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Dyeing properties of a reactive disperse dye carrying acetoxyethylsulphone group

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Abstract

The dyeing and color fastness characteristics of a reactive disperse dye on Nylon fabric, PET fabric and N/P mixture fabric have been examined. The most appropriate pH for the dyeing of Nylon fabric was 7 and suitable dyeing temperature was 100 °C. The build-up on Nylon fabric was good and various color fastnesses were good to excellent due to the formation of the covalent bond. The reactive disperse dye exhibited the similar dyeing properties on PET fabric to a conventional disperse dye. The rate of dyeing of the reactive disperse dye on Nylon fabric was faster than that on PET fabric when both fabrics were dyed simultaneously in a dye bath, but the difference in the color strength between the two fabrics decreased as the pH decreased. The reactive disperse dye was adequate to the one-step, one-bath dyeing of N/P mixture fabric with good color fastnesses. It was also found by HPLC analysis that the rate of β-elimination reaction of the reactive disperse dye at 100 °C increased 8 times as the pH increased by 1.

Keywords: Reactive disperse dye; Acetoxyethylsulphone; β-Elimination reaction; Dyeing; Eco-friendly; Nylon; PET; N/P mixture fabric

1. Introduction

Properties of different fibers can be expressed in a fabric by blend of fibers or mixture weaving. Recently the production of mixture fabrics such as N/P, N/C and P/NP has been increased due to their special handle and unique appearance. Dyeing of mixture fabric requires careful treatments because the component fibers have different dyeing and physical properties. The two-bath dyeing method, even though the processing time is quite long, is frequently employed in dyehouse to secure one-tone effect and acceptable color fastnesses of the mixture fabric. The one-bath dyeing method, which can save considerable processing time and energy, often results in deteriorating quality of dyeing and color fastness, caused by the staining of one fiber with a dye for the other fiber. One of the possible ways to achieve efficient one-bath dyeing of blends or mixture fabrics is the development of a universal dye which alone is capable of dyeing component fibers in a blend or mixture fabric [1,2].

Although disperse dyes can be applied to Nylon fiber, the use of disperse dyes is not popular because of their limited build-up and low fastness properties. Attempts have been made to produce disperse dyes that carry reactive groups, named as reactive disperse dyes, and that have the favorable characteristics of both disperse and reactive dyes [3]. Burkinshaw and Collins examined the dyeing properties of three reactive disperse dyes having sulphatoethylsulphone group, and found that these dyes, when applied at 95 °C and pH 8, exhibited excellent build-up profiles and wash fastness on both conventional and microdenier Nylon 66 fibers [4]. Sunwoo and Burkinshaw synthesized reactive disperse dyes containing ethyleneimine derivatives, and investigated their dyeing and fastness properties on Nylon 66 and PET fibers [5–7].

The dyeing of PET with disperse dye is usually carried out at pH 4–5. Nylon is also dyed in acidic conditions. Hence

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a reactive disperse dye which has good dyeing properties on PET and Nylon fibers in acidic condition might be beneficial to the one-bath dyeing of N/P mixture fabric. In this study, dyeing properties of a reactive disperse dye carrying acetoxyethylsulphone on Nylon fabric, PET fabric, and N/P mixture fabric are reported.

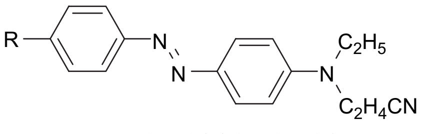
2. Experimental

2.1. Materials

All chemicals such as 4-hydroxyethylsulphone aniline, *N*-cyanoethyl-*N*-ethyl aniline, acetic anhydride, chloroform, acetic acid, sodium hydroxide and sodium hydrosulphite used in the synthesis, HPLC analysis and dyeing were laboratory grade reagents. SD-60 (Borregaard, anionic) was used as a dispersing agent for milling and Disper N-700 (Meisei Chemical, nonionic) was used as a disperse agent for dyeing. Nylon 6 fabric (70d/24f, plain weaved, 214 × 150/5 cm), PET fabric (75d/36f, plain weaved, 210 × 191/5 cm), and N/P mixture fabric (warp, Nylon 70d/24f; weft, PET 150d/192f; N/P = 46/54) were used for dyeing.

2.2. Synthesis of the reactive disperse dye

The chemical structure of the dyes used are shown in Fig. 1. The reactive disperse dye (Dye 1) was synthesized by the following method: 2 g 4-hydroxyethylsulphone aniline was dispersed in 10 ml water and 1.8 ml 35% HCl. The diazonium salt solution was prepared by the addition of 0.69 g $NaNO_2$ into the dispersion and cooled in ice bath. The diazonium salt solution was then slowly added into the solution of *N*-ethylcyano-*N*-ethyl aniline dissolved in 20 ml 5% H_2SO_4. The precipitate was obtained by the addition of reaction mixture into 500 ml water, and washed 3 times with cold water and then dried. The precipitate (0.5 g) and sodium acetate (0.1 g) were then added into 1.2 ml of acetic anhydride. The acetylation reaction was continued for 30 min at 65 °C. Dye 1 was obtained by the addition of the reaction mixture into 50 ml water, and purification through column chromatography (silica gel, chloroform:ethyl acetate = 3:1). The yield of the reaction was 62%. Anal. calcd. for $C_{21}H_{24}N_4O_4S$ (%): C, 58.86; H, 5.65; N, 13.08; S, 7.48; found: C, 58.15; H, 5.98; N, 12.82; S, 7.35. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.84$ (s, 3H, $CH_3{-}CO$); 1.27 (t, 3H, CH_3); 3.60 (q, 2H, CH_2); 2.69 (t, 2H, $CH_2{-}CN$); 3.79 (t, 2H, $N{-}CH_2$); 3.49 (t, 2H, $CH_2{-}SO_2$); 4.43 (t, 2H, $O{-}CH_2$); 6.75 (d, 2H, ArH); 7.92 (d, 2H, ArH); 8.03 (m, 4H, Ar′H).



Dye 1 ; R = $CH_3COOCH_2CH_2SO_2$

Dye 2 ; R = NO_2

Fig. 1. Chemical structure of the dyes used in this study.

A conventional disperse dye (Dye 2) was also synthesized by the normal procedure and used to compare dyeing properties on PET fabric with Dye 1.

2.3. Dyeing

Purified dye and the dispersing agent SD-60 (weight ratio 1:2) were milled to dye dispersion whose particle size were in the range of 0.3–0.6 μm, using glass beads and mechanical stirrer. Dyeing was carried out in the sealed dye pot (Labomat, Mathis), pH was adjusted with buffer solutions according to the substrate (Nylon, 2–11; PET, 4.5; simultaneous dyeing of Nylon and PET, 3–5; N/P mixture, 3–4), and the liquor ratio was 30:1. Temperature was raised from 50 °C to the highest dyeing temperature (Nylon, 100 °C; PET, 120–130 °C; simultaneous dyeing of Nylon and PET, 120 °C; N/P mixture, 120 °C), and dyeing was continued at the highest dyeing temperature for 60 min, 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 of 50:1 for 20 min, rinsed and dried.

2.4. HPLC analysis

The extent of β-elimination reaction of the sulphatoethylsulphone group was analyzed at pH 4, 5 and 6. The dye liquors were prepared by dispersing 2 mg of Dye 1 in 50 ml of buffer solution. The dye liquors were heated to 100 °C and 1 ml aliquots were withdrawn from the dye solution at 10 min intervals and immediately cooled to prevent further reaction. Analysis was carried out at room temperature using HPLC (YoungLin, Korea) with a C18 reverse-phase column and chloroform was used as the mobile phase.

2.5. Measurements of color strength and fastness

The reflectance values of the dyed fabric 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 values using the well-known Kubelka–Munk equation.

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

3. Results and discussion

3.1. Nylon dyeing

The most important factor in Nylon dyeing is the dye bath pH. Dyeings were carried out at 100 °C by varying the pH from 2 to 11 to examine the effect of pH on the dye uptake. *K*/*S* values of the samples before and after reduction clearing, are shown in Fig. 2. Contrary to Nylon/acid dye system, color strength enhances up to pH 7, and then slightly decreases. Dye 1 has an acetoxyethylsulphone group, which can be converted

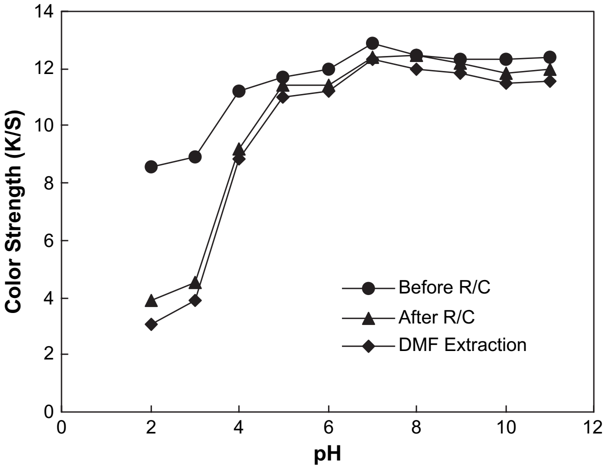


Fig. 2. Effect of dye bath pH on color strength of Nylon fabric dyed with Dye 1.

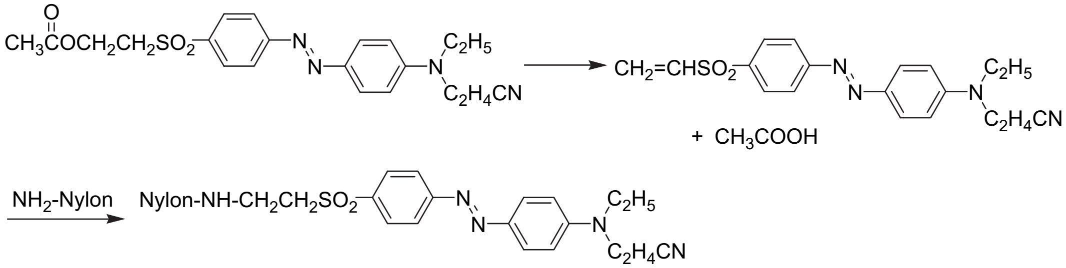
into vinylsulphone group through β-elimination reaction during the dyeing process as in Scheme 1. It is the vinylsulphone derivative which can form the covalent bond with the amino group in Nylon fiber, while the parent dye is not firmly bound to Nylon fiber and subsequently removed by reduction clearing. It can be recognized that the amount of the reactive vinylsulphone derivative increases at the dye bath pHs higher than 5 by examining the difference in *K*/*S* value between samples before and after reduction clearing. This fact suggests that the β-elimination reaction is promoted as the pH increases. Since conventional disperse dyes do not contain any ionic groups, dye–fiber attraction originates in van der Waals forces including hydrogen bonding, dipole–dipole interaction and 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, shown in Fig. 2, are very close to those of the corresponding samples after reduction clearing; that is, the dye in Nylon fiber is not extracted by DMF. This result provides the evidence that Dye 1 is converted into the reactive vinylsulphone derivative and then combined with Nylon fiber not by van der Waals forces, but by the covalent bond. The most appropriate pH for the reactive disperse dye is 7 on the basis of color strength of the dyeings. Considering that acetic acid, ammonium acetate and pH sliding agent are added in the dye liquor to enhance the dye uptake of acid dyes on Nylon, application of Dye 1 is one of the possible ways for the eco-friendly dyeing of Nylon.

Color strength of Nylon fabrics dyed at 60–100 °C at pH 7 are shown in Fig. 3 in order to examine the effect of dyeing temperature on the dye uptake. As the dyeing temperature rises, color strength increases and the difference in the *K*/*S* value between samples before and after reduction clearing decreases. Color strength of the samples dyed at 80–100 °C look very close, so the color fastnesses of Nylon fabric dyed at 80–100 °C, pH 7 and 1% owf are measured and listed in Table 1. The ratings of color fastnesses to washing, rubbing, dry heat and light are in the range of 4–5. The excellent fastnesses are also attributed to the covalent bond characteristics. Even though dyeing of Nylon fabric with Dye 1 can be successfully done in the dyeing temperature of 80–100 °C, we decide the best dyeing temperature for Dye 1 is 100 °C, considering a little higher rating of wash fastness and the practical dyeing temperature of Nylon fiber with acid dyes.

The exhaustion curve of Dye 1 on Nylon fiber at pH 7 are plotted by measuring color strength of the dyed samples which are taken out from the dye pot at the predetermined dyeing times, and are displayed in Fig. 4. The amount of exhausted dye increases sharply as the temperature of dyeing increases and then equilibrates at 100 °C. In the early stage of dyeing up to 90 °C, *i.e.* until 20 min dyeing, the difference in the *K*/*S* value between samples before and after reduction clearing is large, which means that the proportion of the parent dye is still high. The build-up profile is shown in Fig. 5. It is generally known that disperse dyes are not usually applied to Nylon fabrics due to their lower saturation values. However, since Dye 1 is converted to the reactive vinylsulphone derivative, color strength of the dyed sample increases as the concentration of dye increases, which is not the case in Nylon/disperse dye system. It is obvious that as in the case of dyeing cellulosic fibers with the conventional reactive dyes, reaction of the vinylsulphone group with Nylon fiber promotes dye uptake.

3.2. Effect of pH on the β-elimination reaction of sulphatoethylsulphone group

It is evident from the above experimental results that color strength of the sample dyed with Dye 1 is dependent on the dye bath pH which determines the rate of β-elimination of the acetoxyethylsulphone group in the dye structure. The rate of formation of the reactive vinylsulphone derivative is believed as base-catalyzed; thus, the rate and extent of fixation of the dye to the substrate can be expected to increase with increasing pH of application. Fig. 6 shows variation of the peak areas of the parent dye and vinylsulphone derivative



Scheme 1. β-Elimination of Dye 1 into vinylsulphone derivative which can form the covalent bond with Nylon fiber.

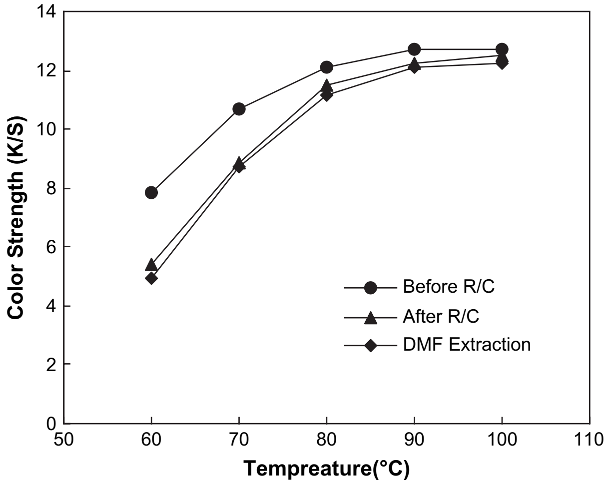


Fig. 3. Effect of dyeing temperature on color strength of Nylon fabric dyed with Dye 1.

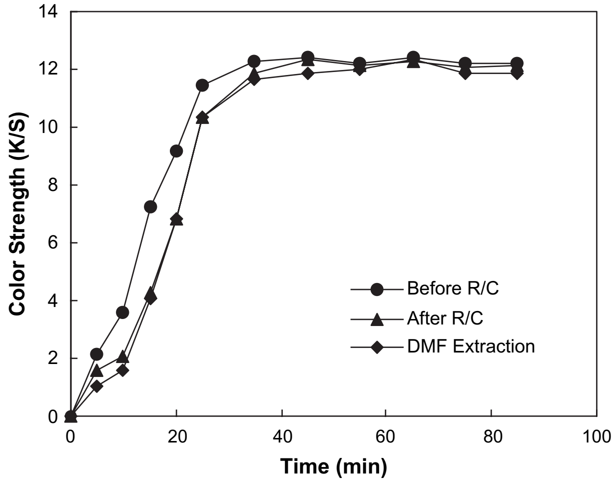


Fig. 4. Exhaustion curve of Dye 1 on Nylon fabric at pH 7.

at pH 4–6 and 100 °C. The values of peak areas of the components determined from the chromatograms are linearly related to their amounts. At pH 4, β-elimination reaction does not occur during the raise of temperature to 100 °C, β-elimination proceeds slowly at 100 °C, and the extent of the reaction after 120 min is as low as 30%. At pH 6, 30% of the parent dye is converted during heating to 100 °C, β-elimination reaction occurs so rapidly at 100 °C that all dye gets reacted after 20 min.

The rate constant of β-elimination reaction (k) is calculated using Eq. (1)

$$\ln\left(\frac{A_0}{A_t}\right) = kt \tag{1}$$

where, A_0 and A_t are values of peak areas of the parent dye at initial state and time t, respectively. The plot of $\ln(A_0/A_t)$ against t is presented in Fig. 7, and yields straight lines passing through the origin with high correlation coefficients, which means the β-elimination reaction is first-order [8]. The rate constants are calculated from the slope of the plot and are listed in Table 2. It reveals that the rate of β-elimination reaction increases 8 times as the pH increases by 1.

3.3. PET dyeing

It is necessary to examine the dyeing properties of the reactive disperse dye on PET fabric before studying N/P mixture fabric dyeing. The amount of adsorbed dyes determined by extraction with hot DMF from PET fabric dyed at several conditions are shown in Fig. 8. Dye 2 is also applied to the substrate and its dyeing properties are compared with those of the reactive disperse dye. Both dyes exhibit fairly good build-up profiles; the dye uptake of two dyes tends to increase linearly as the concentration of dye increases. However, the dye uptakes of 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 bonded to the left benzene ring. Hence, the low dye uptake of Dye 1 is probably caused by the relatively long acetoxyethylsulphone group which can create a difficulty in diffusion of dye molecules into fiber structure. The dye uptakes at 120 °C are 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 3. The ratings of the color fastness of two dyes are excellent. These results reveal that Dye 1 has

Table 1
Color fastnesses of Nylon fabric dyed with Dye 1 at pH 7

Dyeing temperature (°C)	Washing				Rubbing		Dry heat	Light
	PET	Nylon	Wool	Cotton	Dry	Wet	PET	
80	5	5	4/5	5	4/5	4/5	5	4
90	5	5	4/5	5	4/5	4/5	5	4
100	5	5	5	5	5	5	5	4

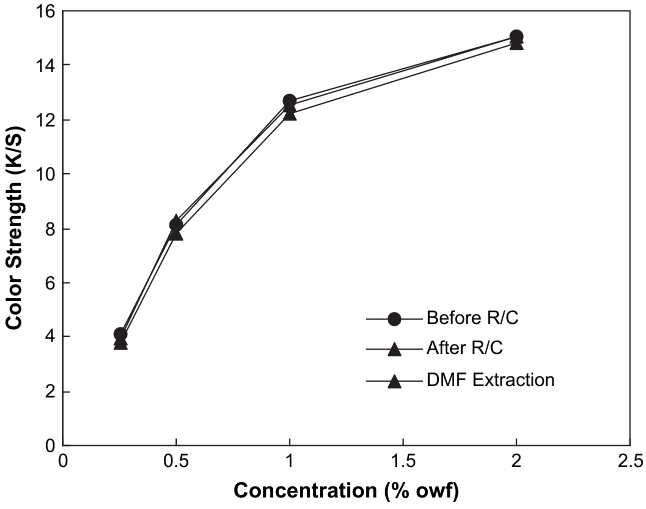


Fig. 5. Build-up profile of Dye 1 on Nylon fabric applied at pH 7 and 100 °C.

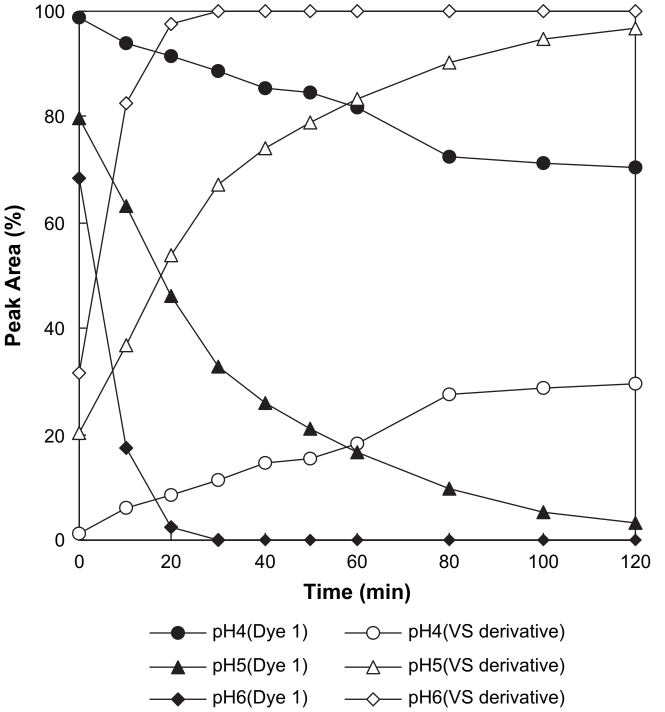


Fig. 6. Effect of pH on the extent of β-elimination reaction of Dye 1 at 100 °C.

the similar dyeing and fastness properties on PET to the conventional disperse dye except the low dye uptake.

3.4. Simultaneous dyeing of Nylon and PET fabrics in a bath

N/P mixture fabric is usually dyed in dyehouse by two-bath method: dyeing PET by disperse dye 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 will be difficult to analyze the dyeing characteristics of each component fiber in the N/P mixture fabric. Hence we first investigate the simultaneous dyeing of Nylon and PET fabrics with Dye 1 in a dye bath. Fig. 9 exhibits the exhaustion curves obtained from an one-step dyeing wherein the same amount of Nylon and PET fabrics are put into a dye pot and then dyed at pH 3–5 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 dyeing since almost all dyes are adsorbed on Nylon in the early stage of dyeing, 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 ways to decrease the difference in color strength between two fabrics is by lowering the pH to decelerate the β-elimination reaction of Dye 1. Color strength of both fabrics dyed at pH 3 and 4 are also shown in Fig. 9. As pH decreases the gap in color strength between two fabrics is narrowed because the formation of reactive vinylsulphone derivative, which can easily form the covalent bond with Nylon fiber, is suppressed.

Table 2
Rate constants of β-elimination reaction for Dye 1 at 100 °C

PH	k (min^{-1})
4	0.0032
5	0.0269
6	0.1625

3.5. N/P mixture dyeing

N/P mixture fabric was dyed with Dye 1 by the one-step, one-bath method at pH 3–4 and 120 °C. As the concentration of dye increases, color strength of dyed N/P mixture fabric, shown in Fig. 10, increases linearly. As expected, color strength of mixture fabric dyed at pH 4 is higher than those at pH 3 at all dye concentrations. The color fastnesses

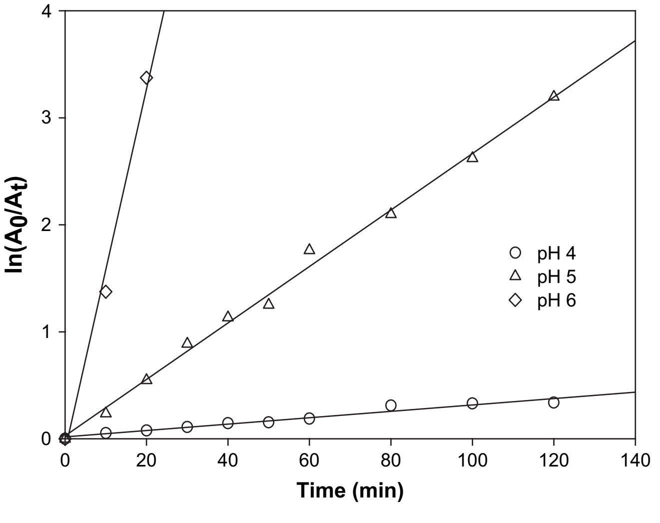


Fig. 7. Effect of pH on the rate of β-elimination reaction of Dye 1 at 100 °C.

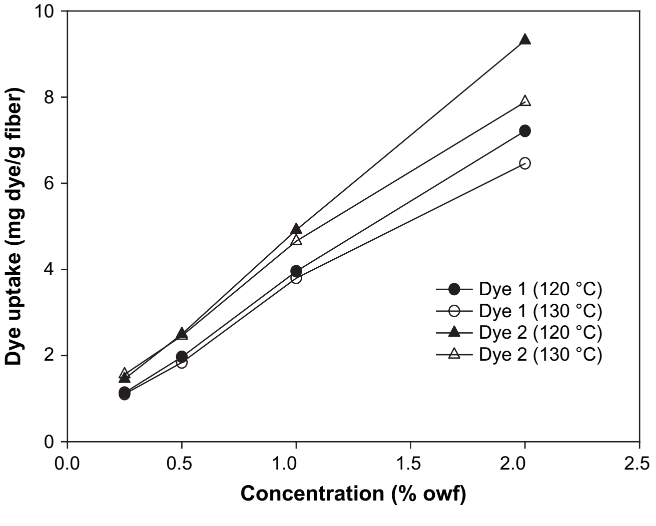


Fig. 8. Build-up profiles of Dyes 1 and 2 on PET fabric.

Table 3
Color fastnesses of PET fabric dyed with Dyes 1 and 2 at 120 °C and pH 4.5

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

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

pH	Washing				Rubbing		Dry Heat	Light
	PET	Nylon	Wool	Cotton	Dry	Wet	PET	
3	5	3/4	3	5	5	4/5	5	4
4	5	4	3/4	5	5	4/5	5	4

of N/P mixture fabric dyed at 120 °C and 1% owf are measured and are listed in Table 4. The ratings of color fastness to washing, rubbing, dry heat and light are good to excellent. Dyeing at pH 4 results in higher color strength and a little better wash fastness, while dyeing at pH 3 can provide one-tone effect. Although the one-step, one-bath dyeing at pH 3 gives the similar color strength to two-component fibers, it is undesirable to get one-tone effect by diminishing the dye uptake on Nylon. Further study is needed to obtain one-tone effect by improving the dye uptake on PET.

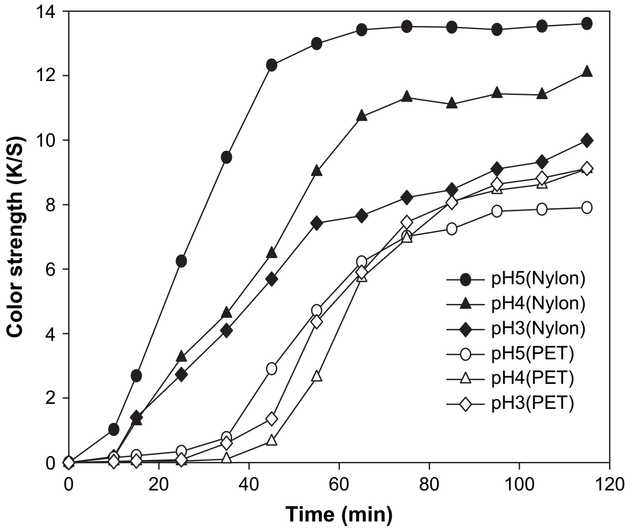


Fig. 9. Effect of pH on color strength of Nylon and PET fabrics on simultaneous dyeing with Dye 1.

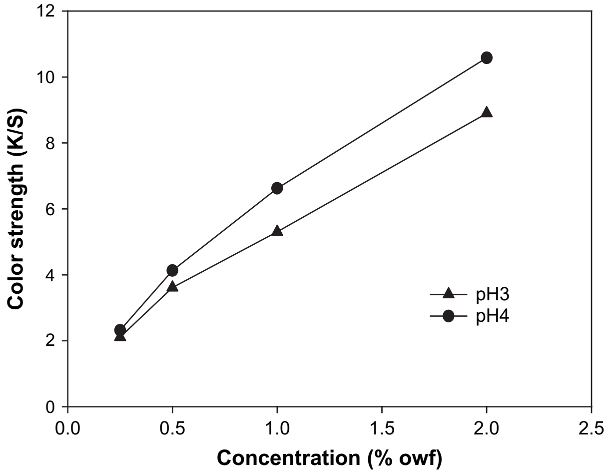


Fig. 10. Build-up profiles of Dye 1 on N/P mixture fabric dyed at 120 °C.

4. Conclusions

The dyeing and color fastness properties of a reactive disperse dye containing acetoxyethylsulphone group on Nylon fabric, PET fabric and N/P mixture fabric have been investigated. The most appropriate pH for the dyeing of Nylon fabric was 7 and suitable dyeing temperature was 100 °C. The build-up on Nylon fabric was good and various color fastness were good to excellent due to the formation of the covalent bond. Comparison of color strength of Nylon extracted by DMF with those of the corresponding samples after reduction clearing, indirectly proved that the reactive disperse dye was converted into the reactive vinylsulphone derivative and then combined with Nylon fiber not by van der Waals forces, but by the covalent bond. It was found by HPLC analysis that the β-elimination reaction was first-order, and that the rate of β-elimination reaction of the reactive disperse dye at 100 °C increased 8 times as the pH increased by 1.

Although the dye uptakes of the reactive disperse dye were lower than those of a conventional disperse dye on PET fabric, the reactive disperse dye exhibited good build-up profiles and the ratings of the color fastnesses were good to excellent. The rate of dyeing of the reactive disperse dye on Nylon fabric was faster than on PET fabric when both fabrics were dyed simultaneously in a dye bath. The difference in color strength between two fabrics decreased as the pH decreased, and dyeing at pH 3 could give the very similar color strength to both fabrics. The reactive disperse dye was adequate to the one-step, one-bath dyeing of N/P mixture fabric when applied at pH 3−4 and 120 °C, and color fastnesses were good. Further study is still needed to provide one-tone effect on N/P mixture fabric not by diminishing the dye uptake on Nylon, but by enhancing the dye uptake on PET.

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