Application of Chitosan/Nonionic Surfactant Mixture in Reactive Dyes for Dyeing Wool Fabrics

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ABSTRACT: The feasibility of wool fabrics pretreated with a chitosan/nonionic surfactant mixture and dyed with reactive dyes was studied. The results showed that the presence of the chitosan/surfactant improved the application to wool, which greatly enhanced the color strength when dyed at 50°C but little change was observed when dyed at 80°C. The higher the concentration of chitosan/surfactant added, the greater was the color strength of the dyed wool fabrics. The amounts found to be optimum for dyeing were 0.5% chitosan and 1.0% surfactant. The washing fastness of the dyed wool fabrics was in the range of grades 4–5, the dry rubbing fastness was in the range of grades 4–5, and the wet rubbing fastness was in the range of grades 3–4. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2859–2864, 2001

Key words: chitosan; wool; reactive dyes; nonionic surfactant

INTRODUCTION

Chitosan is one of the biopolymer chemical compounds[1] produced from the deacetylation process of chitin with shrimp and crab shell content. Its main source is the shell and skin of crabs, shrimp, and ephemera. In addition to these, chitin[2] can also be obtained from shellfish, squid cartilage, and the cell wall of a fungus such as yeast. One hundred billion tons of chitin are produced globally every year. The low purity of chitosan and its low solubility make its application rather limited, and it should be overcome.

In recent years the application of chitosan in industry and science has been widely promoted. The potential for using such a natural high molecule in other areas such as food processing additives, artificial skin, coagulants, and hemostatics are also reported.[3] It was recently used in the wastewater treatment industry as a wastewater treatment agent, mainly to adsorb metal ions.[4] It was also used in the textiles industry. The structure of chitosan is the same as cellulose except for the hydroxyl group, which is substituted with the amino group in case of chitosan.[5] Logically, the main purpose of cotton fabric being treated with chitosan is to enhance the dye uptake of immature cotton and to increase its color strength.[6] In comparision with anionic dyes used in wastewater treatment, the adsorption of metal ion dyes is better and therefore it is being used extensively.[7]

In the present study chitosan was used in combination with cationic dyes in an acid bath in order to substitute a cationic surfactant in dyeing. The most difficult task to control in dyeing wool fabric is its color strength and dyeing fastness. The dyeing quality of dyed wool fabrics can be increased by pretreating the wool fabrics with chitosan in a nonionic surfactant, which fortifies its bonding with the wool fabric surface.[8] The results are reported on using reactive dyes in dyeing treated wool fabrics and its comparison with traditional dyeing methods.

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EXPERIMENTAL

Materials

The specifications of the wool fabrics (supplied by Shinn Hwa Textile Co.) before processing were $64^{s}*64^{s}$ ends (91) and picks (56). The reactive dye used was Cibacron Red F-B (C.I. Reactive Red 184). The chitosan had a molecular weight of 180,000 and a degree of acetylation of 85% (supplied by Sigma). Erkantol NR and Erkantol CW (supplied by Bayer Co.) were used as commercially available without further purification. Avolan REN was used as a leveling agent for the dyeing.

Methods

Process

An exhausted solution was prepared by mixing different concentrations (0.01, 0.05, 0.1, and 0.5% ows) of chitosan and different concentrations (0.1, 0.25, 0.5, and 0.1% ows) of Erkantol NR and Erkantol CW. Solutions were stored for 5 days before use for wool treatment in order to promote interaction between the chitosan and surfactant. Then the wool fabrics were immersed in the treatment solution with shaking in a thermostatically controlled Branson 3210 shaker for 18 h at 40°C with a liquor ratio of 1:20. After the treatment the wool fabrics were squeezed to rolls in order to remove the excess solution and then suspended in a bath containing 5% ammonium hydroxide solution for 10 min in order to precipitate chitosan on the fabrics. The samples were squeezed to rolls again and dried at 50°C in an oven.

Untreated and treated wool fabrics were dyed with 1.5% omf dyes in the presence of 1% oms Avolan REN (pH 9–10) adjusted with 10% sodium carbonate, which is the procedure recommended by the dye manufacturer for dyeing at 80°C; the procedure was slightly modified for dyeing at 50°C. All dyeing was performed using a rapid laboratory dyeing machine at a liquor ratio of 1:20. The fabrics were wetted for 3 min in the dye bath at 30°C before the dyes were added. The 50 and 80°C dyeing temperatures were matched with difference times (10, 20, 30, 60, and 90 min).

Analysis

The dyed wool fabrics were rinsed in tap water and dried, and the color was measured with a Nippon ND-300A spectrophotometer. The color difference of the undyed and dyed wool fabrics was then derived by using the difference value ΔE from the Scofreid formula with the coordinates of Hunter's color space for CIE illumination C with a 2° standard observer.[9] The color difference between the largest and smallest values of the same fabric was obtained; the figures indicated the evenness of the fabrics, according to the regulations of the National Bureau of Standards, was under 2.0, which is acceptable for industrial applications. (The scoring is 0–0.5 indicates a trace, 3–6 appreciable, 0.5–1.5 slight (acceptable), 6–12 much, 1.5–3 noticeable, and 12 and above very much.)

Sample fabrics were tested for washing fastness (according to the JIS L0844 A-4 specification) and rubbing fastness (according to the JIS L0850 A-3 specification).

RESULTS AND DISCUSSION

Effect of Concentration of Chitosan on Color Strength and Evenness of Dyed Wool Fabrics

After desizing and scouring the wool fabric, it was exhausted in different concentrations of chitosan solution (0.01, 0.05, 0.1, and 0.5%) and matched with different concentrations of nonionic surfactant. Then it was allowed to stand for 5 days so that the chitosan and nonionic surfactant would dissolve and mix thoroughly. The wool fabric was then shaken continuously for 18 h at 40°C subjected to dyeing.

Different concentrations of the nonionic surfactant Erkantol NR (1.0, 0.25, 0.5, and 1.0%) were selected. The change in dyeing time at 80°C and the variation of color strength in dyed wool fabrics at different dyeing times is shown in Figure 1. The longer the dyeing time of the wool fabric, the stronger the color. The color strength of the wool fabric that did not undergo pretreatment also increased with a longer dyeing time, and it was even higher than the dyed wool fabrics with chitosan concentrations of 0.01 and 0.05%. It was observed that the color strength of the wool increased with the increase in the concentration of chitosan. The variation in the dyed wool fabrics with the nonionic surfactant Erkantol NR were at concentrations of 0.1, 0.25, 0.5, and 1.0% at 50°C. The variation of the dyed wool fabrics is shown in Figure 2. It can be observed that the color strength of wool fabric pretreated with chitosan increased with the increase in the concentration

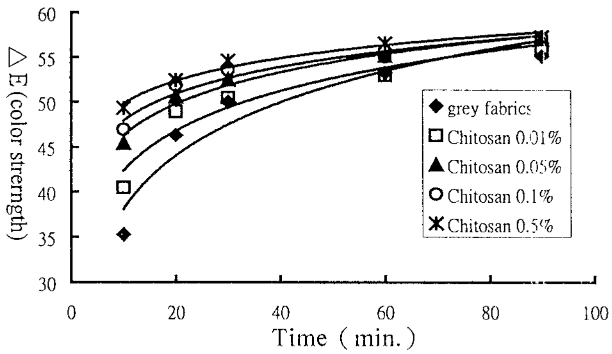

Figure 1 The variation of the color strength for different dyeing times in Erkantol NR (0.5%) on dyed wool fabrics at a dyeing temperature of 80°C with different chitosan concentrations.

of chitosan, which was better than the color strength of raw fabric. It can be suggested from these results that the free amino group in chitosan had hydrogen bonding with the active radical group of the reactive dyes, which in turn increased the dyeing function of the wool fabric. Additionally, wool is an ampholytic fiber so its structure contains a hydroxyl and amide group, which has the potential of forming a hydrogen interaction bond with the amino radical group of chitosan. Such mutual reactions increase the color strength.

Mainly from the point of the wool fabric evenness, the results in Table I show that even when dyeing at high temperature (at 80°C), the evenness of the wool fabrics are all within the acceptable range of 1.5. It is also depicted that dyeing at low temperature (at 50°C), leads to evenness, which is also within the acceptable range of 1.5.

Effect of Concentration of Surfactant on Color Strength and Evenness of Dyed Wool Fabric

The concentrations of the nonionic surfactants Erkantol NR and Erkantol CW were 0.1, 0.25, 0.5, and 1.0%, which matched with the different concentrations of chitosan. It is shown in Figures 3 and 4 that at a concentration of 1.0% chitosan and dyeing at 80 and 50°C, the color strength increases with the increase of surfactant concentration. But as the concentration rose, the color strength was very proximate. This result was due to the fact that the surfactant used in this experiment was nonionic and hence there was no ionic bonding. Also, the purpose of adding this type of surfactant was for penetration and wetting, which is conducive to bonding with chitosan, fibers, and dyes.

From the point of wool fabric evenness, the results in Table I show that when dyeing at high temperature (80°C), the evenness of the wool fabrics was within the acceptable range of 1.5. It is also shown in Table I that the evenness was within the acceptable range of 1.5 when dyeing at a low temperature of 50°C. Therefore, the evenness was excellent. The use of this surfactant can also achieve wetting and penetration and enable chitosan to spread evenly and bond with wool fabrics.

Effect of Types of Surfactant on Color Strength and Evenness of Dyed Wool Fabric

The two surfactants Erkantol NR and Erkantol CW are both nonionic and are wetting and penetrating agents. Thus, in applying chitosan to bond with wool fabrics, these surfactants increase the color strength of reactive dyes. It is shown in Figure 5 that when the dyeing temperature was 80°C, the color strength of the Erkantol CW was much higher than the color strength of the Erkantol NR. When the dyeing temperature was 50°C, the color strength of both the surfactants differed very little, but it was slightly higher in Erkantol CW. When dyeing at 50°C, the color strength tended to increase as the concentration of chitosan increased as shown in Figure 6. In comparing the characteristics of both the surfactants, both have a cellulose radical group. It is shown in

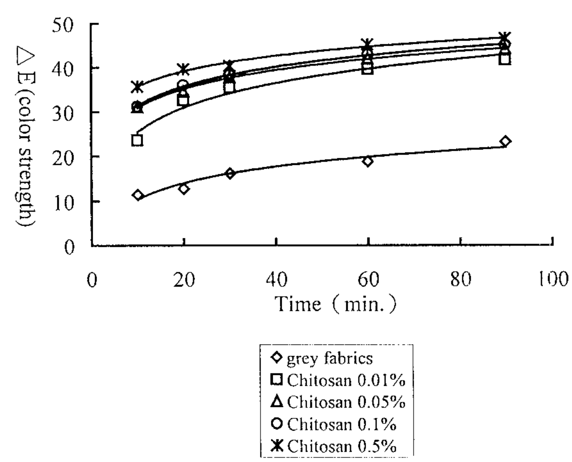

Figure 2 The variation of the color strength for different dyeing times in Erkantol NR (0.5%) on dyed wool fabrics at a dyeing temperature of 50°C with different chitosan concentrations.

Table I Evenness (Δ*E*) of Dyed Wool Fabrics in Erkantol CW at Dyeing Temperatures of 50°C and 80°C

	Chitosan (% o.w.s)															
	0.01				0.05				0.1				0.5			
Erkantol CW concn (% o.w.s)	0.10	0.25	0.50	1.00	0.10	0.25	0.50	1.00	0.10	0.25	0.50	1.00	0.10	0.25	0.50	1.00
ΔE at 80°C	0.25	0.32	0.12	0.22	0.26	0.15	0.31	0.40	0.10	0.20	0.31	0.21	0.30	0.13	0.19	0.20
ΔE at 50°C	0.27	0.17	0.29	0.32	0.28	0.20	0.30	0.29	0.26	0.18	0.34	0.31	0.29	0.23	0.16	0.21

Dyes concn, 1.5% o.m.f; dyeing times, 60 min.

Figure 7 that the structure of chitosan is very similar to the structure of fiber and the hydroxyl radical group of the surfactant and the amine radical group of chitosan form a hydrogen bond, which lead to greater penetration and better dyeing. Because Erkantol CW has a radical group of poly(vinyl chloride) affinity, this additional polar radical increases its opportunity for hydrogen bonding, enabling the color strength of Erkantol CW to be superior to Erkantol NR.

The results from Table I show that when using Erkantol CW and Erkantol NR in dyeing at temperatures of 80 and 50°C, the evenness of the wool fabrics was all within the acceptable range of 1.5. Therefore, the evenness of both was excellent.

Effect of Dyeing Time on Color Strength and Evenness of Dyed Wool Fabrics

Figures 1–4 show that the color strength of wool fabrics increases with an increase in dyeing time. Figure 1 shows that the longer the dyeing time at 80°C, the higher is the bonding effect of chitosan, dyes, and dyed wool fabrics. Very little change was observed in color strength when the dyeing time was 60 min. As shown in Figure 5, at a dyeing temperature of 50°C, the dyeing time was also greatly influenced by the variation of color strength in the wool fabrics.

Effect of Dyeing Temperature on Color Strength and Evenness of Dyed Wool Fabrics

As shown in Figure 1, that when dyeing wool fabrics that were not pretreated, dyeing at 80°C caused their color strength to be very near to the color strength of wool fabric pretreated with chitosan and nonionic surfactant. It is shown in Figure 2 that when dyeing at 50°C, the color strength

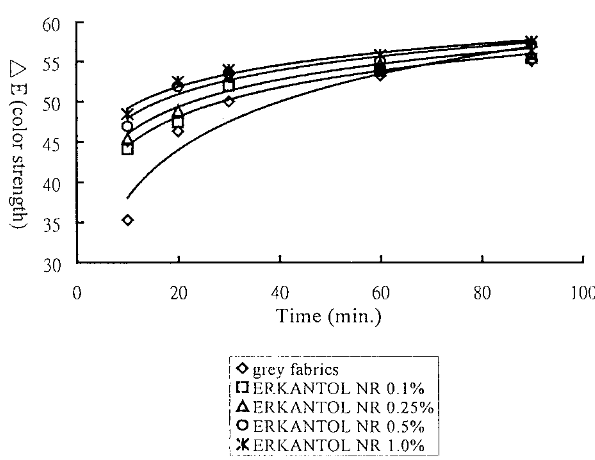

Figure 3 The variation of the color strength for different dyeing times in chitosan (0.1%) on dyed wool fabrics at a dyeing temperature of 80°C with different Erkantol NR concentrations.

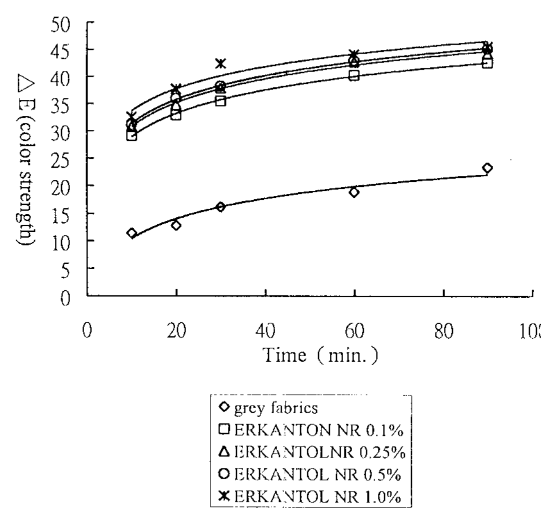

Figure 4 The variation of the color strength for different dyeing times in chitosan (0.1%) on dyed wool fabrics at a dyeing temperature of 50°C with different Erkantol NR concentrations.

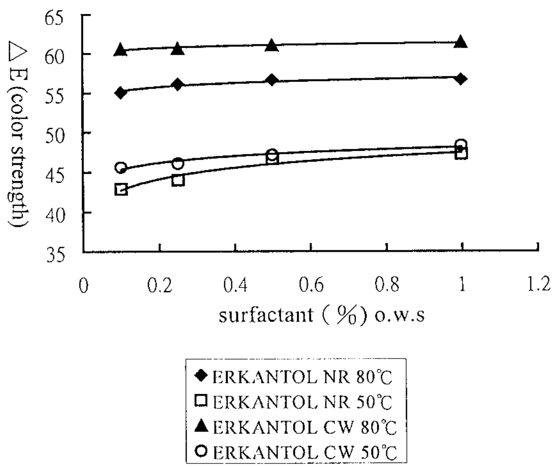

Figure 5 The variation of the color strength for different dyeing temperature in chitosan (0.5%) on dyed wool fabrics with different surfactant concentrations.

of wool fabrics pretreated with chitosan and nonionic surfactant increased more than untreated wool fabrics.

From the above results it can be suggested that the role of chitosan at a low dyeing temperature of 50°C is to increase the color depth of the dyed wool fabrics. But at a high dyeing temperature of 80°C, although it can assist dyeing, as a whole its color strength is not very effective. However, this proves that chitosan can improve the color strength of wool fabrics at low dyeing temperature.

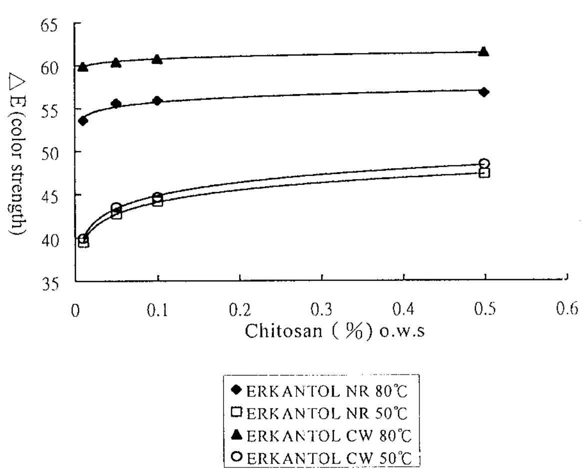

Figure 6 The variation of the color strength for different dyeing temperature in surfactant (1.0%) on dyed wool fabrics with different chitosan concentrations.

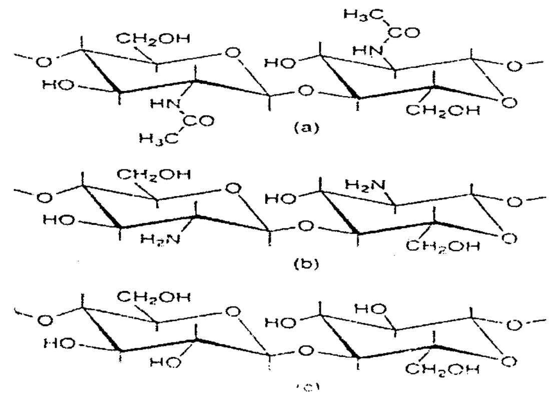

Figure 7 The chemical compositions of (a) chitin, (b) chitosan, and (c) cellulose.

Dyeing Fastness of Dyed Wool Fabrics

Washing Fastness

Washing fastness tests were conducted on each dyed wool fabric as described above at a fixed surfactant concentration of 1.0% matching with different chitosan concentrations. The Table II results show that the washing fastness was almost constant and at grades 4–5, which is independent of dyeing temperature.

Rubbing Fastness

Tests of the rubbing fastness on dyed wool fabrics was carried out as described above at a fixed surfactant concentration of 1.0% with different chitosan concentrations as shown in Table III. The results suggest that dry rubbing fastness could be as high as grades 4–5, while wet rubbing fastness was in the range of grades 3–4.

Table II Washing Fastness of Dyed Wool Fabrics in Different Concentrations of Chitosan

Grade Chitosan (% ows)	Grades at 50°C for 60 min		Grades at 80°C for 60 min	
	SC	CC	SC	CC
0.01	5	4–5	5	5
0.05	4	4–5	4–5	4–5
0.1	4–5	4	5	4–5
0.5	4	4–5	4–5	4–5

Erkantol CW, 1.0%; SC, staining of color; CC, change in color.

Table III Rubbing Fastness of Dyed Wool Fabrics in Different Concentrations of Chitosan

Chitosan (% ows)	Grades at 50°C for 60 min		Grades at 80°C for 60 min	
	Dry	Wet	Dry	Wet
0.01	4–5	4	4–5	4
0.05	4	3–4	4	3–4
0.1	4–5	4	3–4	3–4
0.5	4–5	3–4	3–4	3

Erkantol CW, 1.0% ows.

CONCLUSION

The main aim of this research was to use chitosan in coordination with a nonionic surfactant on dyed wool fabrics with reactive dyes in order to explore the color strength and evenness of dyed wool fabrics. The following conclusions were made from the results of our experiments.

1. The higher the concentration of surfactant, the better is the color strength of dyed wool fabric.
2. At dyeing temperatures of 80 or 50°C, the evenness of the dyed wool fabrics pretreated with chitosan was within the permissible range (i.e., 1.5) and the evenness was excellent.
3. At a dyeing temperature of 50°C, the color strength of dyed wool fabric pretreated with chitosan increased. A dyeing temperature of 80°C showed no significant change in the color strength.
4. The color strength of the surfactant Erkantol CW was found to be superior to the color strength of Erkantol NR.
5. The washing fastness of dyed wool fabrics pretreated with chitosan can reach grades 4–5.
6. The dry rubbing fastness of dyed wool fabrics pretreated with chitosan can reach grades 4–5, and the wet rubbing fastness can reach grades 3–4.

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