Fibers and Polymers 2006, Vol.7, No.4, 352-357

Dyeing of Cotton and Polyester/Cotton Blend with Disperse Dyes Using Sodium 2-(2,3-dibromopropionylamino)-5-(4,6-dichloro-1,3,5-triazinylamino)-benzenesulfonate

Mikyung Kim, Seokhan Yoon*, Taekyeong Kim[1], Jin-seok Bae, and Namsik Yoon[1]

Korea Dyeing Technology Center, Daegu 703-834, Korea
[1]*Department of Textile System Engineering, Kyungpook National University, Daegu 702-701, Korea*
(Received September 21, 2006; Revised November 2, 2006; Accepted November 9, 2006)

Abstract: The cotton fabrics were pretreated by sodium 2-(2,3-dibromopropionylamino)-5-(4,6-dichloro-1,3,5-triazinylamino)-benzenesulfonate (**DBDCBS**) at alkaline condition of room temperature and then dyed with four disperse dyes having amino groups (C.I. Disperse Yellow 9, C.I. Disperse Red 11, C.I. Disperse Blue 56 and C.I. Disperse Violet 1) at acidic condition of high temperature. A novel hetero-bifunctional bridge compound, **DBDCBS**, has two reactive groups such as dichloro-s-triazinyl group and α, β-dibromopropionylamido group. The first has reactivity towards hydroxy group of cellulosic fiber and the second shows reactivity towards amino groups of disperse dye containing amino groups. The results indicate that it is possible to dye polyester/cotton blend at one-bath dyeing using one kind of disperse dye containing amino groups. Therefore, two kinds of dyeing methods such as two-bath process one-bath dyeing and one-bath process one-bath dyeing were investigated and their dyeabilities were compared. The differences between these two methods were negligibly small so that perfect one-bath one-step dyeing of polyester/cotton blend by one kind of disperse dye was achieved.

Keywords: Polyester, Cotton, One-bath dyeing, Bifunctional compounds, Disperse dye

Introduction

Blends dyeing such as polyester/cotton is usually carried out by two-bath or one-bath-two-step dyeing method employs proper dyes and chemicals for each fibers [1]. However, these dyeing methods are relatively long and complicated. The process of one-bath-two-step dyeing process is shorter than the two-bath method but there are some problems such as lower dyeability from migration and poor reproducibility since different kinds of dyes are used in the same bath. In this regard, several researches have been conducted to improve the dyeability of blended fabrics [2-7].

Especially, there was a try to develop new reactive dyes for PET/cotton blend. Dyeing of cotton by conventional reactive dyes is usually carried out at alkaline conditions under 80 °C but this is a totally different condition from that of PETs. Dyeing of PET is carried out at acidic condition over 120 °C by using disperse dyes. This means that one-bath dyeing method is impossible to apply to polyester/cotton blends. Therefore, there is another method of one-bath dyeing that conventional disperse dyes and newly developed reactive dyes which can be attached at acidic or neutral condition around 100~130 °C are added simultaneously to the same bath [5-8].

This method is possible to reduce the dyeing process but two different dyes should be still used. Also, the preparation of new reactive dyes is complicated and not economical since their chemical intermediates are very expensive and there are still possibilities of hydrolysis of dyes.

*Corresponding author: seokhan@dyetec.or.kr

The synthesis of bi-functional compounds, sodium 2-(2,3-dibromopropionylamino)-5-(4,6-dichloro-1,3,5-triazinylamino)-benzenesulfonate (**DBDCBS**), including dichlorotriazine and α, β-dibromopropionylamido in their structures, and dyeing result by 1,4-diaminoantraquinone (C.I. Disperse Violet 1) and **DBDCBS** were reported in previous papers [8]. The results indicate that it is possible to dye polyester/cotton blend at one-bath using C.I. Disperse Violet 1.

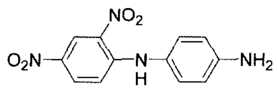
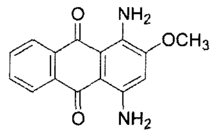
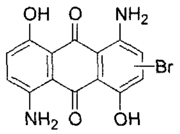
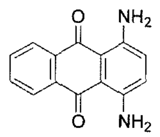
In the present study, perfect one-bath dyeing of cotton/PET blend by using a new hetero-bifunctional compound (**DBDCBS**) and one kind of disperse dyes, in which there are advantages such as process improvement and simplicity, was evaluated. Therefore, in order to identify the possiblility of one-bath dyeing of cotton/PET blend, dyeability of treated cotton fabrics was examined by using disperse dyes containing various amino groups at each different conditions based on previous studies.

Experimental

Materials

Standard white cotton, PET and scouring whitened polyester/cotton blend (Plain, T/C=65/35, 75d/20's, 106 × 48/inch, 176 g/m^2) were used for the experiments according to KS K 0905 regulation. Four disperse dyes containing amino groups, C.I. Disperse Yellow 9 (Reagent grade), C.I. Disperse Red 11 (Industrial grade, Lumacel Pink FF3B), C.I. Disperse Blue 56 (Industrial grade, Dianix Blue FBLE) and C.I. Disperse Violet 1 (Industrial grade, Lumacel Heliotrope R), were employed as shown in Table 1. The 2,5-diamino benzenesulfonic acid, 2,3-dibromopropionyl chloride and 2,4,6-trichloro-

Table 1. Structures of the disperse dyes used in experiments

Dye	Structure
C.I. Disperse Yellow 9	
C.I. Disperse Red 11 (Lumacel Pink FF3B)	
C.I. Disperse Blue 56 (Dianix Blue FBLE)	
C.I. Disperse Violet 1 (Lumacel Heliotrope R)	

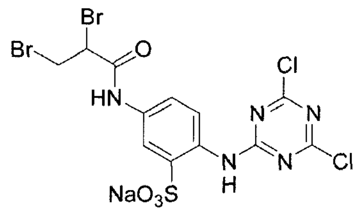


Figure 1. The structure of hetero-bifunctional bridge compound (**DBDCBS**).

1,3,5-triazine, used for the synthesis of Hetero-bifunctional compounds, were first grade and used without further purification.

Preparation of Hetero-bifunctional Reactive Compound

The novel reactive compound shown in Figure 1 was prepared to apply to cotton and polyester/cotton blend. The same mole ratio of 2,5-diaminobenzenesulfonic acid, 2,3-dibromopropionyl chloride and 2,4,6-trichloro-1,3,5-triazine were used at ice-bath to synthesize sodium 2-(2,3-dibromo-propionylamino)-5-(4,6-dichloro-1,3,5-triazinylamino)-benzene-sulfonate (**DBDCBS**) (Figure 1). The detailed synthetic method of the **DBDCBS** and its corresponding analysis data were described in the previous paper [9].

Dyeing of DBDCBS Treated Cotton Fabrics Using Disperse Dyes Containing Amino Groups

DBDCBS Treatment of Cotton Fibers

Each cotton fabric (1.0 g) was treated with 10 % o.w.f. **DBDCBS**, 10 g/*l* sodium carbonate, and 200 g/*l* sodium sulfate at 30 °C for 1 hour. The liquor ratio was 1:20. The treated samples were washed more than three times by 80 °C distilled water to remove the unattached **DBDCBS** entirely before dyeing.

Disperse Dyeing of DBDCBS Treated and Untreated Cotton Fabrics

DBDCBS treated and untreated cotton fabrics (1.0 g) were dyed with 4 disperse dyes containing amino groups, as shown in Table 1 (3 % o.w.f. C.I. Disperse Yellow 9, 5 % o.w.f. C.I. Disperse Red 11, C.I. Disperse Blue 56 and C.I. Disperse Violet 1) at 110 °C for 1 hour and washed with acetone and distilled water three times. In order to identify the bonding strength between amino group contained disperse dyes and treated and untreated cotton fabrics, after removing the unattached dyes entirely by using 20 m*l* DMF(N,N-dimethylformamide) over 90 °C for 1 hour.

Conditional Dyeing of DBDCBS Treated Cotton Fabric by Disperse Dyes

A **DBDCBS** treated cotton fabric (1.0 g) was dyed with four disperse dyes (0.5~15.0 % o.w.f.) at 1:50 liquor ratio, 50~120 °C, pH 3~11 and washed with acetone and distilled water three times, then dried.

Fastness Evaluation of Disperse Dyed Cotton Fabrics

DBDCBS treated cotton fabrics were dyed with four disperse dyes of each 3 % o.w.f. at 115 °C for 1 hour. Their wash fastness (KS K 0430 A-1 : 2001), light fastness (AATCC 16E), and rubbing fastness (KS K 0650 : 2001) were evaluated.

One-bath Dyeing of Polyester/Cotton Blend

One-bath Dyeing of DBDCBS Treated Polyester/Cotton Blend : Two-bath Process One-bath Dyeing (Figure 2)

In order to dye polyester/cotton blend fabrics by one-bath

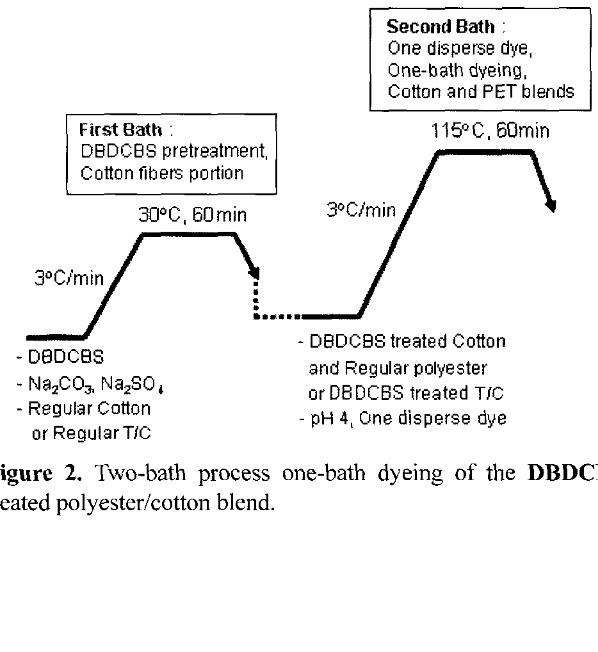


Figure 2. Two-bath process one-bath dyeing of the **DBDCBS** treated polyester/cotton blend.

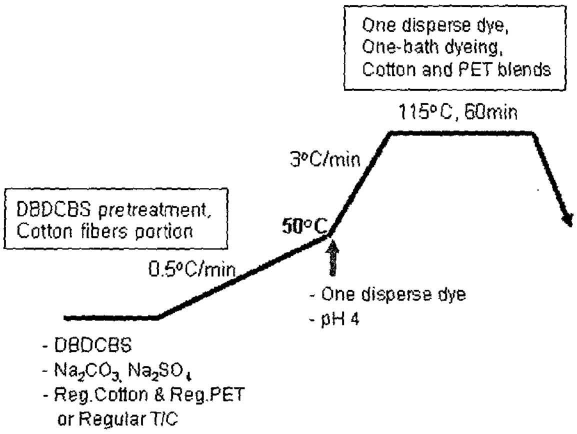


Figure 3. One-bath process one-bath dyeing of the **DBDCBS** treated polyester/cotton blends.

dyeing method, polyester/cotton blend was first treated with **DBDCBS** and then dyed with a disperse dye in a different bath. This process is called two-bath process one-bath dyeing. Each 1.0 g cotton fabrics and polyester/cotton blends were treated with 10 % o.w.f. **DBDCBS**, 10 *g/l* sodium carbonate, and 200 *g/l* sodium sulfate at 1:20 liquor ratio, 30 °C, 60 minutes, and washed more than three times by 80 °C distilled water to remove the unattached **DBDCBS** entirely before dyeing.

After this process, the **DBDCBS** treated cotton fabric (0.5 g) and conventional PET fabric (0.5 g) were dyed in one pot at 1:50 liquor ratio, pH 4, and 115 °C for 60 minutes using 3 % o.w.f. yellow dye, 5 % o.w.f. red, blue and violet dyes.

Also, the **DBDCBS** treated polyester/cotton blend (1.0 g) was dyed with the same conditions and all dyed fabrics were washed with acetone three times to remove the unattached dyes and washed again with distilled water.

One-bath Dyeing of Untreated Polyester/Cotton Blend Fabrics : One-bath Process One-bath Dyeing (Figure 3)

Untreated cotton fabric (0.5 g), conventional PET fabric (0.5 g), and 10 % o.w.f. **DBDCBS** were added in one pot with 10 *g/l* sodium carbonate and 200 *g/l* sodium sulfate at alkaline conditions. The temperature was raised slowly (0.5 °C/min) and acetic acid was added to control pH 4 as soon as the temperature reach 50 °C. 3 % o.w.f. yellow dye and 5 % o.w.f. red, blue and violet dyes were added, and the temperature was raised up to 115 °C (2.5 °C/min) and maintained for 60 minutes, for simultaneous dyeing and **DBDCBS** treatment in one-bath.

Also, the same process using untreated polyester/cotton blend (1.0 g) was conducted to compare with two-bath process one-bath dyeing. All dyed fabrics were washed with acetone and distilled water and their color strength was evaluated.

Color Strength Measurement of Dyed Fabrics

The color strength of all dyed fabrics was measured using spectrophotometer (Datacolor SF 600 Plus, Datacolor, USA) and K/S values at every 10 nm in 380~720 nm were summed up to calculate total K/S value.

Results and Discussion

Dyeing Properties of DBDCBS Treated Cotton Fabrics Using Disperse Dyes Containing Amino Group

Figure 4 shows reaction mechanism of the **DBDCBS** with cellulosic fibers and disperse dyes containing amino groups. Disperse dyes, typical hydrophobic dyes, have affinity with hydrophobic fibers such as nylon but do not have affinity with cellulose fibers. However, there seems to have possibilities that **DBDCBS** treated cotton fabrics are bonded covalently with disperse dyes containing amino groups. The **DBDCBS** compound has two reactive groups in its structure. One is trichlorotriazine type reactive group forming covalent bond easily with cellulose fiber at 30~40 °C, alkaline condition. The other is α,β-dibromopropionylamido reactive group forming covalent bond with amino groups at 90 °C under acidic condition. The Dichloro-*s*-triazinyl group in **DBDCBS** form covalent bonds with hydroxyl groups in cotton fabrics and α,β-dibromopropionylamido group remaining inside the **DBDCBS** molecules forms stable bonding with compounds having amino groups. Disperse dyes basically do not soluble in water but they should have slight solubility at certain dyeing temperature. For this reason, some hydrophilic groups such as -OH and -NH_2 are included in dye structure. In this regard, the reactive dyeing of **DBDCBS** treated cotton fabrics would be possible by disperse dyes containing amino group. Therefore, **DBDCBS** treated polyester/cotton blend is judged to be dyed in one-bath by one kind of disperse dye.

Figure 5 shows the comparison of color strength of **DBDCBS** treated and untreated cotton fabrics to identify the stability of covalent bond between dyes and fabrics. These

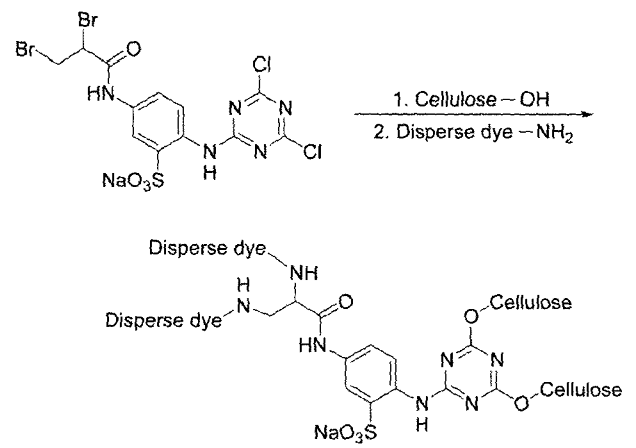


Figure 4. Reaction mechanism of the **DBDCBS** with cellulosic fibers and disperse dyes containing amino groups.

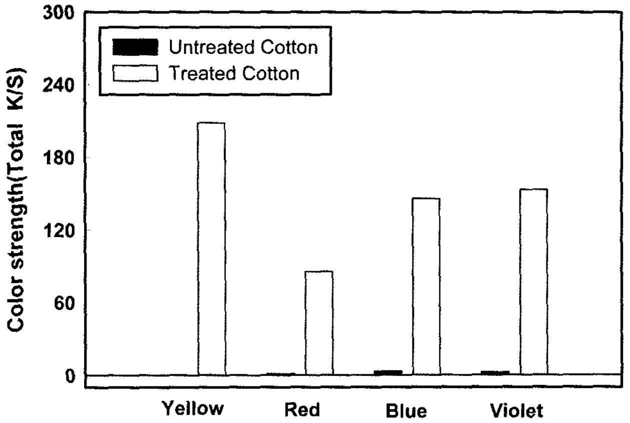


Figure 5. Color strength of the **DBDCBS** treated and untreated cotton fabrics after disperse dyeing (3 % o.w.f. C.I. Disperse Yellow 9, 5 % o.w.f. C.I. Disperse Red 11, C.I. Disperse Blue 56 and C.I. Disperse Violet 1) at 110 °C, pH 4 for 1 hour and then **DMF** treatment.

fabrics were dyed with disperse dyes containing amino groups and then washed with acetone and high temperature **DMF**. In the case of **DBDCBS** treated cotton fabrics, deep coloration was achieved by all disperse dyes but in the case of untreated fabrics, almost no coloration was achieved. This explains that almost no affinity between the untreated fabrics and disperse dyes exist. Also, it can be identified that some absorbed dyes from migration during **DMF** washing are extracted, solved, or detached.

On the contrary, dyeability of **DBDCBS** treated cotton fabrics is superior for all four disperse dyes as well as no desorption exists after high temperature **DMF** treatment. As expected from previous papers, reactive dyeing was thought to be carried out that **DBDCBS** forms covalent bond with hydroxyl group in cotton fiber at alkaline condition of room temperature and then combines again with amine group in disperse dyes at acidic condition of high temperature.

Theoretically, one α, β-dibromopropionylamido can react with two amino groups but the reactivity between α, β-dibromopropionylamido and amino groups is influenced by steric effect of the compound containing **DBDCBS** and amino groups. Therefore, the dyeability comparison of each dye is not needed in this study since the differences are seems to result from these steric hindrance and purity of dyes.

The conditional dyeing characteristics of **DBDCBS** treated cotton fabrics according to temperature, pH, and build-up properties were examined in detail and shown in Figure 6-8.

Figure 6 shows the dyeability of **DBDCBS** treated cotton fabrics within the pH range of 3~11, controlled by acetic acid and 20 % sodium carbonate. The concentration of four disperse dyes used was 1 % o.w.f.. The dyeability of disperse dyes used was better at acidic condition than at alkaline condition. Under acidic conditions, the bromine at the end of

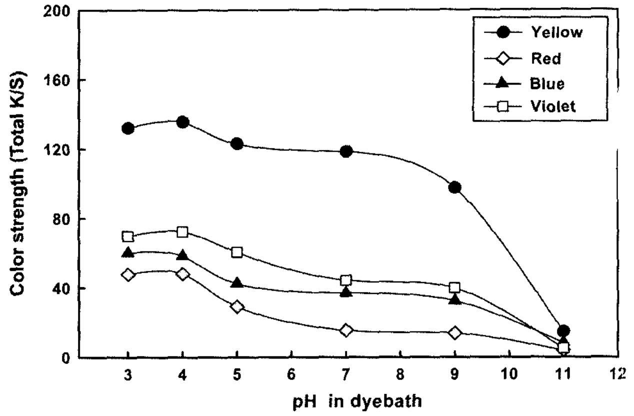


Figure 6. Effect of pH on the color strength of **DBDCBS** treated cotton fabrics dyed with various disperse dyes having amino groups (Dye conc.; 1.0 % o.w.f., dyeing temp.; 110 °C, dyeing time; 1 hour).

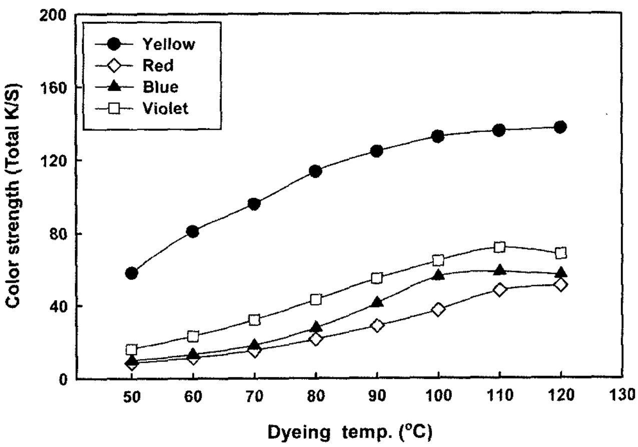


Figure 7. Effect of dyeing temperature on the color strength of **DBDCBS** treated cotton fabrics dyed with various disperse dyes having amino groups (Dye conc.; 1.0 % o.w.f., dyeing pH; 4, dyeing time; 1 hour).

DBDCBS molecule reacts with the amino groups of disperse dyes by substitution. However, dyeing at pH 4 seems to be appropriate since cotton fabrics tend to be easily brominated at high temperature acidic conditions. Disperse dyes are generally known to be unstabled and decomposed at alkaline condition. This is another reason to control the pH at acidic condition. Also, there exist anionic groups derived from sulfone groups in **DBDCBS** molecular structure and their dyeabilities are increased since the amino groups in disperse dyes are cationized temporarily under acidic condition. As a result, the more α, β-dibromopropionylamido groups in **DBDCBS** treated cotton fabrics react with amino groups in disperse dyes.

Figure 7 indicate the dyeability of **DBDCBS** treated cotton fabrics within temperature range of 50~120 °C. The concentration of four dyes used was 1 % o.w.f. and the pH was 4.

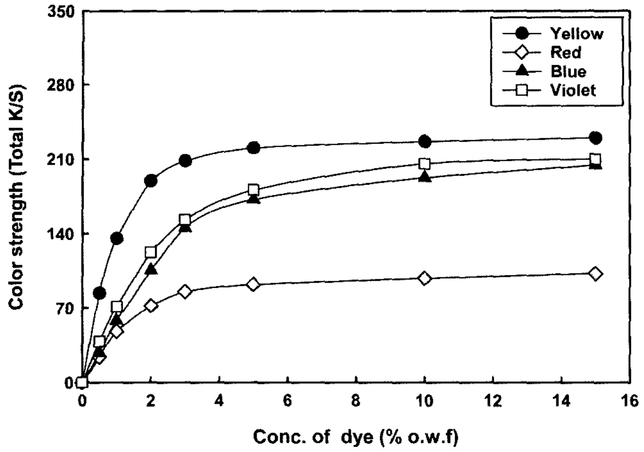


Figure 8. Effect of build-up properties on the color strength of **DBDCBS** treated cotton fabrics dyed with various disperse dyes having amino groups (Dyeing temp.; 110 °C, dyeing pH; 4, dyeing time; 1 hour).

The color strength of all disperse dyes was radically increased as temperature goes up and was maximum at 110 °C. In the case of Disperse Blue 56 and Disperse Violet 1, the color strength was decreased at the temperature more than 110 °C. The higher the dyeing temperature, the more disperse dye can react with α,β-dibromopropionylamido groups in **DBDCBS** treated cotton fabric.

To investigate the build up properties of disperse dyes used, the dyeability of dyes was examined up to 15 % o.w.f. concentration and the results are shown in Figure 8. All disperse dyes show increasing tendency at this concentrations. Especially, the dyeability was increase radically up to 3 % o.w.f. and was maximum around 5 % o.w.f.

Table 2. Fastness evaluation of the **DBDCBS** treated cotton fabrics dyed with the disperse dyes having amino groups

Fastness to		Disperse Yellow 9	Disperse Red 11	Disperse Blue 56	Disperse Violet 1
Washing					
Change in color		4	4-5	4-5	4-5
Staining	- Acetate	3-4	4-5	4-5	4-5
	- Cotton	4	4-5	4-5	4-5
	- Nylon	3-4	4	4-5	4-5
	- Polyester	3-4	4	4-5	4-5
	- Acrylic	4-5	4-5	4-5	4-5
	- Wool	4	4-5	4-5	4-5
Rubbing					
Change in color	- Dry	4	4	4	4
	- Wet	3	3	4	4
Light					
Change in color		3	3	4	4

Fastness Properties of Cotton Fabrics by One-bath Method

It is expected that the fastness would be relatively good because of covalent bond formation between disperse dyes having amino groups and **DBDCBS** treated cotton fabrics.

Table 2 shows the result of wash-, light-, and rubbing fastness tests. Overall, the fastness properties were practically good except when yellow dyes were used. From these results, practical possibilities in one-bath dyeing of polyester/cotton blend using hetero-bifunctional compound **DBDCBS** and disperse dyes can be justified.

Dyeing Characteristics of Polyester/Cotton Blend Fabrics by One-bath Dyeing Process

Usually two-bath dyeing process using disperse dyes and reactive dyes separately was employed for the dyeing of polyester/cotton blend. However, in this study, one-bath dyeing process using one kind of dye was investigated.

Polyester/cotton blend can be dyed with disperse dyes after **DBDCBS** treatment since a similar reactive mechanism forming a covalent bond will be applied to cotton. The conventional disperse dyeing mechanism will be possible on PET simultaneously. However, there still remains complication of two-bath since this dyeing process needs a separate **DBDCBS** pre-treatment process on cotton before dyeing.

Therefore, two kinds of one-bath dyeing methods, two-bath process one-bath dyeing (Figure 2) and one-bath process one-bath dyeing (Figure 3), were investigated. The first method employs two baths. One is for **DBDCBS** treatment and the other is for dyeing. The second method employs only one bath in which **DBDCBS** treatment and dyeing are carried out continuously.

The color strength of dyed cotton and polyester/cotton blend by two-bath process one-bath dyeing and one-bath process one-bath dyeing was compared in Figure 9 and 10. In the case of one-bath process one-bath dyeing method, the color strength was slightly lower than that of two-bath process one-bath dyeing method. The reason for this result seems that unattached **DBDCBS** reacts with disperse dyes

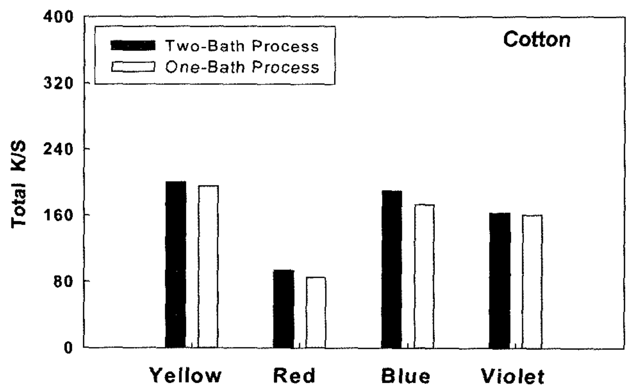


Figure 9. Effect of one-bath dyeing process on the color strength of the **DBDCBS** treated cotton fabrics dyed with various disperse dyes having amino groups.

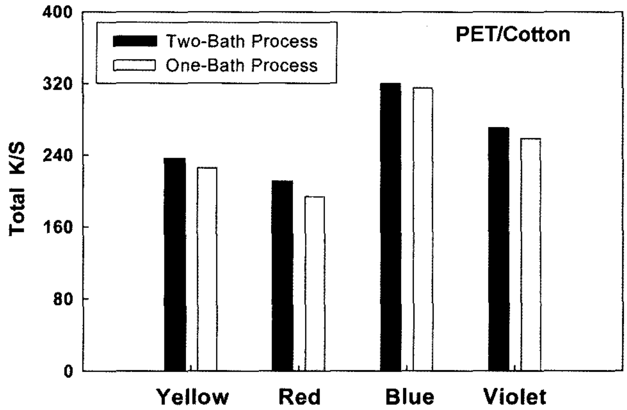


Figure 10. Effect of one-bath dyeing process on the color strength of the polyester/cotton blend fabrics dyed with various disperse dyes having amino groups.

and hindered dyeing process. However, the differences of color strength were negligibly small while there are many economic and process advantages in one-bath process one-bath dyeing. Therefore, one-bath process one-bath dyeing method was adopted and conducted.

Conclusion

In the present study, the perfect one-bath dyeing method using a hetero-bifunctional compound (**DBDCBS**) to dye polyester/cotton blend by disperse dyes having amino groups was tried based on the previous papers. The dyeability and fastness properties of **DBDCBS** treated cotton fabrics were relatively good for all disperse dyes used but the dyeability of untreated cotton fabrics was very unsatisfactory.

Therefore, two kinds of dyeing methods, two-bath process one-bath dyeing, which uses a separate bath for the **DBDCBS** treatment, and one-bath process one-bath dyeing, in which **DBDCBS** treatment and dyeing are carried out in one bath continuously, were investigated and their dyeabilities were compared. The differences of color strength between these two methods were negligibly small so that one-bath dyeing of polyester/cotton blend by one kind of disperse dye was achieved.

Acknowledgement

The authors acknowledge the support of this research by the Jung-Moo Academic Scholarship Foundation of Stiftung.

References

1. S. J. Kim, D. W. Jeon, and J. I. Lee, *J. Korean Soc. Clothing & Textiles*, **30**(2), 275 (2006).
2. J. M. Cardamone and J. D. Turner, *AATCC Review*, **32**(6), 49 (2000).
3. S. D. Kim, J. L. Lee, C. H. Ahn, K. S. Kim, and K. S. Lee, *J. Korean Soc. Dyers & Finishers*, **16**(1), 26 (2004).
4. W. K. Sung, *J. Korean Soc. Dyers & Finishers*, **10**(2), 82 (2004).
5. S. N. Croft, D. M. Lewis, R. Orita, and T. Sugimoto, *J.S.D.C*, **108**(4), 195 (1992).
6. T. Sugimoto, *J.S.D.C*, **108**(4), 497 (1992).
7. J. Y. Kim, K. P. Lee, H. M. Park, M. S. Yoon, and K. H. Cho, *J. Korean Soc. Dyers & Finishers*, **16**(5), 1 (2004).
8. J. Bae, J. H. Park, J. Koh, and S. D. Kim, *Fibers and Polymers*, **7**(2), 174 (2006).
9. T. K. Kim, S. H. Yoon, and M. K. Kim, *J. Korean Soc. Dyers & Finishers*, **18**(3), 121 (2006).