

Dyeing of Polyester with Reactive Dyestuffs Using Nano-Chitosan

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ABSTRACT

The main objective of this work is to investigate the effect of nano-chitosan on the dyeing of polyester fabric with reactive dyes. Polyester fabric was treated with alkali and coated with nano-chitosan. Afterwards all samples were dyed with reactive dyes. The water absorption and bending resistance of pristine polyester, alkaline and chitosan-treated polyester were measured. In order to investigate surface chemical bonding, FTIR/ATR was employed. Surface morphology of fabrics was observed using scanning electron microscopy (SEM). Wettability and bending behavior of the treated polyester increased compared to the untreated one. The color difference between the dyed blank and chitosan-treated samples was estimated using a spectrophotometer. The data obtained shows it is possible to use reactive dyes to dye polyester fabrics finished with nano-chitosan and the resulting fabrics will exhibit acceptable washing and rubbing fastness.

Keywords: chitosan, reactive dye, polyester, alkaline treatment, dyeing process.

INTRODUCTION

Polyester fibers have been widely used in textile industries due to their low production costs, high strength, easy-care properties, dimensional stability, high thermal stability and chemical resistance. However, polyester fibers show a hydrophobic character and swell to a very small extent in water, making access by dyestuff molecules to the fiber difficult. This together with the absence of active chemical groups makes it difficult to dye polyester with dyestuffs other than disperse dyes [1-4]. Dyeing polyester with disperse dye is performed by using temperatures around 130°C, by dyeing at boiling temperature in the presence of a carrier, or using supercritical CO₂ fluid dyeing. Many carriers have significant problems such as toxicity, unpleasant odor, sensitization of human skin and environmental contamination. It will be possible to eliminate disperse dye stuffs and carriers through surface modification of polyester.

Surface modification of textile fibers is one of the most useful methods of textile treatment. By the modification of the fiber surface only, deterioration of fiber quality and bulk properties is minimized [4-6].

Chitosan is a linear, semi-crystalline polysaccharide derived by deacetylation of chitin. Chitosan also has free amino groups which make it a positively-charged polyelectrolyte at pH below 2–6 and contribute to the higher solubility compared to chitin.

Polyester must be alkaline treated to form crosslinks with chitosan. This results in positive dye sites on the fiber surface. Polyester undergoes nucleophilic substitution and is hydrolyzed by aqueous sodium hydroxide. The hydroxyl ions attack the electron – deficient carbonyl carbons of the polyester to form an intermediate anion. Chain scission follows and produces hydroxyl and carboxylated end groups. As a result, anionic dyes such as direct, acid and reactive dyes can easily be absorbed by electrostatic attraction due to the created cationic nature of the fiber surface treated by chitosan. The incorporation of nano-scale entities into textile surfaces leads to a strong interfacial interaction and results in significant improvement in properties of the material [7-12].

The current work investigates the dyeability and color performance of nano-chitosan treated polyester fabric dyed with reactive dye.

EXPERIMENTAL

Materials and Methods

One hundred percent scoured and bleached plain-woven polyester fabric (160gr/m²) was used. Medium molecular weight chitosan powder with DD=75-85% was obtained from Aldrich. Sodium tripolyphosphate, sodium hydroxide, Glauber salt, soda ash, citric acid and acetic acid were purchased from Merck. Reactive dye stuff was commercial dye (Bezactive green S-4B) from Bezama Company.

To investigate chemical bonding, FTIR/ATR technique (Tensor 27, Bruker) was employed. The adsorption infrared spectroscopy was recorded at 1 cm^{-1} intervals in the wave number range 500–4000 cm^{-1} .

Surface modification of non-treated, hydrolyzed and chitosan treated fabrics was observed using a bal-tech scd 005 scanning electron microscope, at an acceleration voltage of 26kV and magnification of 2500X. Wettability of fabrics was determined according to international standard method AATCC-39-1980. The time of disappearance of spherical shape of a water drop being poured from a burette on fabrics was measured. Bending tests to measure the stiffness of fabrics were carried out according to ASTM-D 1388 standard test method, in which a fabric of specified width and length is slid at a specified rate in a direction parallel to its long dimension until the leading edge projects from the edge of a horizontal surface. The length of the overhang is measured when the tip of the specimen is depressed under its own mass from this measured length; the bending length and flexural rigidity are then calculated.

Dyeing of polyester fabric was carried out in lab dyeing machine (Copower Technology, Ltd., Model: H-24M). The color depth was analyzed by spectrophotometer (X-Rite Color-Eye 7000A) on CIE system (International Commission on Illumination). Rubbing fastness (Electronic crock meter) and washing fastness were measured under international standard ISO-105/X-198(E) and ISO-105-C03-1982(E), respectively.

To synthesize nano-chitosan, chitosan 1% concentration was dissolved in 2% w/v acetic acid followed by sonification at 45 watts for 30 min. Then a 1% concentration of sodium tripolyphosphate was added to the chitosan solution slowly while the sonification was carried out. The resulting solution was centrifuged at 7000 r.p.m for 30 min. The residue was washed off with distilled water, centrifuged and dried. A schematic view of the process is shown in *Figure 1*.

In order to improve the adhesion of chitosan and nano-chitosan to the surface of polyester fabric, an alkaline pretreatment was applied based on a recipe mentioned in previous work [1, 5]. Polyester samples were treated in 10% o.w.f concentration of NaOH for 60min at boil with liquor ratio 1:20. After washing, samples were naturalized in acetic 1% acid at a ratio of 1:20 for 15 min at room temperature. *Figure 1*

shows the steps involved in preparing chitosan via chemical hydrolysis following surface treatment of polyester fabric.

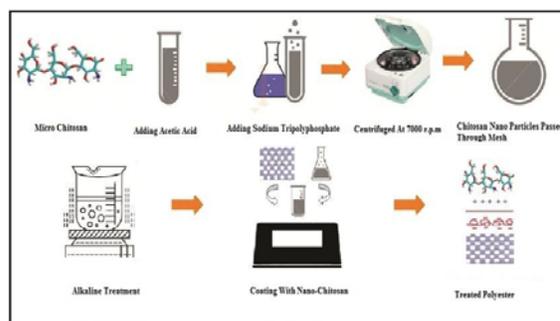


FIGURE 1. Diagram of nano-chitosan preparing and surface treatment of polyester.

Three different percentages of nano-chitosan (2%, 4% and 6% o.w.f) were used to treat fabrics. Neat polyester and alkaline treated one were immersed in an 8 % (o.w.f) concentration of citric acid (as cross linking agent) and chitosan or nano-chitosan for 30 min at 50°C. The liquor ratio was 1:50. Then, samples were dried at 80°C for 5 min and subjected to thermo fixation at 120°C for 2 min. All samples washed in detergent for 5 min at 50°C so unbounded chitosan could be removed.

The weight differences in samples after alkaline treatment and nano-chitosan coating were measured according to Eq. (1):

$$W \% = \left| \frac{W_1 - W_2}{W_1} \right| * 100 \quad (1)$$

Where $W\%$ is the percentage difference in the weight of the fabric and W_1 and W_2 are weights of the fabric before and after treatment, respectively.

The bending test was carried out according to the standard ASTM-D-1388 test method. A sample of specified width and length was placed on the top of the device and covered with a ruler. The fabric and the ruler were moved together until the sagging edge of the fabric touched the inclined plane. The length indicated on the ruler was recorded as the bending length.

The water droplet adsorption time test was done according to the AATCC-39 1980 standard test method. A drop of water was poured from the burette to the surface of fabric. The time to disappearance of the water drop was measured.

Samples of treated and untreated polyester weighing 2 grams were dyed using 1% (o.w.f) reactive dye in a sample dyeing machine according to exhaust method and dyeing curve shown in Figure 2 (liquor ratio 1:20, soda ash 8gr/lit and glauber salt 10gr/lit) [10].

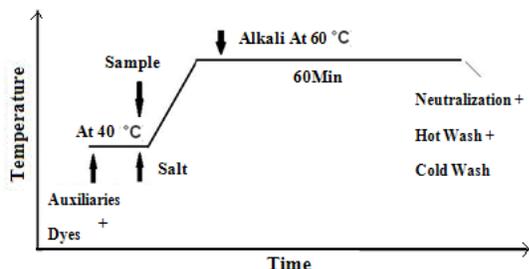


FIGURE 2. Dyeing curve of samples with reactive dye.

The depth of the dyed fabrics was analyzed by measuring K/S values of samples. The K/S ratios of the samples were determined by spectrophotometry using the Kubelka – Munk equation as follows [10, 11]:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (2)$$

Where R is reflectance percentage, K is absorption co-efficient and S is scattering coefficient of dyes.

RESULTS AND DISCUSSION

Physical Properties

Table I shows weight differences, bending lengths and water absorption times of alkaline treated and untreated polyester fabrics. After alkaline treatment of polyester fabric, water droplet adsorption reached 2.18 Sec. This could be due to the physical or chemical changes on alkaline-treated polyester fiber. Alkaline treatment changes the surface structure of fiber by creating pores and cracks. This enhances the hydrophilicity of PET and promotes surface wetting. In addition to physical changes, the alkaline hydrolysis causes chain cleavage as OH⁻ attacks ester-bonded carbonyl carbon resulting in hydroxyl (-OH) and -COO groups on the fiber surface as shown in Figure 3) [5].

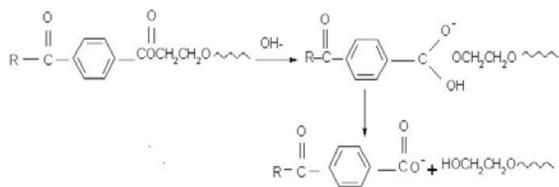


FIGURE 3. Alkaline treatment of polyester fiber.

The bending strength shows the stiffness or softness of fabric, which directly affect hand. As can be seen in Table I, the bending length decreased from 2.8 cm to 1.9 cm after alkaline treatment, which means the fabric is more flexible than untreated polyester. This result is in agreement with previous work [8,12]. Bending length slightly decreased in nano-chitosan treated fabrics compared to that of alkaline treated fabric. This slight decrease in bending length could be a result of penetration of nano-chitosan into the pores of polyester fiber, which would not affect the flexibility of fabric significantly [8].

TABLE I. Weight difference, bending length and Water absorption results.

	Weight difference (%)		Bending length(cm)	Water adsorption time(s)
PET	-----		2.8	4.12
Alkaline treated PET	31.5%	-	1.9	2.18
Nanochitosan(%) Treated				
	2	2.9%	+	1.8
	4	3.1%	+	1.63
	6	3.6%	+	1.46

Fourier Transform-Infrared Spectroscopy (FTIR/ATR)

Figure 4 shows the spectra of a) untreated b) alkaline treated and c) chitosan treated polyester. The presence of strong peaks between 700 cm⁻¹ and 1700 cm⁻¹ is in agreement with previous research [5]. From Figure 4(a) the stretching vibration bands of C=O at 1017.32 cm⁻¹ and C-O-C at 1341.68 cm⁻¹ are attributed to the ester groups of polyester. In Figure 4(b) a peak appearing at 2361.33 cm⁻¹ confirms the presence of carboxylic groups (-COOH) in the alkaline treated polyester. In Figure 4(c) disappearance of a peak related to carboxylic groups indicates the nano-chitosan reacted strongly via hydrogen bonding with polyester [5,10].

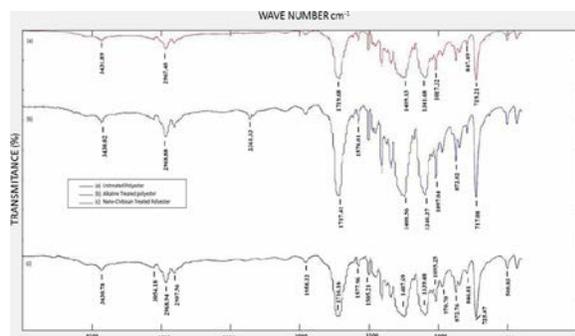


FIGURE 4. FTIR/ATR spectra of (a) polyester, (b) Alkaline polyester, (c) Alkaline Polyester Coated with nano-Chitosan.

Scanning Electron Microscopy (SEM)

Figure 5 shows SEM micrographs of a) untreated polyester, b) alkaline treated polyester, c) 2%, d) 4% and e) 6% nano-chitosan treated polyester. The polyester fiber has a smooth surface, while alkaline treatment made some pores and scars on the surface of polyester (Figures 5a and 5b). The pores made by alkaline hydrolysis could be sites for penetration of nano-chitosan. This phenomenon can be seen clearly in Figure 5 (c-e). When the content of nano-chitosan increased to 6% the pores were almost filled by chitosan nanoparticles shown in Figure 5e.

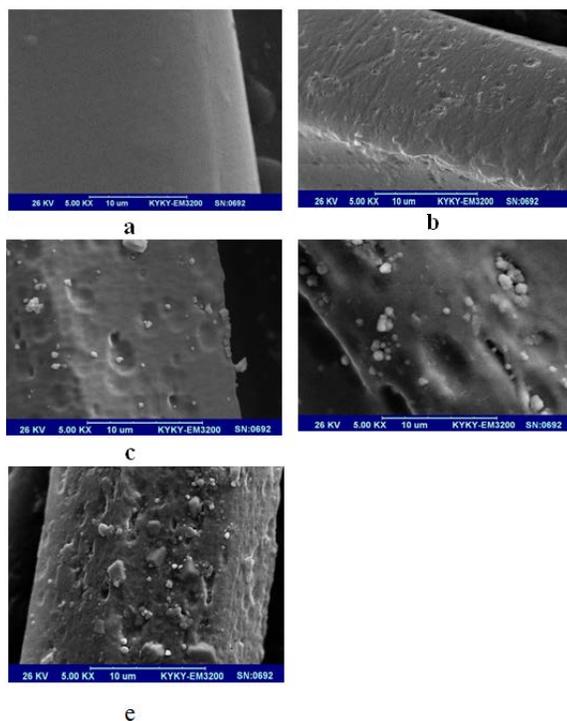


FIGURE 5. SEM micrographs of a) polyester, b) alkaline polyester, c) 2% nano-chitosan, d) 4% nano-chitosan and e) 6% nano-chitosan treated polyester.

Color Depth Analysis

The K/S values show the depth of color of dyed fabric. Figure 6 shows that after nano-chitosan treatment it is possible to dye polyester with reactive dye. Moreover, increased nano-chitosan concentration provided higher depth of shades.

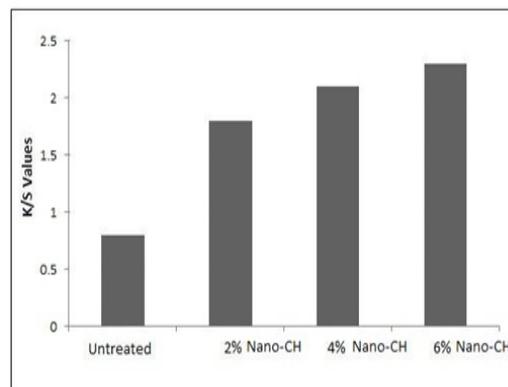


FIGURE 6. Changes in color difference of untreated and treated fabric.

Color Fastness

The color fastness results are presented in Table 3. The fastness ratings of nano-chitosan treated and untreated polyester are almost the same. However, the wet rubbing fastness is lower than the dry fastness. Alkaline pretreatment of fabrics improved the chemical bonding between nano-chitosan and polyester. Hence, the increase in dye-sites caused improvement of dye fastness.

TABLE III. Color fastness to rubbing and washing.

Nano-chitosan treated(%)	Rubbing fastness		Washing fastness Color staining
	dry	wet	
0	3	3	4
2	4.5	4	4
4	4.5	4	4.5
6	4	3	4

CONCLUSION

In this study, polyester fabric was alkaline treated and then coated with nano-chitosan, which was prepared via chemical hydrolysis. Alkaline and nano-chitosan treatments caused improvement in wettability and bending length. Penetration of nano-chitosan into pores resulting from alkaline treatment along with strong hydrogen bonds between chitosan and polyester made it possible to dye polyester with a reactive dyestuff. Increasing nano-chitosan content resulted in higher dye adsorption. Dyed samples

showed good dry-rubbing and washing fastness and moderate wet-rubbing fastness. According to these results, reactive dyeability of polyester at low temperatures in the absence of a carrier provides a more environmentally friendly alternative to traditional polyester dyeing methods.

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