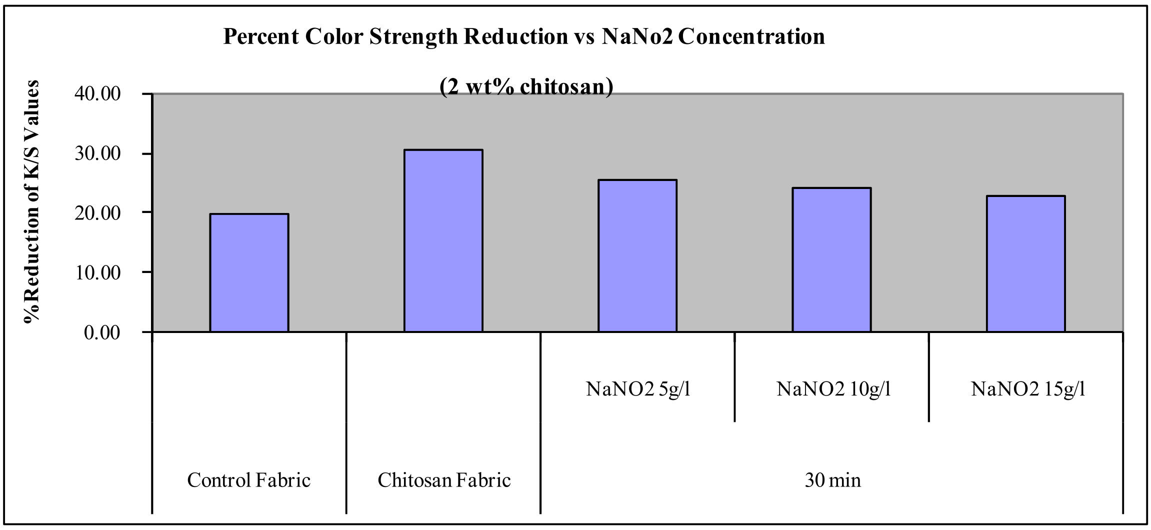
Table 2. Crocking fastness of dyed chitosan-fabrics after treatment with various concentrations of sodium nitrite (2 wt% chitosan)

$NaNO_2$ (g/l)	Dye Concentration							
	0.5% owf		1% owf		1.5% owf		2% owf	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Control	5	4-5	5	4-5	4-5	4	4-5	4
Non (chitosan-fabric)	4-5	4	4-5	3-4	4	3-4	3-4	3
5	4-5	4-5	4	4	4-5	4	4-5	3-4
10	4-5	4-5	4-5	4	4	4	4-5	4
15	4-5	4-5	4-5	4-5	4	4	4	4

Table 3. Light fastness rating and color difference of dved chitosan-fabrics after treatment with various concentrations of sodium nitrite (2 wt% chitosan)

$NaNO_2$ conc. (g/l)	Light fastness rating	Color difference(ΔE)
-	5 (fabric without chitosan coating)	19.68 (fabric without chitosan coating)
0	5	30.70
5	5	25.69
10	5	24.20
15	5	22.74

Figure 3. Percent color loss by light of dyed chitosan-fabrics against sodium nitrite concentration



The disadvantages of coating of chitosan onto cotton fabric such as decreased fastness properties and fabric stiffness arising from the formation of coating film were minimized by partial removal of surface-chitosan with sodium nitrite under mild condition. The results showed that sodium nitrite concentration of 10 g/L and treatment time of 30 mins. at 30°C were the optimum conditions for controlling the surface chitosan removal, yielding good results in terms of properties of dyed fabrics.

Acknowledgement

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