Fibers and Polymers 2005, Vol.6, No.3, 229-234

Digital Ink-jet Printing for Chitosan-treated Cotton Fabric

P. S. R. Choi, C. W. M. Yuen, S. K. A. Ku, and C. W. Kan*

Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

(Received December 6, 2004; Revised April 11, 2005; Accepted May 29, 2005)

Abstract: In this paper, chitosan was suggested for using as a replacement for sodium alginate in the pretreatment print paste for digital ink-jet printing for cotton fabric. Pretreatment print pastes prepared from the mixture of chitosan and acetic acid with the appropriate viscosity gave satisfactory prints on the cotton fabric. Chitosan-treated cotton fabrics were digitally ink-jet printed with four different colors and the color fastness rating of the printed fabrics was satisfactory. Experimental results revealed the possibility of pre-treating the cotton with chitosan to replace the sodium alginate normally present in the pre-treatment print paste recipe.

Keywords: Digital ink-jet printing, Chitosan, Sodium alginate, Thickener, Pretreatment print paste

Introduction

The advantages of digital ink-jet printing are well known and the process has grown recently. Digital ink-jet printing offers benefits such as speed, flexibility, creativity and cleanliness [1,2]. In conventional textile printing of cotton fabric with reactive dyes, the reactive dyes are applied with the alkali and other chemicals in the form of a print paste. However, due to the specific purity and conductivity requirements for ink-jet printing [3], none of the conventional printing chemicals can be directly incorporated into the ink formulation. As a result, the cotton fabric was pretreated with the printing chemicals prior to the stage of digital ink-jet printing.

Recently, sodium alginate is commonly used for preparing thickener in the pretreatment print paste for digital ink-jet printing with reactive dyes due to its ready solubility and excellent stability even after high-temperature fixation treatments [4]. In addition, the extent of interaction of sodium alginate with reactive dyes is very small. Similar to alginate, chitosan is also widely used as a novel biomaterial. As a natural polymer, alginate and chitosan are biocompatible, biodegradable and non-toxic [5]. Previous study reported that chitosan could be applied to different textile area [6] and one of the areas was applying it to conventional textile printing for improving the dye uptake and color fastness. Therefore, the aim of this paper was to study the possibility and effectiveness of chitosan in replacing the sodium alginate as a thickener in the pretreatment print paste for digital ink-jet printing for cotton fabric.

Experimental

Fabric

100 % singed, desized, scoured and bleached cotton plain weave fabric of 136 g/m^2 with 133 ends/inch (40s) and 72 picks/inch (40s) was used.

*Corresponding author: cwkan1@netvigator.com

Preparation of Pretreatment Print Paste

Chitosan in solid form was supplied by Sigma Co. (USA). A stock solution of chitosan with medium viscosity (~150 mPa·s) was prepared by dissolving 5 g of chitosan completely into 500 m*l* of 10 % acetic acid. The amount of chitosan used in the pretreatment print paste was measured directly from the stock chitosan. Suitable amounts of urea and sodium bicarbonate ($NaHCO_3$) were also added to the pretreatment print paste. In order to study the effect of individual parameter in each color, a $L_9(3)^4$ orthogonal analysis was used with the detailed experimental arrangement shown in Tables 1 and 2. The pretreatment print pastes were prepared in accordance

Table 1. Factors and levels used in orthogonal analysis

Factor	Pretreatment print paste gradient			Post-treatment
Level	Chitosan	Urea	Sodium bicarbonate	Steaming time
I	15 m*l*	5 g	2 g	3 min
II	25 m*l*	10 g	4 g	5 min
III	40 m*l*	20 g	8 g	10 min

Table 2. Experimental arrangement

Test run	Pretreatment print paste gradient			Post-treatment
	Chitosan	Urea	Sodium bicarbonate	Steaming time
1	I	I	I	I
2	I	II	II	II
3	I	III	III	III
4	II	I	II	III
5	II	II	III	I
6	II	III	I	II
7	III	I	III	II
8	III	II	I	III
9	III	III	II	I

with the requirements stated in Table 2 and made up to the final weight of 150 g with deionized water. In addition, a control pretreatment print paste with weight of 200 g deionized water was prepared containing 150 g sodium alginate, 10 g urea and 8 g sodium bicarbonate [4].

Fabric Pretreatment

The pretreatment print paste was padded onto the cotton fabric using a padding machine (Labortex Co. Ltd.) with the pressure of 2.6 kg/m^2 and padding speed of 2.5 rpm until a finally pick-up of 80 % was achieved. The chitosan pretreated fabrics were dried in an oven at 80 °C and cured at 170 °C for 1.5 minute while the control fabric was dried in the oven at 80 °C. All the pretreated fabrics were conditioned before digital ink-jet printing.

Digital Ink-jet Printing and After-treatment

A digital ink-jet printer (Mimaki Tx2-1600, Mimaki Engineering Co., Ltd.) was used and it was a piezo electric drop-on demand printer. Four commercially available reactive dyes with colors of Cyan (C), Magenta (M), Yellow (Y) and Black (K) were used without further purification. The reactive dyes inside the ink had different reactive systems in which Magenta, Yellow and Black contains vinylsulphone reactive system while Cyan contains triazine reactive system [7,8].

A pattern of 80 mm × 80 mm square was printed for each single color with 360 dpi × 360 dpi for easy comparison. After digital ink-jet printing, the printed fabrics were air-dried and then steamed at 110 °C for fixing the color. The steaming time chosen was employed in accordance with the experimental arrangement stated in Table 2 and the steaming time for control fabric was 5 minutes [4]. The steamed fabrics were finally washed in 10 g/*l* nonionic detergent until all unreacted dyes and chemicals were removed.

Color Yield Measurement

The printed fabrics were conditioned before color yield measurement with a Macbeth Color Eye 7000A Spectrophotometer. The fabric was folded twice for ensuring opacity and measured twice, i.e., measured on both the warp and weft directions. The measured results were then averaged.

The color yield expressed as a K/S value from the wavelength of 400 nm to 700 nm with 20 nm interval within the visible spectrum was calculated. The K/S values were summed with the use of equation (1). The higher the K/S (sum) value, the more the dye-uptake will be resulting in better color yield.

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

where

K: absorption coefficient, depending on the concentration of colorant

S: scattering coefficient, caused by the dyed substrate

R: reflectance of the colored sample

Determination of Colorfastness of Printed Fabric

The colorfastness of the printed fabrics to light, laundering and crocking were assessed by AATCC Test Method 16-2001, 20 AATCC fading units (AFU), AATCC Test Method 61-2001 and AATCC Test Method 8-2001, respectively.

Outline Sharpness Measurement

In order to compare the outline sharpness of the prints, the width of the printed pattern in both warp and weft directions were measured using an optical light microscope (Nikon Optiplot-Pol) with a magnification of 400.

Results and Discussion

The optimum condition of the pretreatment print pastes containing chitosan and steaming time was obtained by means of the orthogonal analysis and the results were summarized in Table 3.

Effect of Chitosan and Acetic Acid

Figure 1 clearly shows that the Black color had the best color yield followed by Cyan, Magenta and Yellow colors. When the amount of chitosan used in the pretreatment print paste was increased, the color yields of the printed fabrics were enhanced correspondingly. This concluded that chitosan could serve the function of increasing the color yield of ink-jet printing and this behavior could be explained on the basis that the amino groups present in the chitosan take up a proton from the slightly acidic dyebath to form the $-NH_3^+$ groups. These $-NH_3^+$ groups being electropositive in nature facilitate the transfer of the negatively charge dye anion from the bath onto the fabric, thereby improving the color fixation [9].

In addition, the results also show the color yield of these four different colors under the influence of various amounts of acetic acid used in the pretreatment print paste. It was apparent that the amount of chitosan used is proportional to the amount of acetic acid used in pretreatment print paste. Figure 1 showed that when increasing the amount of acetic acid used in the pretreatment print paste, the color of the digital ink-jet printed cotton fabric could be deepened with the maximum color yield achieved in 40 m*l* of chitosan used in the pretreatment print paste.

Effect of Sodium Bicarbonate

Similar to the dyeing process, alkali is used in the printing process for the reactive dye color development of all shades [9, 10]. The presence of alkali is essential to produce ionization of accessible cellulose hydroxyl groups which can then react with the reactive dyes in the fixation stage. Sodium bicarbonate has been the preferred alkali because it is cheap and can give sufficient pretreatment print paste stability with most of the reactive dyes available in the markets [9,10]. During steaming, sodium bicarbonate loses carbon dioxide and increases the

Table 3. Orthogonal table for the optimization of each color

Test run	Substrate			Post-treatment	Color yield (*K/S*)			
	Chitosan	Urea	$NaHCO_3$	Steaming time	C	M	Y	K
1	I	I	I	I	62.93	40.82	35.62	114.76
2	I	II	II	II	70.27	52.89	47.38	132.75
3	I	III	III	III	56.08	32.04	27.77	91.3
4	II	I	II	III	65.22	45.77	44.84	130.25
5	II	II	III	I	76.93	55.05	55.82	152.57
6	II	III	I	II	57.42	35.14	35.86	95.46
7	III	I	III	II	77.42	71.28	58.02	174.17
8	III	II	I	III	76.62	54.07	49.09	134.06
9	III	III	II	I	64.95	41.92	42.82	117.04
Cyan (C)								
ΣI	189.28	205.57	196.97	204.81				
ΣII	199.57	**223.82**	200.44	**205.11**				
ΣIII	**218.99**	178.45	**210.43**	197.92				
Different	29.71	45.37	13.46	7.19				
Magenta (M)								
ΣI	125.75	157.87	130.03	137.79				
ΣII	135.96	**162.01**	140.58	**159.31**				
ΣIII	**167.27**	109.10	**158.37**	131.88				
Different	41.52	52.91	28.34	27.43				
Yellow (Y)								
ΣI	110.77	138.48	120.57	134.26				
ΣII	136.52	**152.29**	135.04	**141.26**				
ΣIII	**149.93**	106.45	**141.61**	121.70				
Different	39.16	45.84	21.04	19.56				
Black (K)								
ΣI	338.81	419.18	344.28	384.37				
ΣII	378.28	**419.38**	380.04	**402.38**				
ΣIII	**425.27**	303.80	**418.04**	355.61				
Different	86.46	115.58	73.76	46.77				

Figures in **bold** form showed the greatest value among the values in the levels of different factors used.

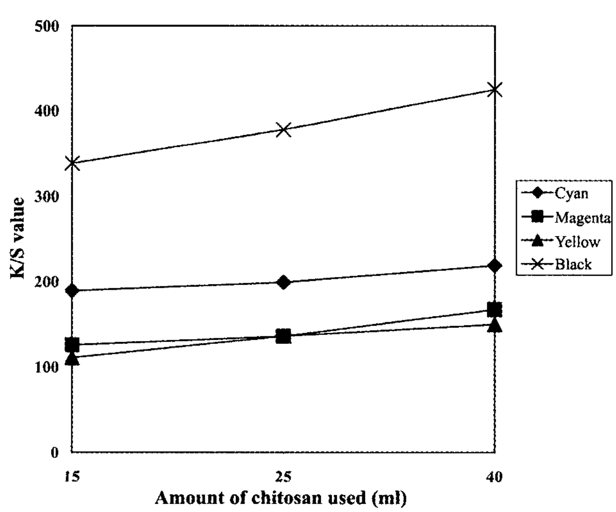

Figure 1. Effect of the amount of chitosan used on the color yield of different colors.

ionization of cellulose which thus promotes the dye-fiber interaction in the fixation stage.

From Figure 2, it was also noted that the Black color had the best color yield followed by Cyan, Magenta and Yellow. However, the effects of Cyan, Magenta and Yellow colors were not significant when compared with the Black color. Generally speaking, when the amount of the sodium bicarbonate used in the pretreatment print paste was increased, the color yields of the printed fabrics were increased. Furthermore, it was noted that the neutralization effect was not significant in the pretreatment print paste because when both amount of acetic acid and sodium bicarbonate increased, no significant reduction of the final color yield was observed.

Effect of Urea

Urea is essential in the pretreatment print paste because during the steaming process, particularly during the use of superheated steam right after the fabric is digitally ink-

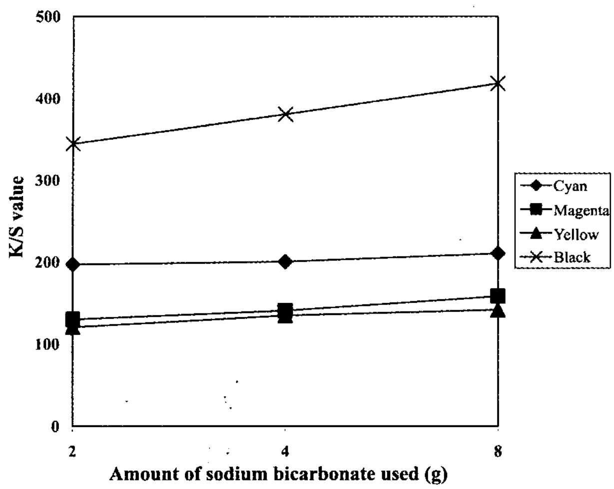

Figure 2. Effect of the amount of sodium bicarbonate used on the color yield of different colors.

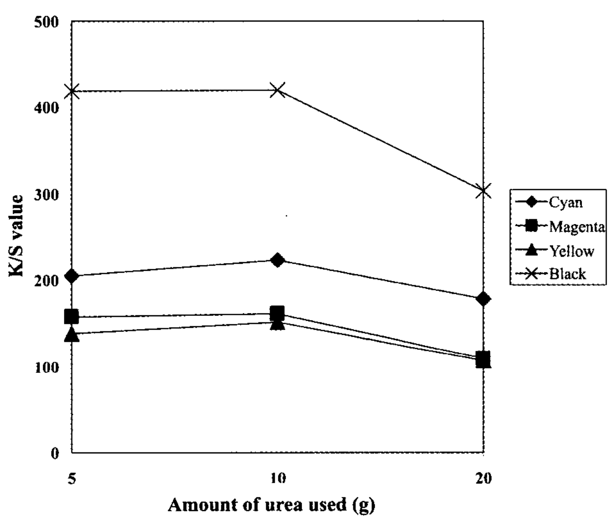

Figure 3. Effect of the amount of urea used on the color yield of different colors.

printed. It swells the cotton fibers so that the dye can penetrate the fibers rapidly [10-12]. Therefore, urea acts as a solvent for the reactive dye and also it performs as a moisture-absorbing agent in the pretreatment print paste to increase the moisture regain during the steaming process [10-12]. Thus, urea accelerates the migration of dye from the thickener film into the cotton fiber and the urea also reduces the yellowing of cotton under hot, dry alkaline conditions.

Figure 3 shows the color yield of different colors under the influence of various amounts of urea used in the pretreatment print paste. The results showed that the urea could deepen the color of the ink-jet printed cotton fabric with the maximum color yield at the amount of 10 g in the pretreatment print paste. In comparison, the Black color obviously showed the greatest color yield followed by the Cyan, Magenta and finally Yellow colors. The order of effect was similar to that of the results reported previously [4,10]. However, an interesting observation in Figure 3 was that when the amount of urea used in the pretreatment print paste was more than 10 g, the color yield of the ink-jet printed fabrics would decrease. When the amount of urea used was further increased to 20 g, the color yield of the ink-jet printed fabric dropped significantly which was paler than that of 5 g of urea used. Such drop of color yield with respect to the increasing amount of urea used in the pretreatment print paste might be due to the increase of moisture regain of the fibers during the steaming process. Owing to the hygroscopic nature, urea was used as a moisture-absorbing agent during the steaming process. A large amount of urea used in the pretreatment print paste could enhance the moisture absorption and also cause the hydrolysis of reactive dye during the steaming process. Furthermore, the reactive inks of Magenta, Yellow and Black have a dye structure of vinylsulphone type. This type of dye has a tendency to become deactivated in the presence of urea. So the decrease in color yield was believed probably to be due to the thermal decomposition of urea to biuret and ammonia followed by the conversion of the vinylsulphone dye to the inactive aminoethylsulphone rather than a direct reaction between the dye and urea [7].

Effect of Steaming Time

Steam serves as a convenient source of both water and heat which can be transferred rapidly and uniformly over the surface areas of the ink-jet printed cotton fabrics. Superheated steam is used because it shows the advantages of faster heating, shorter fixation time and fewer colors spread [10].

Figure 4 reflects the effect of steaming time on the color yield of different ink-jet printed colors on the cotton fabric. The Black color showed the best color yield followed by Cyan, Magenta and Yellow with the same sequence shown

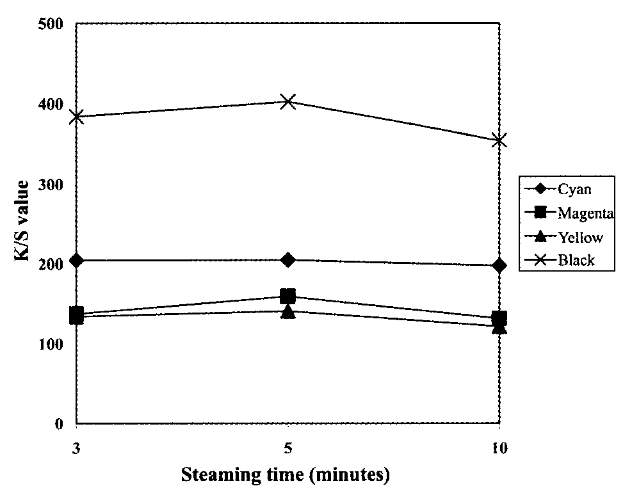

Figure 4. Effect of steaming time on the color yield of different colors.

in the previous sections. It was noted that the optimum *K/S* values of all colors were obtained at the steaming time of 5 minutes. However, when the steaming time was extended to more than 5 minutes, the color yield of the digital ink-jet printed fabrics would be reduced to different extents. The reduction of color yield at prolonged steaming time might be a combined effect of both chemicals and steaming time used. With regard to the prolonged steaming time at high temperature, i.e., 110 °C, decomposition of urea would occur producing ammonia and biuret-type products inside the steaming chamber [13]. Owing to the reaction of reactive dyes with ammonia and the loss of alkali, lower color yield would be obtained under these conditions. Furthermore, prolonged steaming time would also provide sufficient moisture for the moisture-absorbing agent, i.e., urea, to absorb it. As a result of the combination effect, hydrolysis might occur and reduce color yield.

Optimum Condition with Using Chitosan as Thickener

Orthogonal analysis is a useful and simple technique for analyzing the process variables or factors involved in a production process. Previous studies [14-17] showed that it could provide a simple and convenient way for finding out the optimum condition and the level of importance of different factors in a production process.

After considering the results obtained from the orthogonal analysis as shown in Table 3, it was concluded that all four factors studied, chitosan, urea, sodium bicarbonate, and steaming time could affect the *K/S* value by contributing different effect on the final color yield. However, the level of importance based on the orthogonal analysis [4,16,17] was in the order of urea > chitosan > sodium bicarbonate > steaming time. Based on the results of the orthogonal analysis, the optimum condition with using chitosan as thickener for the pretreatment print paste and steaming time was concluded as chitosan = 40 m*l*, urea = 10 g, sodium bicarbonate = 8 g and steaming time = 5 minutes.

Table 4. Color yield of chitosan-treated fabric with the use of optimum condition

Color	Cyan	Magenta	Yellow	Black
Control fabric [4]	110.75	95.66	90.30	260.88
Chitosan-treated fabric	88.60	76.53	72.24	208.70

In order to verify the accuracy of the newly developed optimum condition, further experiments were conducted with the use of a control fabric and the results were shown in Table 4.

The results shown in Table 4 demonstrated clearly that the cotton fabric treated with chitosan under the optimum condition achieved a better color yield when compared with those shown in Table 3. Nevertheless, about 80 % of final color yield was obtained for each color with cotton fabric treated with chitosan when compared with the control fabric. On the whole, the optimum condition for chitosan treatment for cotton fabric could still achieve a high level of color yield in digital ink-jet printing.

Colorfastness of the Digital Ink-jet Printed Cotton Fabric

Although the control fabric had a better color yield than the chitosan-treated cotton fabric, the chitosan-treated fabric under optimum condition treatment had a better colorfastness properties than the control fabric, i.e., at least 1/2 step better. The ratings of different colorfastness of the fabrics were shown in Table 5.

The improvement in the colorfastness in the case of the finished fabric containing chitosan may be associated with the introduction of primary amino groups into the cellulosic fiber structure. Most probably these groups are deposited in the crevices between the fibers and so they may impart a cationic surface which attracts the oppositely charged reactive dye anions [18]. As a result, the digital ink-jet printability of the chitosan-treated cotton fabric was improved.

Outline Sharpness of the Digital Ink-jet Printed Fabric

The outline sharpness of the digital ink-jet printed pattern was measured by optical analysis method and the results were shown in Table 6 below.

Clearly, the digital ink-jet printed patterns in the direction of warp were thicker than those in the weft direction, both in the control and chitosan-treated fabrics. This might be due to the differential wicking effect caused by the warp and weft yarns. When considering the width of the printed pattern, the patterns printed on chitosan-treated cotton fabrics were narrower than the control fabric in both warp and weft directions. This can be attributed to reduce spreading of the printed

Table 5. Colorfastness results of digital ink-jet printed cotton fabrics

Runs	Light (20 AFU) (C/M/Y/K)	Crocking		Washing							
		Wet (C/M/Y/K)	Dry (C/M/Y/K)	Staining (C/M/Y/K)						Color change (C/M/Y/K)
				Acetate	Cotton	Nylon	Polyester	Acrylic	Wool	
Control fabric [4]	4/3/4/3	3/3/3/3	4/4/4/4	4/4/4/4	4/4/4/4	4/4/4/4	4/4/4/4	4/4/4/4	4/4/4/4	3/4/4/4
Chitosan-treated fabric	4-5/4/4-5/4	4/4/4/4	4-5/4-5/ 4-5/4-5	4-5/4-5/ 4-5/4-5	4/4-5/ 4-5/4-5	4-5/4-5/ 4-5/4-5	4-5/4-5/ 4-5/4-5	4-5/4-5/ 4-5/4-5	4-5/4-5/ 4-5/4-5	4/4-5/4-5/ 4-5

Table 6. Outline sharpness of digital ink-jet printed cotton fabric

	Color							
	Cyan		Magenta		Yellow		Black	
	Warp (mm)	Weft (mm)	Warp (mm)	Weft (mm)	Warp (mm)	Weft (mm)	Warp (mm)	Weft (mm)
Control fabric [4]	82	81	82	81	82	81	82	81
Chitosan-treated fabric	81	80	81	80	81	80	81	80

reactive inks due to the strong ionic attraction between cationic cotton and anionic reactive inks. As results, chitosan treatment enhanced the outline sharpness of the prints.

Conclusions

The evaluation of chitosn as a thickener in pretreatment print paste for digital ink-jet printing was conducted. Based on different color fastness observations, chitosan basically could work as a replacement of sodium alginate in conventional pretreatment print paste for digital ink-jet printing. However, the color yield was not as good as that of using sodium alginate in conventional pretreatment print paste recipe previously developed for digital ink-jet printing fabric. Nevertheless, the color fastness properties and the outline sharpness of the prints of cotton fabric were improved and enhanced by the chitosan treatment.

Acknowledgments

The authors would like to acknowledge the Research Grants Council of Hong Kong for the financial support of this work.

References

1. M. van Parys, *MelliandTextilberichte/International Textile Reports (Eng. Ed.)*, **83**(6), E96 (2002).
2. S. Gupta, *Ind. J. Fiber and Text. Res.*, **26**(1&2), 156 (2001).
3. P. S. Choi, C. W. M. Yuen, S. K. A. Ku, and C. W. Kan, *Textile Asia*, **35**(2), 50 (2004).
4. C. W. M. Yuen, S. K. A. Ku, P. S. Choi, and C. W. Kan, *Research Journal of Textile and Apparel*, **7**(2), 43 (2003).
5. Y. Qin, *Textiles Magazine*, **31**(2), 14 (2004).
6. S. A. Bahmani, G. C. East, and I. Holme, *J. Soc. Dyers Colour.*, **116**(3), 94 (2000).
7. C. W. M. Yuen, S. K. A. Ku, P. S. R. Choi, and C. W. Kan, *Text. Res. J.* (in press).
8. C. W. M. Yuen, S. K. A. Ku, P. S. R. Choi, C. W. Kan, and S. Y. Tsang, *Research Journal of Textile and Apparel* (accepted for publication).
9. B. N. Bandyopadbyay, G. N. Sheth, and M. M. Moni, *International Dyer*, **11**, 39 (1998).
10. H. Gutjahr and R. R. Koch in "Textile Printing", 2nd ed. (L. W. C. Miles Ed.), pp.139-195, Society of Dyers and Colourists, Bradford, 1994.
11. W. B. Achwal, *Colourage*, **49**(12), 33 (2002).
12. W. Chen, G. Wang, and Y. Bai, *Textile Asia*, **33**(12), 37 (2002).
13. L. W. C. Miles in "Textile Printing", 2nd ed. (L. W. C. Miles Ed.), pp.275-300, Society of Dyers and Colourists, Bradford, 1994.
14. S. Sui, P. Zhu, M. Zhao, and P. Wang, *Journal of Northwest Institute of Textile Science and Technology*, **2**(8), 165 (1994).
15. H. L. I. Lam and K. P. S. Cheng, *Research Journal of Textile and Apparel*, **2**(1), 21 (1998).
16. K. W. Yeung, K. Chan, Q. Zhang, and S. Y. Wang, *Journal of Hong Kong Institution of Textile and Apparel*, **1**(1), 10 (1997).
17. C. W. M. Yuen, S. K. A. Ku, P. S. R. Choi, and C. W. Kan, *Fibers and Polymers*, **5**(2), 117 (2004).
18. T. Oktem, *Coloration Technology*, **119**(2), 241 (2003).