ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

NEW METHOD OF UNION DYEING OF COTTON/NYLON BLENDED FABRIC USING CHITOSAN NANOPARTICLES

KALIYAMOORTHI Karthikeyan[1], THANGAVELU Ramachandran[1]

[1]Karpagam University, Department of Textile Engineering, Coimbatore, Tamilnadu, 641021, India

Corresponding author: K. Karthikeyan, E-mail: karthi_info3@yahoo.co.in

Abstract: *Dyeing of fabric blends such as Cotton/Nylon (C/N) is presently dyed by two-bath or one-bath two-step dyeing. Cellulose fibers when immersed in water produce a negative electrokinetic potential. The negative charge on the fiber repels the anionic dye ions and consequently the exhaustion of the dye bath is limited. When the fabric is treated with chitosan (polyacrylamide), the primary hydroxyl groups of cellulose is partially modified into amide groups, which intern leads the cellulose to act like as polyamide fiber. As a naturally deriving substance, chitosan has several beneficial properties such as being nontoxic and biodegradable. Absorption of acid dyes by chitosan is mostly by electrostatic interactions, the larger surface area of chitosan nanoparticles is advantageous for enhancement of dyeability of textile material. Experimental work was carried out on finding the possibility of one bath dyeing of chitosan pretreated cotton/nylon fabric with acid dyes. The effect of chitosan pretreatment on dyeability, fastness, and few physicochemical properties has been investigated, and results are presented. The cotton/nylon sample treated with 0.3% of chitosan nanoparticles had higher K/S values, washing, and crocking fastness. Also observed, dyed fabric had antibacterial potential due to the antibacterial property of chitosan. New method of union dyeing showed level dyeing having good fastness properties and offers the option of cost effective and eco-friendly.*

Key words: *amide groups, acid dyes, chitosan, colour strength, pH, oxidation*

1. INTRODUCTION

Good solidity of hue and depth is more critical in 50:50 blends and in union fabrics, such as nylon warp stretch fabrics, containing cotton or nylon/ cotton wefts for swim wear and narrow fabrics, rain wear or work wear. Nylon/cotton is also used in socks. Nylon being a polyamide contains many amide groups in its structure. It also contains free amine groups at the ends of its polymeric chains, although the number of these free amine groups is less than the number of carboxylic groups, and the fiber possesses a negative charge unless in the appropriate pH region[1].

These amide and amine groups provide excellent hydrogen bonding sites and are the main factors contributing to the substantively of the dye molecules. Acid dyes have very little affinity for cotton, but cationic cotton can be dyed readily with acid dyes. The ammonium groups act as dye sites [2]. Conventional dyeing method of the cotton/nylon blend fabric carried out by two-bath or one-bath two-step dyeing with reactive / acid dyes (duration of 3 hours).

Chitosan is the deacetylated derivative of chitin. Chitin is the second most abundant polysaccharide found next to cellulose, the main component in the shells of crustaceans.Chitosan has the same backbone with cellulose except for its acetamide group instead of a hydroxy group. Chitosan is ß-1, 4-linked linear polysaccharides, and most of its glucopyranose residues are 2, 2-deoxy-b-D-glucopyranos [3]. Chitosan can easily adsorb anionic dyes, such as acid dyes, by electrostatic attraction due to its cationic nature in an acidic condition.

The use of chitosan, a polycationic biopolymer, is more eco-friendly [4]. The dye enhancement activity of Chitosan nanoparticles was seldom reported. Unique characters of nanoparticles for their small size and quantum size effect supposedly promised Chitosan nanoparticles to exhibit superior dyeability improvement [5].

Cellulosic fabrics can be oxidized by several oxidizing agents such as hydrogen peroxide (H2O2), sodium persulphate (Na2S2O8) and potassium periodate (KIO3). Oxidation of cellulosic fabric using sodium metaperiodate (NaIO4) has been extensively investigated in the literature, since it leads to selective cleavage at the C2 and C3 vicinal hydroxyl groups to yield a product with 2, 3-dialdehyde units along the polymer chain. The latter is an important functional polymer for further derivatisation to specialized products. Potassium periodate is known to selectively convert 1, 2-dihydroxyl groups to a pair of aldehyde groups without significant side reaction and is widely used in structural analysis of carbohydrates [6].This oxidizing agent was used successfully for surface oxidation of cotton fiber in the preparatory process with chitosan nanoparticles to produce chitosan coated cotton fiber.

A novel one step process is devised for preparation of modified fabrics; the fabric is treated in an aqueous solution containing the oxidant and chitosan [7]. Therefore, with blended fabrics or mixed fabrics, using cationic cellulosic fiber and regular cotton, two-tone effects can be obtained in one-bath dyeing. Meanwhile, this phenomenon gives a possibility to one-bath dyeing for blended fabrics, using cationic cellulosic fiber and nylon [8]. The main objective of this research is to explore the possibilities of union dyeing of cotton /Nylon fabric with acid dyes by introducing amino group in oxidized cotton using chitosan nano-particles and also enhancing antibacterial properties of dyed fabrics.

2. EXPERIMENTAL

2.1 Materials

Ready for dyeing 50/50 Cotton/Nylon (C/N) blended fabric with the weights of 150 g/m^2 was used. Chitosan (Degree of deacetylation (DD) = 92.5%, Molecular Weight=1000kD) and C.I.Acid Red 138 was used respectively for pretreatment and dyeing. All other reagents are commonly used laboratory reagent grade.

2.2. Preparation of chitosan nanoparticles

Chitosan was dissolved in a dilute aqueous acetic acid solution of 0.5 % (w/v). Aqueous ammonia was then dropped into the chitosan solution to precipitate the chitosan. The obtained gel-like swollen chitosan was washed to neutral with deionised water, and was then transferred into a 25 mL volumetric flask. The total volume of liquid was added to 25 mL with deionized water. An ultrasound processor (Cole Parmer – Qsonica) with a probe of 6mm diameter was used and it was put into the volumetric flask. Ultrasound treatment was conducted under an ice-water bath at 25W for 15 min. Finally, a milky emulsion was obtained.

2.3. Pretreatment with chitosan and sodium periodate

Pre-washed cotton/nylon blend fabrics were soaked for 30 minutes at 40 ºC in chitosan nano-emulsion at five different concentrations 0.01%, 0.05%, 0.1%, 0.3 and 0.5% (w/v) with 50 mg/100ml of sodium periodate (1:50). Then cotton/nylon blend fabric washed several times with water and dried.

2.4 Dyeing

Dyeing of the pretreated blend fabrics were carried out in the laboratory dyeing machine by exhaust method. Fabrics were dyed with 3% C.I.Acid Red 138 in a bath containing 9 %of Ammonium acetate, and 3% hydrochloric acid of 10%, with a liquor ratio of 1:20. Firstly, salt and acid were added to water and the dyeing bath was warmed at 60º C, then the samples were immersed in the dyeing bath and the dyeing continued for 10 min, followed by adding dye solution and the dyeing continued for 15 min., then the temperature was raised to boiling through 20 min, the dyeing was continued at this temperature for 30 min, finally the dyeing was stopped and the dyeing bath was cooled.

2.5 Evaluation of the dyed cotton fabrics

The color strength (K/S) of the treated sample using the undyed samples as blank was determined using X-rite spectrophotometer, according to Kubelka- Munk equation.

$$K/S = (1-R)^2 / 2R \quad (1)$$

The color difference (ΔE) and relative color strength between chitosan treated dyed and untreated dyed samples were also calculated according to Eq. (2)

Realtive colour strength (%) = K/S value of Tretated sample / K/S value of Untreated sample (2)

2.6 Antibacterial Efficiency

AATCC100-2012 test method was used to analyze the antibacterial activity of the treated cotton/nylon blend fabrics. The organisms taken for this study were *Staphylococcus aureus* (*S.aureus*) and *Escherichia coli (E.coli*). To evaluate the antibacterial activities of the treated fabrics, the reduction in colony number between the treated and untreated samples after incubation was determined with two specimens for each organism.

3. RESULT AND DISCUSSION

3.1. Colour Strength

K/S value of a dyed material has a close relationship to the amount of dye absorbed by the fabric. K/S values and the relative color strength of cotton/nylon dyed samples with C.I.Acid Red 108 are shown in *Table 1*. It was observed that the color measurements of untreated cotton/nylon fabric have the lowest values. This was because cotton fibers when immersed in water produce a negative zeta potential. The negative charge on the fiber repels the C.I.Acid Red 138 dye ions and consequently the exhaustion of the dye bath was limited which lead to the decrease of the color measurements. The color measurements of cotton/nylon blends increased with the Chitosan pretreatment.

Table 1: *K/S Values of dyed samples*

Chitosan concentration (%)	ΔE	K/S	Relative colour strength (%)
0	-	12.246	100
0.01	1.494	16.786	137
0.05	1.796	17.724	145
0.1	1.909	18.967	154
0.3	2.321	20.989	171
0.5	2.307	20.693	169

This enhancement in (K/S) values of chitosan treated cotton/nylon fabrics shows that the chitosan has an incremental effect in dyeing processes. The improved dye ability is postulated due to the presence of amide groups (-CONH2) available from the polyacrylamide (chitosan). It is observed (*Table 1*) that by increasing the chitosan concentration the (K/S) values has been increased up to 0.3% and then decreased. This detraction in (K/S) values of chitosan treated cotton fabric is associated with the saturation of cotton/nylon fabrics by chitosan.

3.2. Colour Fastness Properties

For evaluation of colour fastness of dyed fabrics, the following test methods were performed with three repeats and average values given in table 2.

- Colour fastness to Washing, according to ISO 105 C06:2010
- Colour fastness to Rubbing, according to ISO 105 X12:2002
- Colour fastness to Light, according to ISO 105 B02:2013

Table 2: *Colour fastness properties*

Chitosan concentration (%)	Wash Fastness			Wet Rub Fastness	Light Fastness
	Colour change	Staining on Cotton	Staining on Nylon		
0	3-4	3-4	2-3	3	4
0.01	4	4-5	4-5	4	4
0.05	4	4-5	4-5	4	4
0.1	4	4-5	4-5	4	4
0.3	4	4-5	4-5	4	4
0.5	4	4-5	4-5	4	4

The attachment of the dye molecules onto the partially-modified cellulosic substrate is by ionic bonding since no dyes strips out from the dyed sample. This is also indicative through the wash fastness properties. The fastness values of all such dyed samples are quite improved whereas untreated sample shows poor washing and crocking fastness properties.

3.3. Physical properties

Dyed cotton/ nylon samples were tested for various fabric properties such as air permeability and tensile strength. For Air permeability testing, ten measurements carried out in each sample using TEXTEST FX 3300 Air Permeability Tester and average value given in table 3. It is inferred from the table 3 that there is a change in air permeability of the nano chitosan treated cotton fabric as compared to the untreated one. It is perhaps due to the attachment of chitosan to all over the whole structure of the fabric. The slight losses of air permeability in the pretreated fabrics have not affected intact breathability of the cotton fabrics which is important requirement for comfort properties.

Table 3: *Physical properties*

Chitosan concentration (%)	Tensile Strength-Warp (N)	Air Permeability ($l/m^2/s$)
0	459.5	350.5
0.01	397.4	304.5
0.05	395.6	298.7
0.1	392.2	293.2
0.3	389.8	290.9
0.5	398.5	289.7

For Tensile strength, five measument taken in warp direction and it is obvious from table 3 that tensile strength loss slightly significant after the process. The slight loss of strength is mainly due to the oxidation and stiffening of the molecular backbone after cross-link formation.

3.4. Antibacterial Activity

The antibacterial activities of cotton/nylon fabrics have been tested with prepared two specimens for each analysis and figure 1 represents average reduction values against both *E. coli* and *S. aureus*. These data show that treated fabrics had bacterial reduction. The antibacterial activity of cotton treated with chitosan was considerably decreased after dyeing due to the blocking of the cationic groups of the chitosan and fibers by dye molecules. The reduction values exhibited by chitosan treated and subsequently dyed fabrics are higher than un-dyed samples which prove that chitosan treatment enhances the antibacterial activity of the dyed fabrics. It has been observed that the antibacterial action of treated samples is due to chitosan nanoparticles.

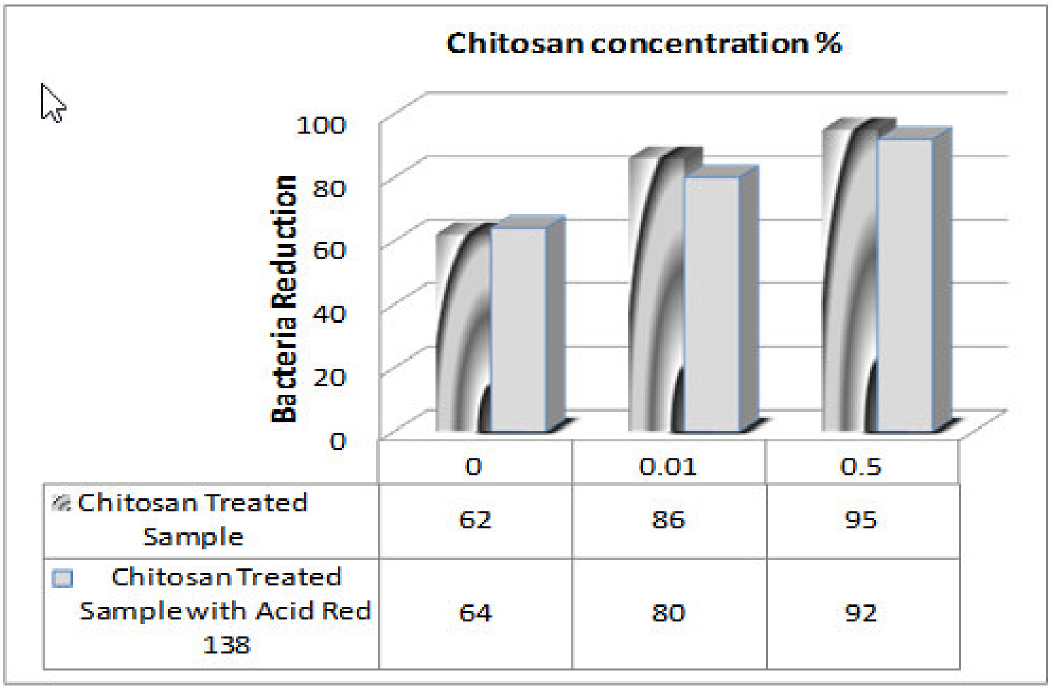

Fig. 1: *Graphical representation of antibacterial activity results*

4.CONCLUSIONS

This paper described the ability to dye cotton/nylon blend fabric in one step, one dyeing bath with shortened time. It was found that the pretreatment of cotton/nylon fabrics with chitosan nanoparticles enhanced the dye uptake and also increased the antibacterial activity of cotton/nylon fabrics compared with untreated fabric. The improved dye ability of cotton to acid dye is postulated due to the presence of amide groups available from the chitosan. Based on the depth of shade values, it was found that by increasing chitosan nanoparticles concentration up to 0.3% (w/v), there was significant improvement of relative color strength. Moreover, colorfastness properties to washing and wet crocking of the treated samples were improved. Union dyeing of cotton/ nylon fabrics with acid dyes using biodegradable modification agent such as chitosan is an environmental friendly approach in the field of textile dyeing industry.

REFERENCES

[1] Wu, Yen-Ping, “Cotton/Nylon mixed fabric - The art of warp weft heterochromatic”, D*yeing and Finishing*, vol. 24, 2002, pp. 23-26.

[2] Shang Run-ling, “One-bath dyeing of cotton/nylon mixture with reactive and acid dyes”, Dyeing and Finishing, 2010, 2101-16.

[3] Yang, H.C.; Wang, W.H.; “Preparation and application of nanochitosan to finishing treatment with anti-microbial and anti-shrinking properties”, *Carbohydrate Polymers* 79, 2010, pp.176-179

[4] Liu, X.D., Nishi, N., Tokura, S., & Sakairi, N. “Chitosan coated cotton fiber preparation and physical properties”, Carbohydrate Polymers, 44, 2001, 233.

[5] Hu Z.G., Chan W.L., Szeto Y.S., “Dyeability improvement of silk with chitosan nanoparticles”, Abstract of the 230th ACS National Meeting, Washington DC, August 2005.

[6] Varma, A.J. & Kulkarni, M.P.”Oxidation of cellulose under controlled conditions”, Polymer Degradation and Stability, 2002 77, pp.25-27

[7] Ristić, N., Ristić I., “Cationic Modification of Cotton Fabrics and Reactive Dyeing Characteristics”, Journal of Engineered Fibers and Fabrics, 2012, 115.

[8] Tsai, U-Yueh, Wen, Ying & Hsieh, Hsing, “Cotton/Nylon mixed fabric active single bath dye”, *Dyeing and Finishing*, vol. 24, 2002, pp. 27-28.

[9] ISO 105 B02: Colour fastness to artificial Light: Xenon arc fading lamp test, 2013.

[10] ISO 105 C06: Colour fastness to domestic and commercial laundering, 2010

[11] AATCC 100: Antibacterial Finishes on Textile Materials: Assessment of, 2012, 166-168.