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Dyeing and Fastness Properties of a Reactive Disperse Dye on PET, Nylon, Silk and N/P Fabrics

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Abstract: Dyeing and color fastness properties of a reactive disperse dye containing an acetoxyethylsulphone group on PET, Nylon, silk and N/P fabrics were examined. The reactive disperse dye exhibited almost the same dyeing properties on PET fabric as a conventional disperse dye except the level of dye uptake. The most appropriate pH and dyeing temperature for the dyeing of Nylon fabric were 7 and 100 °C respectively. The build-up on Nylon fabric was good and various color fastnesses were good to excellent due to the formation of the covalent bond. Application of the reactive disperse dye on silk fabric at pH 9 and 80 °C yielded optimum color strength. The rate of dyeing on Nylon fabric was faster than that on PET fabric when both fabrics were dyed simultaneously in a dye bath, accordingly color strength of the dyed Nylon was higher. The reactive disperse dye can be applied for one-step and one-bath dyeing of N/P mixture fabric with good color fastness.

Keywords: Reactive disperse dye, Acetoxyethylsulphone, Dyeing, Eco-friendly, PET, Nylon, Silk, N/P fabric

Introduction

There have been many efforts in textile industry to produce new materials which possess special appearances or functionality by combining two or more types of fiber. The combination of different fibers can be performed by blend of fibers or mixture weaving. Polyester/cotton and polyester/wool blends are highly popular apparel fabrics, and recently the production of mixture fabrics such as N/P, N/C and P/NP has increased. There are four major types of colored effect achieved by dyeing blends or mixture fabrics: (a) solid effect (component fibers are dyed as closely as possible to the same hue, depth and brightness); (b) reserve effect (only one fiber is dyed and the other is kept as white as possible); (c) shadow effect (the two fibers are dyed to the same hue and brightness but the different depth); (d) contrast effect (the two fibers are dyed to the same depth but the different hue) [1].

It is required of careful treatments to color blends or mixture fabrics because the component fibers have different dyeing properties. The two-bath dyeing method is frequently employed in dyehouse to secure acceptable color fastness. Taking polyester/cotton blends as an example, current processes consist of dyeing the polyester portion with disperse dyes at 130 °C, reduction clearing, resetting the bath, reactive dyeing the cotton portion, and final clearing unfixed dye. Such processes are expensive and time-consuming. Hence dye chemists and dyers have been trying to develop universal dyes which have affinity for several fibers to streamline dye manufacturing and to contribute to quick dyeing operation. Lewis and coworker have suggested disperse dyes as colorants for this purpose, and they explained incorporation of the necessary dye sites within natural fibers by a pretreatment with a chemical like benzoyl chloride as a key requirement [2].

An alternative approach to universal dyes would involve designing disperse dyes that contain reactive group [3]. This type of disperse dye is named as a reactive disperse dye, and it has the favorable characteristics of both disperse and reactive dyes. Burkinshaw and Collins studied the dyeing properties of three reactive disperse dyes having sulphatoethylsulphone group, and found these dyes exhibited excellent build-up profiles and washfastness on both conventional and microdenier Nylon 66 fibers [4]. Sunwoo and Burkinshaw synthesized a series of reactive disperse dye containing ethyleneimine derivatives, and investigated their dyeing and fastness properties on Nylon 66 and PET fibers [5-7]. Kim and coworkers examined synthesis of a reactive disperse dye having a bromoacrylamide group and its dyeing property [8].

In this study, dyeing and fastness properties of a reactive disperse dye containing an acetoxyethylsulphone group on PET, Nylon, silk and N/P fabrics are reported.

Experimental

Materials

All chemicals used in the synthesis of dyes and dyeing were laboratory grade reagents. SD-60(Borregaard, anionic) and Disper N-700(Meisei Chemical, nonionic) were used as dispersing agents for milling and for dyeing respectively. PET fabric (75 d/36 f, plain weaved, 210 × 191/5 cm), Nylon 6 fabric (70 d/24 f, plain weaved, 210 × 191/5 cm), silk fabric (crepe de chine, 16 mm, 45"), N/P mixture fabric (warp, Nylon 70 d/24 f; weft, PET 150 d/192 f; N/P = 46/54) were used for dyeing.

Synthesis of a Reactive Disperse Dye

The chemical structure of two dyes used is shown in Figure 1. The synthetic route for a reactive disperse dye (Dye 1) was diazotization of 4-hydroxysulphone aniline and

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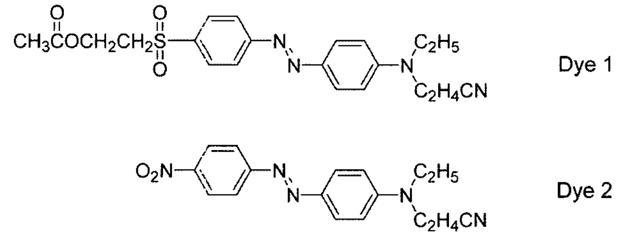


Figure 1. Chemical structures of the dyes used in this study.

subsequent coupling with N-cyanoethyl-N-ethyl aniline followed by acetylation with acetic anhydride. The detailed synthetic procedure, analysis of the chemical structure, and HPLC study on the β-elimination reaction are described in a previous paper [9]. A conventional disperse dye (Dye 2) was also synthesized by coupling of N-cyanoethyl-N-ethyl aniline with diazonium salt of 4-nitroaniline, and used to compare dyeing properties on PET fabric with Dye 1.

Dyeing

Purified dyes and the dispersing agent SD-60 (weight ratio 1:2) were milled to make dye dispersion whose particle size was in the range of 0.3-0.6 μm, using glass beads and mechanical stirrer. Dyeing was carried out in the sealed dyepot (Labomat, Mathis), pH was adjusted with buffer solutions according to the substrate (PET, 4.5; Nylon, 2~11; silk, 2~11; simultaneous dyeing of Nylon and PET, 4~5; N/P, 4), and a liquor ratio was 30:1. Temperature was raised from 50 °C to the highest dyeing temperature (PET, 120~130 °C; Nylon, 100 °C; silk, 80 °C; simultaneous dyeing of Nylon and PET, 120 °C; N/P, 120 °C), and dyeing was continued at the highest dyeing temperature for 60 min, and then the temperature was lowered to 80 °C. Dyed fabric was reduction cleared in an aqueous solution containing 2 g/*l* sodium hydroxide and 2 g/*l* sodium hydrosulphite at 80 °C using a liquor ratio 50:1 for 20 min.

Measurements of Color Strength and Fastness

The reflectance values of the dyed fabrics were measured using a Color-Eye 3100 (Macbeth, USA) under illuminant D65 using 10 ° standard observers. Color strength (K/S) was calculated from the reflectance value using Kubelka-Munk equation. The dye uptake on PET was calculated by extraction with hot DMF and pre-determined calibration curve.

Fastness to washing, light, dry heat, rubbing and perspiration were measured using AATCC 61 IIA, AATCC 16A, AATCC 117, AATCC 8 and AATCC 15 methods respectively.

Results and Discussion

PET Dyeing

Dyeing properties of the reactive disperse dye on PET fabric are examined in the first place. The amount of adsorbed dyes determined by extraction with hot DMF from PET fabric dyed at several conditions are presented in Figure 2. Dyeing properties of Dye 2 are compared with those of the reactive disperse dye. Both dyes exhibit fairly good build-up profiles because the dye uptake of two dyes tends to increase linearly as the concentration of dye increases. However, the amounts of adsorbed Dye 1 are lower than those of Dye 2 at all dye concentrations examined. The only difference in chemical structure between two dyes is a substituent; Dye 1 has an acetoxyethylsulphone group instead of a nitro group. Hence, the low dye uptake of Dye 1 is probably caused by the bulky acetoxyethylsulphone group which can give a difficulty in diffusion of dye molecules into fiber structure. The dye uptake at 120 °C is higher than at 130 °C, which means both dyes belong to low energy type disperse dye whose molecular weight is relatively small. The color fastnesses of PET fabric dyed at 120~130 °C and 1 %owf are listed in Table 1. The ratings of the color fastness of two dyes are excellent. These results tell that Dye 1 has the similar dyeing and fastness properties on PET to the conventional disperse dye except the level of the dye uptake.

Nylon Dyeing

The dye bath pH is known to be a very important factor in

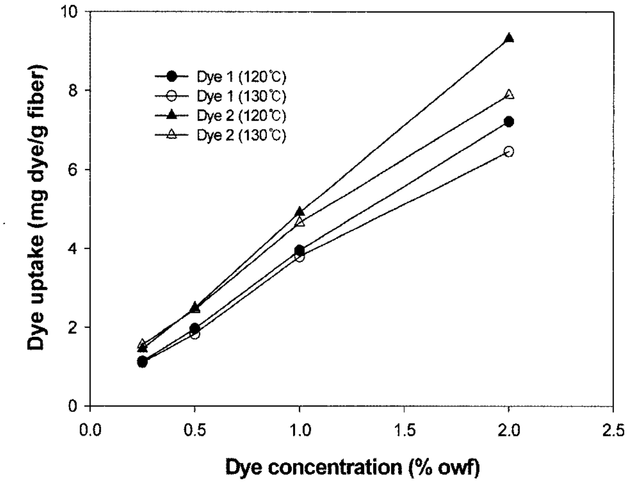


Figure 2. Build-up profiles of dyes 1 and 2 on PET fabric.

Table 1. Color fastness of PET fabric dyed with dyes 1 and 2 at 120 °C and pH 4.5

Dye	Washing				Rubbing		Dry heat	Light
	PET	Nylon	Silk	Cotton	Dry	Wet	PET	
1	5	5	4	5	4/5	4/5	4/5	4
2	5	4/5	4	5	4/5	4/5	4/5	4

Nylon dyeing. Dyeings are performed at 100 °C varying pH from 2 to 11 to investigate the effect of pH on color strength. K/S values of the samples before and after reduction clearing are shown in Figure 3. Color strength enhances as the dye bath pH increases and reaches the highest value at pH 7. Dye 1 contains an acetoxyethylsulphone group, which can be converted into a vinylsulphone group through β-elimination reaction during dyeing process as shown in Scheme 1 [8]. The vinylsulphone derivative can form covalent bond with the amino end group of Nylon fiber through nucleophilic addition reaction, while the parent dye is not firmly bound to Nylon fiber and subsequently removed by reduction clearing. The difference in K/S value between samples before and after reduction clearing decreases at pH region of 5 to 11, suggesting that the β-elimination reaction takes place actively at pH higher than 5. Since conventional disperse dyes do not contain any ionic groups, dye-fiber attraction mainly originates in dispersion forces, so they can be completely extracted from the dyed fabric by hot DMF. The K/S values of the samples extracted by DMF are also given in Figure 3, and they are very close to those of the corresponding samples after reduction clearing, meaning that most dyes in Nylon fiber are fixed strongly and that Dye 1 is converted into the reactive vinylsulphone derivative and then reacted with Nylon fiber. It can be said that the most appropriate pH for Nylon dyeing with Dye 1 is 7 on the basis of color strength of the dyed samples. Considering that acetic acid, ammonium acetate and pH sliding agent are usually added in the conventional acid dye solution to secure the high dye uptake on Nylon, application of Dye 1 can be regarded as one of eco-friendly dyeing system for Nylon fabric.

Dyeings are carried out at pH 7 varying the dyeing temperature from 60 °C to 100 °C to investigate the effect of temperature on the dye uptake, and K/S values are presented in Figure 4. As the dyeing temperature increases, color strength increases, lowering K/S difference between samples before and after reduction clearing. Color strength of the samples dyed at 90 and 100 °C are very close to each other, so color fastnesses of Nylon fabric dyed at pH 7, 1 %owf and two temperatures are measured and listed in Table 2. The ratings of fastness to washing, rubbing, dry heat and light are good to excellent. The excellent fastnesses must be related to the covalent bond formed between dye molecule and fiber.

The build-up profile is shown in Figure 5. It is generally accepted that disperse dyes are not usually applied to Nylon fabrics since their saturation values are low. However, color strength of Nylon dyed with Dye 1 increases with increasing dye concentration almost proportionally. It is evident that the reaction of the vinylsulphone group with Nylon fiber promotes

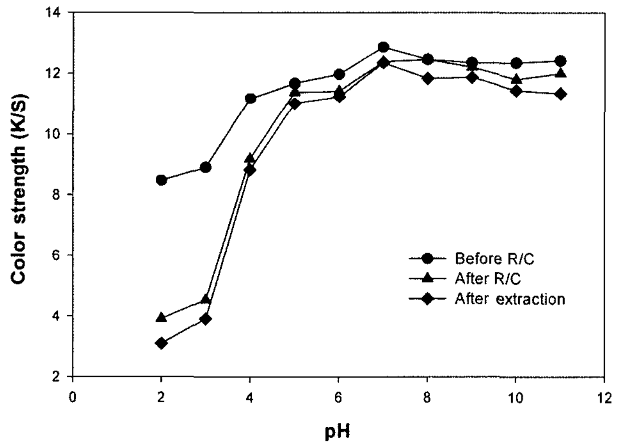


Figure 3. Color strength of nylon fabric dyed with dye 1 at different pHs.

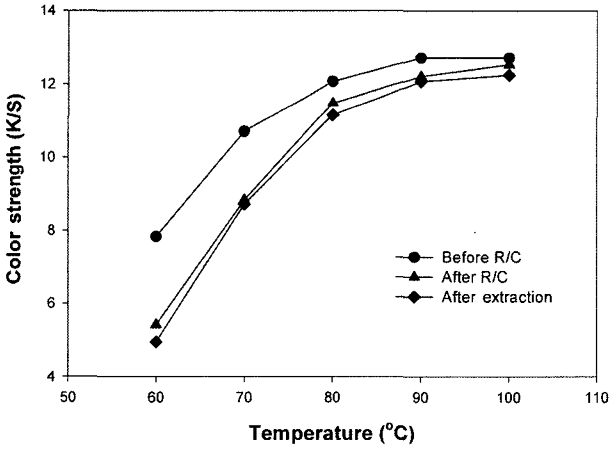
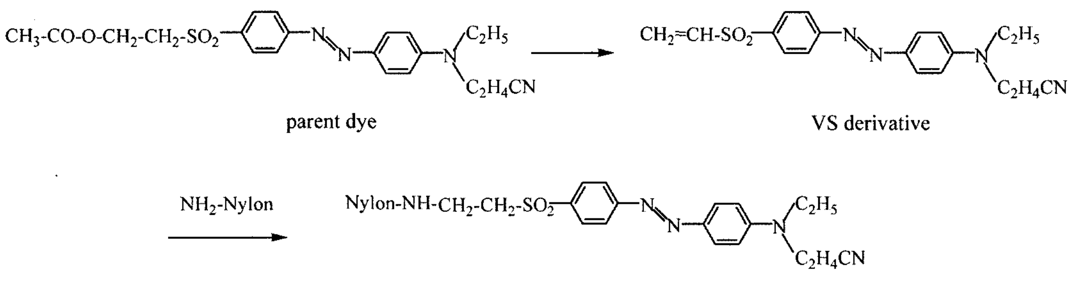


Figure 4. Color strength of nylon fabric dyed with dye 1 at different temperatures.



Scheme 1. Reaction mechanism of a reactive disperse dye with nylon fiber.

Table 2. Color fastness of nylon fabric dyed with dye 1 at pH 7

Dyeing temp. (°C)	Washing				Rubbing		Dry heat	Light
	PET	Nylon	Silk	Cotton	Dry	Wet	PET	
90	5	5	3/4	4/5	4/5	4/5	5	4
100	5	5	3/4	4/5	4/5	5	5	4

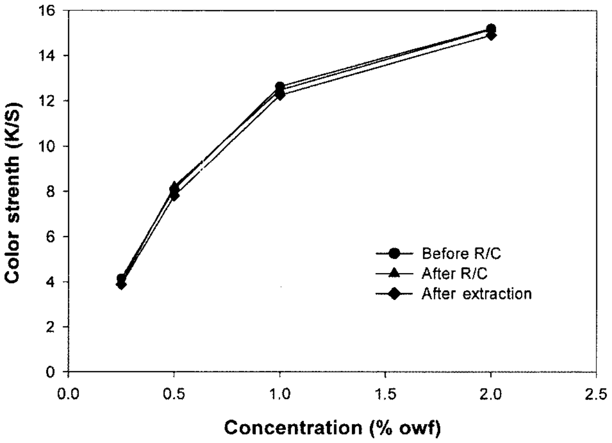


Figure 5. Build-up profile of dye 1 on nylon fabric.

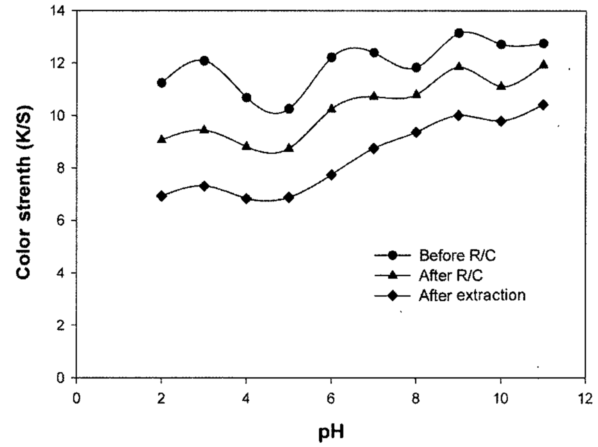


Figure 6. Color strength of silk fabric dyed with dye 1 at different pHs.

the dye uptake.

Silk Dyeing

Silk has amino groups like Nylon fiber, so that its dyeing properties are expected to vary according to the dye bath pH. Dyeings at different pH of 2 to 11 were carried out at 80 °C with 1 %owf dye in order to examine the pH effect on the dye uptake, and K/S values are presented in Figure 6. While color strength of samples before reduction clearing changes irregularly as pH increases, however it can be noticed that the lowest and highest color strengths are at pH 5, near the isoelectric point of silk, and at pH 9 respectively. Compared to Nylon dyeing in Figure 3, the difference in K/S value between samples before and after reduction clearing is large, and the difference in K/S value between samples after reduction clearing and after DMF extraction is even bigger, suggesting that some dyes did not form covalent bond with silk fiber. Considering the fact that the number of amino group in silk fiber is more than Nylon fiber, these results are unexpected. It might be caused partly by the slow rate of β-elimination reaction due to relatively low dyeing temperature of 80 °C, and partly by the fact that the highly hydrophobic reactive disperse dye do not have a high affinity for the hydrophilic silk fiber.

Silk fabrics are dyed at 40~80 °C at pH 9 in order to examine the effect of dyeing temperature on the dye uptake, and the results are shown in Figure 7. The highest dyeing temperature is set to 80 °C because silk fabric is usually dyed with acid dyes at this temperature in order to minimize damage of silk during dyeing process. As the dyeing temperature rises, color strength is getting high, and the difference in the K/S value between samples before and after reduction clearing is getting small. It is found that the most appropriate pH for silk dyeing is 9, and the best temperature is 80 °C on the basis of color strength of the samples. Color fastnesses of silk fabric dyed at 80 °C, pH 9 and 1 %owf are measured and listed in Table 3. Fastness to washing is good to excellent except staining on silk, and the ratings of fastness to rubbing, perspiration and light are in the range of 4 to 5.

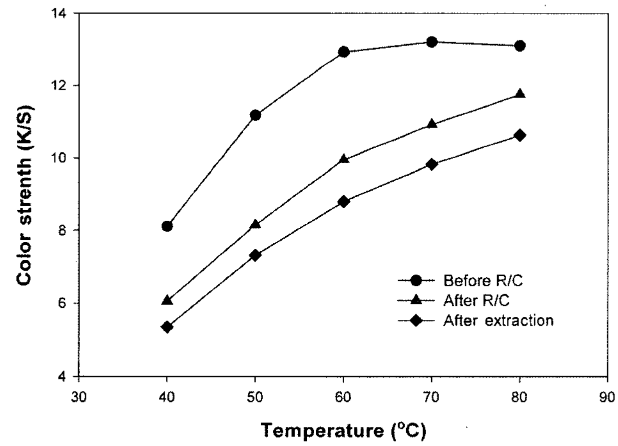


Figure 7. Color strength of silk fabric dyed with dye 1 at different temperatures.

N/P Mixture Dyeing

N/P mixture fabric is usually dyed in dyehouse by two-

Table 3. Color fastnesses of silk fabric dyed with dye 1 at 80 °C and pH 9

Washing				Rubbing		Perspiration		Light
PET	Nylon	Silk	Cotton	Dry	Wet	Acidic	Alkaline	
5	4	2/3	5	5	4/5	5	5	4

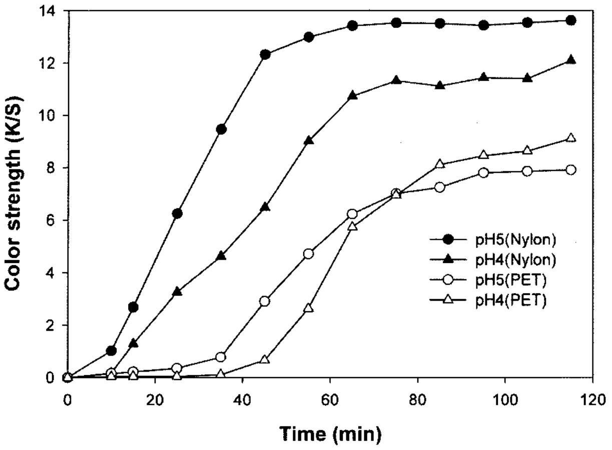


Figure 8. Color strength of nylon and PET fabrics in simultaneous dyeing with dye 1 at pH 4 and 5.

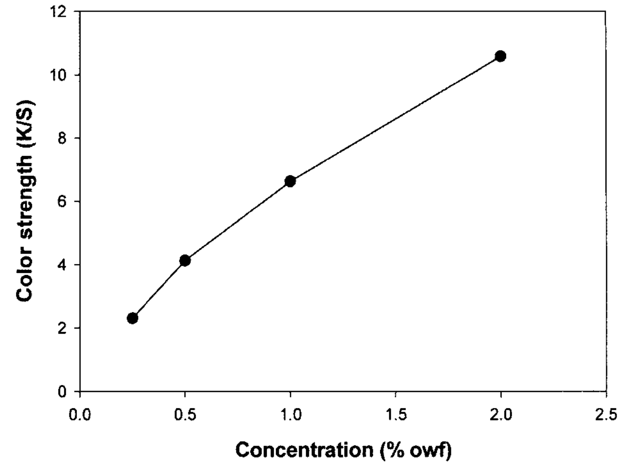


Figure 9. Build-up profile of dye 1 on N/P mixture fabric dyed at pH 4 and 120 °C.

bath method: dyeing PET by disperse dyes at 120 °C and pH 4~5, followed by dyeing of Nylon with acid dyes at 100 °C in acidic condition. If one-step, one-bath dyeing method using Dye 1 is tried, it would be difficult to analyze the dyeing characteristics of each component fiber in N/P mixture fabric. Hence we first examine the simultaneous dyeing of Nylon and PET fabrics with Dye 1 in a dye bath. Figure 8 shows exhaustion curves obtained from an one-step dyeing with same amount of Nylon and PET fabrics are dyed at the pH region of 4 to 5 and 120 °C. In the case of dyeing at pH 5, the difference in color strength between two fabrics is quite wide. The dye adsorption on Nylon is actually completed after 45 min, and then the dye starts to be adsorbed on PET. As a result the same tone of the color on both fabrics is hard to obtain by the simultaneous dyeing at pH 5. One of the possible way to decrease the difference in color strength between two fabrics is lowing pH to decelerate the β-elimination reaction of Dye 1. Color strength of both fabrics dyed at pH 4 is also presented in Figure 8. As pH decreases the gap in color strength between two fabrics reduced because the formation of reactive vinylsulphone derivative is suppressed.

N/P mixture fabric is dyed with Dye 1 by the one-step, one-bath method at pH 4 and 120 °C, and the results are shown in Figure 9. As the concentration of dye increases, color strength of dyed N/P mixture fabric increases linearly. Color fastnesses of N/P mixture fabric dyed at 120 °C and 1 %owf are measured and listed in Table 4. Fastness to washing is good to excellent except staining on silk, and the ratings of fastness to rubbing, dry heat and light are in the range of 4 to 5.

Conclusions

The dyeing and color fastness properties of a reactive disperse dye carrying an acetoxyethylsulphone group on PET, Nylon, silk, and N/P fabrics have been investigated. Although the amounts of adsorbed dye were lower than a conventional disperse dye at all dye concentrations examined, the reactive disperse dye exhibited good build-up profile on PET and color fastnesses ratings were good to excellent. The most appropriate dyeing conditions for Nylon fabric were pH 7 and 100 °C. The build-up on Nylon was good and color fastnesses were good to excellent due to the formation of the covalent bond. Comparing color strength of the dyed Nylon extracted by DMF with those of corresponding samples after reduction clearing, the reactive disperse dye was proved to be combined with Nylon fiber by covalent bond. Optimum

Table 4. Color fastnesses of N/P mixture fabric dyed with dye 1 at 120 °C

pH	Washing				Rubbing		Dry heat	Light
	PET	Nylon	Silk	Cotton	Dry	Wet	PET	
4	5	4	2/3	5	5	4/5	5	4

color strength for silk dyed with the reactive disperse dye was obtained at pH 9 and 80 °C and color fastnesses were good to excellent. The dyeing rate of Nylon was faster than that of PET when both fabrics were dyed simultaneously in a dye bath with higher color strength unsurprisingly. It was found that the reactive disperse dye may be a good candidate adequate for the one-step and one-bath dyeing of N/P mixture fabric with good color fastnesses.

References

1. J. Shore, "Blends Dyeing", pp.10-19, SDC, Bradford, 1998.
2. D. M. Lewis and P. J. Broadbent, *J.S.D.C.*, **113**, 159 (1997).
3. H. S. Freeman and J. Sokolowska, *Rev. Prog. Coloration*, **29**, 8 (1999).
4. S. M. Burkinshaw and G. W. Collins, *Dyes and Pigments*, **25**, 31 (1994).
5. K. H. Sunwoo and S. M. Burkinshaw, *J. Korean Soc. Dyers Finishers*, **8**, 361 (1996).
6. K. H. Sunwoo and S. M. Burkinshaw, *J. Korean Soc. Dyers Finishers*, **8**, 385 (1996).
7. K. H. Sunwoo and S. M. Burkinshaw, *J. Korean Soc. Dyers Finishers*, **8**, 445 (1996).
8. K. S. Kim, S. D. Kim, J. L. Lee, and K. H. Lee, *J. Korean Fiber Soc.*, **38**, 683 (2001).
9. S. D. Kim, Y. H. Lee, B. S. Lee, and J. Y. Jaung, *J. Korean Fiber Soc.*, **39**, 723 (2002).