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Dyeing Properties of Nylon, PET, and N/P Mixture Fabric with Reactive-disperse Dyes Having a Sulfatoethylsulfone Group

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Abstract: The dyeing and color fastness properties of two reactive-disperse dyes containing a sulfatoethylsulfone group on nylon, PET and N/P mixture fabrics were examined. The rate of dyeing on nylon fabric was greatly dependent upon dye bath pH. The final dye uptakes at all pH, however, were as high as 97 %. Color strength of the dyed nylon fabric linearly increased up to 0.5 %owf and then slowed down over 1 %owf dyeing. Washing and rubbing fastness of the dyed nylon fabric were excellent, but grade of light fastness was moderate. Dyeability of the reactive-disperse dyes on PET fabric was not much affected by pH, and *K/S* values of PET fabric dyed at pH 5-8 were lower than those of nylon fabric at all pH examined. Build-up and color fastnesses properties on PET fabric showed the same tendency with nylon fabric. The rate of dyeing of the reactive-disperse dyes on nylon fabric was faster than on PET fabric when both fabrics were dyed simultaneously in the same dye pot, resulting in higher color strength of nylon than PET. The reactive-disperse dyes were found to be adequate to the one-bath, one-step dyeing of N/P mixture fabric when applied at pH 5 and 120 ^{o}C.

Keywords: Reactive-disperse dye, Sulfatoethylsulfone group, One bath dyeing, N/P mixture fabric

Introduction

Fabrics, made of two or more fibers, are commonly manufactured and used for various purposes in textile industry. There are several reasons for the development of these fabrics: economy, the dilution of an expensive fiber by combining with a cheaper substitute; durability, the incorporation of a more durable component to extend the useful life of a relatively fragile fiber; physical properties, a compromise to take advantage of desirable performance characteristics; color, the development of novel garment or fabric designs incorporating multicolor effects; appearance, the attainment of attractive appearance and tactile qualities using combinations of fibers of different luster or denier which still differ in appearance even when dyed uniformly to the same color [1]. Combination of different fibers in a fabric is performed by blending, conjugation spinning or mixture weaving.

Dyeing of mixture fabric is required of careful treatments because the component fibers have different dyeing and physical properties [2-4]. 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, which can save considerable processing time and energy, often results in deteriorating quality of dyeing and color fastness, caused by the staining 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 [5].

Disperse dyes containing a reactive group are called reactive-disperse dyes. Those are a type of universal dyes since they have possibilities to apply to several different types of fibers, and sulfatoethylsulfone (SES) group is one of the typical reactive group. Dohmyou reported dyeing properties of temporarily solubilized disperse dyes containing SES group to polyester(polyethylene terephtalae or PET)/silk blends in earlier study [6]. Burkinshaw and Collins also studied the improvement of washing fastness on nylon fiber with reactive disperse dyes having SES group [7]. Lee *et al.* synthesized temporarily solubilized SES azo disperse dyes and investigated dyeing properties on PET [8,9] and PET/cotton blends [10]. Youssef and Mousa researched about comparison between monofunctional and bifunctional SES reactive-disperse dyes on nylon [11-13].

The dyeing of PET with disperse dyes is usually carried out at pH 4-5. Nylon is also dyed in acidic conditions. Hence a reactive-disperse dye which has good dyeing properties on PET and nylon fibers in acidic condition might be beneficial to one-bath dyeing of nylon/PET (N/P) mixture fabric. A reactive-disperse dye carrying acetoxyethylsulfone group was tested to the dyeing of N/P mixture fabric [14]. In this study, the reactive-disperse dyes, which contain a SES group, are synthesized and their dyeing properties on nylon, PET and N/P mixture fabric are investigated.

Experimental

Materials

All chemicals such as aminophenyl-4-(β-sulfatoethylsulfone), *N*,*N*-diethylaniline, sodium hydroxide, sodium hydrosulphite, sodium nitrite, and *N*-benzyl-*N*-methylaniline used in the synthesis of dyes and dyeing were laboratory grade reagents. Nylon 6 fabric (70 d/20 f, plain weaved, 106×84/inch^2), PET fabric (75 d/24 f, plain weaved, 100×74/inch^2), N/P mixture fabric (warp, nylon 6, SD Filament DTY 70 d/68 f; weft,

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PET SD Filament DTY 150 d/288 f; nylon/PET=53/47) were used for dyeing.

Synthesis of Dye 1

Two dyes were synthesized in this study. Chemical structures of them are shown in Figure 1 and their properties are listed in Table 1. 7.78 g (0.025 mol) aminophenyl-4-(β-sulfatoethylsulfone) was added into 300 m*l* distilled water and 6 m*l* 35 % HCl and then temperature was lowered to 0 °C. The diazonium salt solution was prepared by the addition of 1.94 g (0.0275 mol) $NaNO_2$ dissolved in 20 m*l* water. 3.79 g (0.025 mol) N,N-diethylaniline was slowly added into diazonium salt solution and stirred for 2 h under 5 °C. After solution of the reaction mixture was allowed to warm to room temperature, pH was adjusted to 5-6 with sodium acetate solution, and 30 g NaCl was added to precipitate the dye. Precipitated dye was filtered and vacuum dried at room temperature. Dried dyes were dissolved in DMF and filtered to eliminate the salts and impurities. Dye was reprecipitated by adding chloroform into dye solution dissolved in DMF. The yield of reaction was 59.21 %. ^{1}H-NMR (DMSO-d_6, 400 MHz), δ1.15 (6H, t, CH_3), 3.47 (4H, q, N-CH_2), 3.67 (2H, t, CH_2-SO_2), 3.98 (2H, t, O-CH_2), 6.82 (2H, d, Ar-H), 7.81 (2H, d, Ar-H), 8.01 (4H, q, Ar-H). LC-MSD (acetonitrile: 0.1 %formic acid=9:1), ESI$^+$ m/z=442, ESI$^-$ m/z=440.

Synthesis of Dye 2

The same reaction procedures were applied except using 4.97 g (0.025 mol) *N*-benzyl-*N*-methylaniline as a coupler. The yield of reaction was 83.40 %. ^{1}H-NMR (DMSO-d_6, 400 MHz), δ3.19 (3H, s, N-CH_3), 3.66 (2H, t, CH_2-SO_2), 3.98 (2H, t, O-CH_2), 4.76 (2H, s, N-CH_2), 6.89 (2H, d, Ar-H), 7.21 (2H, t, Ar-H), 7.23 (1H, t, Ar-H), 7.34 (2H, d, Ar-H), 7.81 (2H, d, Ar-H), 8.01 (4H, q, Ar-H). LC-MSD (acetonitrile: 0.1 % formic acid=9:1), ESI$^+$ m/z=490, ESI$^-$ m/z=488.

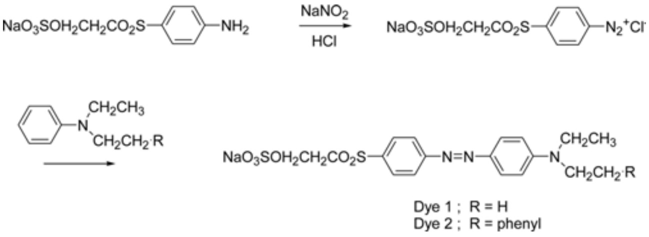


Figure 1. Reaction scheme and chemical structure of the dyes used in this study.

Table 1. Reaction yield, melting point, mass, molecular weight, and color of Dye 1 and 2

Dye	Yield (%)	M.P. (°C)	Mass (m/z)	MW (g/mol)	Color
Dye 1	59.21	204	441	463.50	Orange
Dye 2	83.40	235	489	511.55	Orange

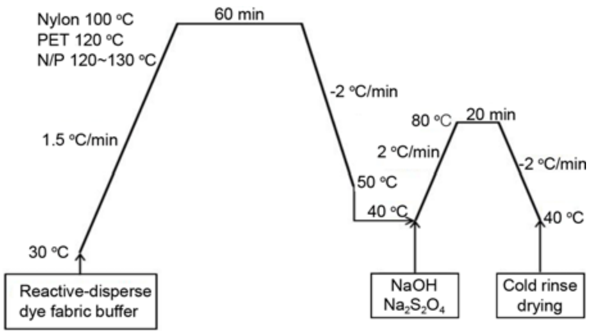


Figure 2. Typical dyeing procedure used in experiments.

Dyeing

Dyeing was carried out in the sealed dyepot (Labomat, Mathis) and a liquor ratio was 20:1. pH was adjusted with buffer solutions. Temperature was raised at the rate of 1.5 °C/min from 30 °C to the highest dyeing temperature (nylon 100 °C, PET 120 °C, simultaneous dyeing 120 °C, N/P mixture fabric 120 °C), and dyeing was continued at the highest temperature for 60 min, then the temperature was lowered to 50 °C. Dyed fabric was reduction cleared (R/C) in an aqueous solution containing 2 g/*l* sodium hydroxide and 2 g/*l* sodium hydrosulfite at 80 °C using a liquor ratio 40:1 for 20 min, rinsed and dried. Fabrics were heat setted at 180 °C for 30 s. Dyeing procedures of nylon, PET, and N/P mixture fabrics are shown in Figure 2. Build-up property was studied at various dye concentrations (0.25, 0.5, 1, 2 %owf), and the rate of dyeing was also investigated with Dye-O-Meter (DyeMax-L, Dyetex engineering).

Measurements of Color Strength and Fastness

The reflectance values of the dyed fabric were measured using a spectrophotometer (ColorEye 7000A, X-Rite) under illuminant D65 using 10 ° standard observers. Color strength (*K*/*S*) was calculated from the reflectance value using the well-known Kubelka-Munk equation.

Fastness to washing, light and rubbing were measured using ISO 105-C06 A2S:1994(E), AATCC Test Method 165 and AATCC 16E, respectively.

Results and Discussion

Nylon Dyeing

The dye bath pH is a very important factor in nylon dyeing. Dyeings are performed at 100 °C varying pH from 4 to 8 with Dye 1 and exhaustions at each pH are measured every 5 min by Dye-O-Meter system, and shown in Figure 3. The rate of absorption of dye at early stage of dyeing is very dependent on the dye bath pH, the order is pH 4 > pH 5 > pH 8 > pH 7 > pH 6, and the dyeing at pH 6 reaches saturation point 40 min later than at pH 4. But, the final exhaustions at all pH are over 97 %, meaning the dyeability of Dye 1 on nylon fiber is excellent.

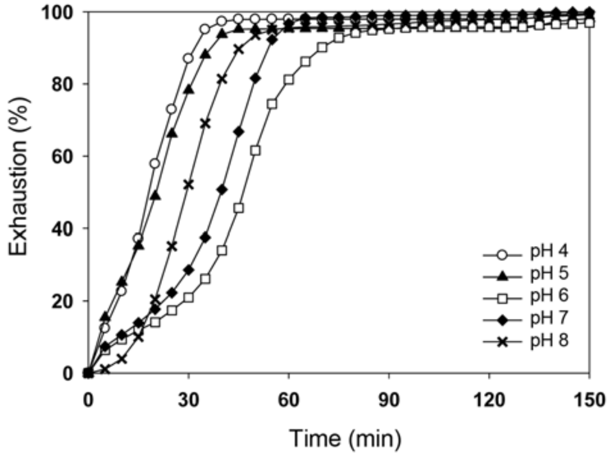
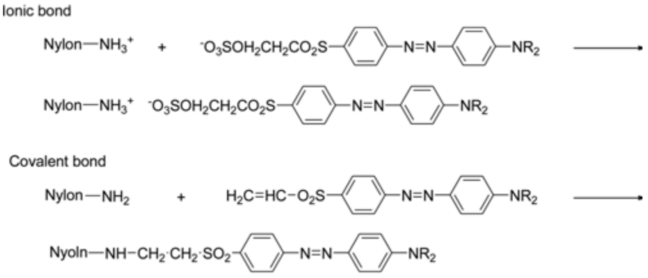
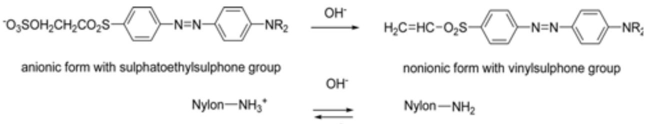


Figure 3. Dyeing behavior of Dye 1 on nylon at various pH.

It is well known that water soluble SES group is converted into the reactive VS group during dyeing process, and that the rate of conversion increases as both dye bath pH and dyeing temperature increase. The VS group forms a covalent bonding with amino group in nylon fiber by nucleophilic addition reaction. Thus, the rate of dyeing between the reactive-disperse dyes containing a SES group and nylon fiber is closely related to the following factors: the rate of absorption of the dyes on the fiber surface through electrostatic interaction and the rate of formation of covalent bond between dye and fiber, as shown in Scheme 1. These two interactions are key factors that decide the dyeing rate, and the combination of both factors with different ratio might result in the exhaustion curves with different rates at pH 4-8. When the dye bath pH is low, dye molecules tend to remain as anionic form with SES group and nylon fiber possesses positive charge due to the protonation of amino group as depicted in Scheme 2. The reason of rapid rate of dyeing at pH 4 and 5 might be that the cations on nylon fiber quickly attract the dye anions by electrostatic interaction. On the other hand, when the dye bath pH is alkaline, SES group in dye molecule is rapidly converted into nonionic VS group, and nylon fiber does not carry positive charge, and nucleophilicity of the amino group in nylon fiber becomes high. The nucleophilic addition reaction between amino groups on the nylon fiber and VS groups on the dye takes place. This is the reason for the moderate rate of dyeing at pH 8. The slowest rate of dyeing at pH 6 might be caused by the state of nylon fiber which is neither cationic nor strongly nucleophilic to attract dye molecules.



Scheme 1. Two important interactions between reactive-disperse dye and nylon fiber.



Scheme 2. Effect of pH on the state of reactive-disperse dye and nylon fiber.

Investigating build-up properties of the reactive-dispersive dyes on nylon fiber are performed at pH 5, 100 °C with dye concentration of 0.25, 0.5, 1, 2 %owf. The color strength of dyed nylon fabric is measured and presented by *K*/*S* values in Figure 4. The dyeing characteristics of Dye 1 and 2 are much alike. Higher *K*/*S* values are obtained with both dyes as the dye concentration increases. The slope of color strength, however, slows down over 1 %owf dyeing. Dye 2 has one more benzene ring in a coupling component than Dye 1, which makes Dye 2 more hydrophobic. It can be known from the results that increasing the hydrophobicity does not influence the dyeing properties of the reactive-disperse dyes used. *K*/*S* values after R/C are almost the same with those after dyeing, which can be used as an indirect evidence of forming covalent bonds between nylon fiber and the reactive-disperse dyes. Grades of fastness to washing, light and rubbing of dyed nylon fabric with Dye 1 and 2 are shown in Table 2. Washing fastness and rubbing fastness are good to excellent with grade 4-5, while light fastness is moderate: grade 3-4 for Dye 1 and grade 3 for Dye 2.

PET Dyeing

It is necessary to examine dyeing properties of the reactive-disperse dye on PET fabric before studying N/P mixture

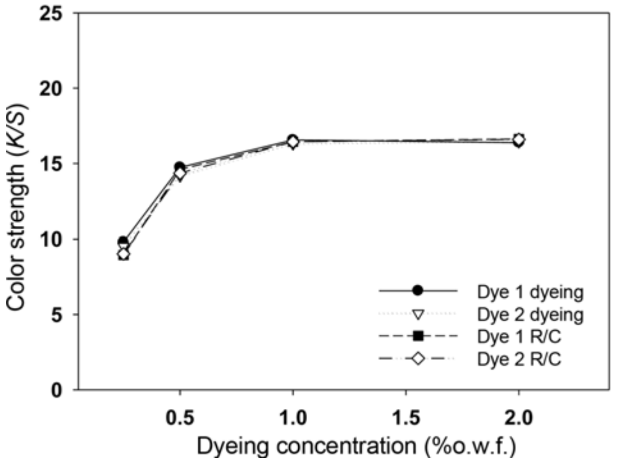


Figure 4. Build-up properties of Dyes 1 and 2 on nylon.

Table 2. Fastness to washing, light, and rubbing of Dye 1 and 2 on nylon

Dye	%o.w.f.	Washing							Light	Rubbing	
		Color change	Staining							Dry	Wet
			Wool	Acryl	PET	Nylon	Cotton	Acetate			
Dye 1	0.25	5	5	5	5	5	5	5	3-4	5	5
	0.5	5	5	5	5	5	5	5	3-4	4-5	4-5
	1	5	5	5	5	5	5	5	3	4-5	4-5
	2	5	5	5	5	4-5	5	4-5	3	4-5	4-5
Dye 2	0.25	4-5	5	5	5	5	5	5	3	5	5
	0.5	4-5	4-5	5	4-5	4-5	4-5	4-5	3	5	5
	1	4-5	4-5	4-5	4-5	4-5	4-5	4-5	3	4-5	4-5
	2	4-5	4	4-5	4	4	4-5	4	3	4-5	4-5

fabric dyeing. PET dyeing is performed at 120 °C varying the dye bath pH from 4 to 8 with Dye 1 and then reduction-cleared. Effect of pH on color strength of PET dyed with Dye 1 at various pH is shown in Figure 5. *K*/*S* values of PET fabric dyed at pH 5-8 are about 11.7, those values are somewhat lower than *K*/*S* values of nylon dyed with Dye 1. The dyeability on PET is not much affected by pH except at pH 4. Hydrophobic PET fabric is not dyed well with Dye 1 as long as Dye 1 possesses SES group which is very polar. The reactive-disperse dye can be attracted by PET through van der Waals force after SES group is converted into VS group. Slow conversion of SES group into VS group attributes to the lowest color strength of PET dyed at pH 4.

Color strength of PET fabrics dyed with the reactive-disperse dyes at four different dye concentrations are shown in Figure 6. Both dyes exhibit very similar build-up properties: the dye uptake tends to increase linearly up to 0.5 %owf and then slow down over 1 %owf dyeing. We expect Dye 2 to show higher dye uptake than Dye 1 since it has one more benzene ring which enhances hydrophobicity and subsequently interacts more strongly with PET fiber. However, difference in dyeing properties between two dyes is scarcely observed. It can be explained by the slow diffusion of Dye 2, which has higher molecular weight than Dye 1, into compactly packed PET fiber. Grades of fastness to washing, light and rubbing of the dyed PET fabrics with Dye 1 and 2 are shown in Table 3. Washing and rubbing fastness are very good to excellent, but grade of light fastness is moderate.

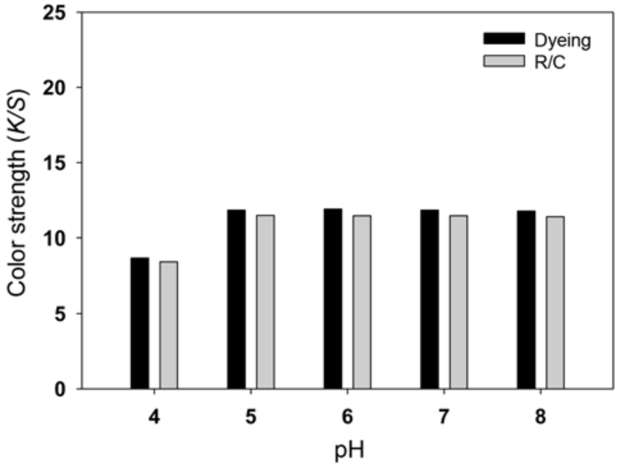


Figure 5. Effect of pH on the color yield of Dye 1 on PET.

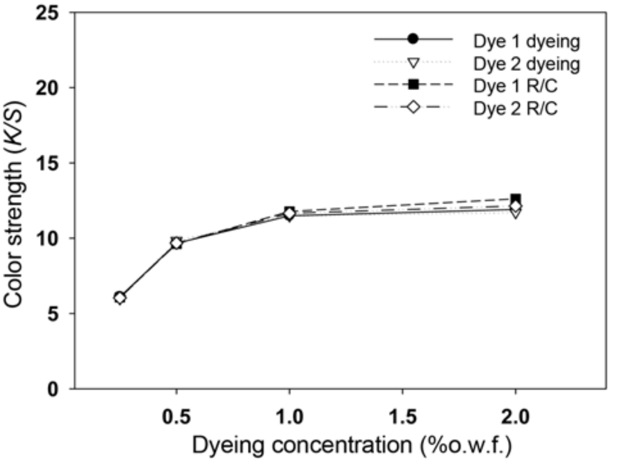


Figure 6. Build-up properties of Dyes 1 and 2 on PET.

N/P Mixture Fabric Dyeing

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-bath, one-step dyeing method using a reactive-disperse dye is applied, it will be difficult to analyze the dyeing characteristics of each component fiber in N/P mixture fabric. Hence the simultaneous dyeing of nylon and PET fabrics with Dye 1 in a dye bath is tried. Nylon and PET fabrics are prepared as the weight ratio of nylon and PET fibers in N/P mixture fabric (nylon/PET=53/47, w/w) and dyed in the same bath. Dyeing is performed at 120 °C varying pH from 4 to 7 with Dye 1 and *K/S* values of each fabric are represented in Figure 7. It is found that color strength of nylon fabric are much higher than those of PET fabric at all

Table 3. Fastness to washing, light, and rubbing of Dye 1 and 2 on PET

Dye	%o.w.f.	Washing							Light	Rubbing	
		Color change	Staining							Dry	Wet
			Wool	Acryl	PET	Nylon	Cotton	Acetate			
Dye 1	0.25	5	5	5	5	5	5	5	3-4	5	5
	0.5	5	5	5	5	5	5	5	3-4	4-5	5
	1	5	5	5	5	5	5	5	3-4	4-5	5
	2	5	5	5	5	5	5	5	3-4	4-5	5
Dye 2	0.25	4-5	5	5	5	5	5	5	3	4-5	4-5
	0.5	4-5	5	5	5	5	5	5	3	4-5	4-5
	1	4-5	4-5	4-5	4-5	5	5	5	3	4-5	4-5
	2	4-5	4-5	4-5	4-5	5	5	4-5	3	4-5	4-5

pH examined: *K*/*S* values of dyed nylon are 16-17, they are not affected by pH; *K*/*S* values of PET dyed at pH 5-7 are about 8, they are a little higher than those at pH 4. Comparing results of the simultaneous dyeing to those of the homogeneous dyeing, nylon does not show much difference in its color strength, whereas *K*/*S* values of PET are decreased a lot.

It is necessary to raise the dye uptake on PET fabric to reduce the color differences between two fabrics. For this reason, a diffusion agent, Univadine PB, is applied. The diffusion agent used at this study is an anion aromatic hydrocarbon mixture and it is known for relaxing the PET structure and accelerating the dye diffusion. The simultaneous dyeing of nylon and PET fabrics with the diffusion agent is performed at pH 5 with 1 %owf of Dye 1, and the results are shown in Figure 8. It is found that there is no difference in color strength of nylon fabric whether the diffusion agent is used or not, and that PET, by contrast, shows certain amount of increasing in *K*/*S* value with 1-2 g/*l* of the auxiliary. The effect of the diffusion agent is not sufficient enough to secure one-tone effect between two fabrics.

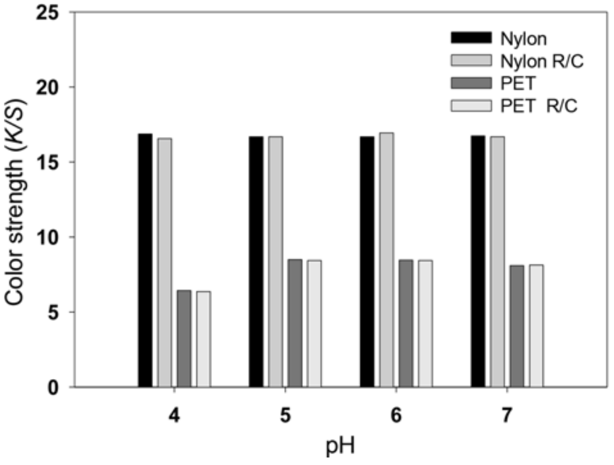


Figure 7. Effect of pH on the color yield of Dye 1 on nylon and PET in the simultaneous dyeing.

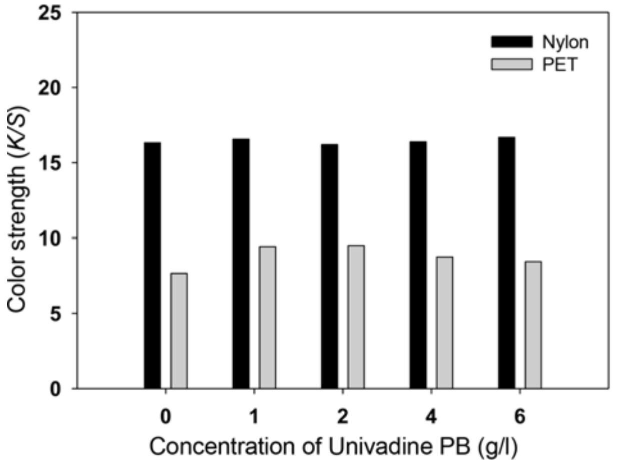


Figure 8. Effect of diffusion agent on the distribution of Dye 1 between nylon and PET in simultaneous dyeing.

We choose pH 5 for dyeing of N/P mixture fabric, considering practical dye bath pH of nylon and PET fabrics. The exhaustion curves of Dye 1 and 2 obtained by the simultaneous dyeing at pH 5, are plotted by measuring color strength of the dyed samples which are taken out from the dye pot at the predetermined dyeing time, and are displayed in Figure 9 in order to examine distribution of dye between two fibers as a function of dyeing time. Nylon exhibits so good dyeing properties with the reactive-disperse dyes that it absorbs dye molecules even at lower temperatures as soon as the dyeing process starts. The amount of exhausted dye increases sharply as the dyeing temperature increases, and reaches saturation at 90 °C, i.e. dyeing time 60 min. On the other hand, PET shows poor dyeing properties with the reactive-disperse dyes and starts to absorb dye at 90 °C. In other words, PET just gets started to absorb the dye when nylon finishes the exhaustion of dye and there is, actually, not much amount of the dye left at the dye bath useful to PET fabric. Consequently, the amount of dye uptake on nylon is far more than that on PET. Two factors attribute to slow rate of PET dyeing: one is the compact structure of PET fiber that needs

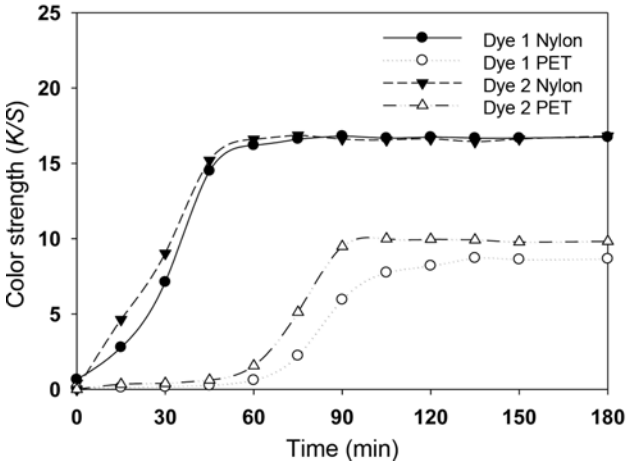


Figure 9. Distribution of dyes between nylon and PET fiber in the simultaneous dyeing.

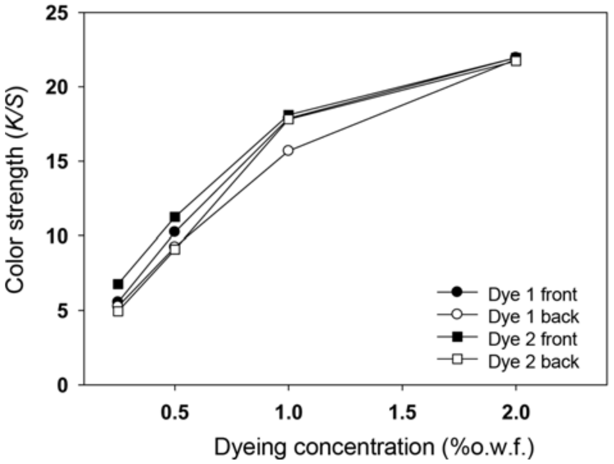


Figure 10. Build-up properties of Dyes 1 and 2 on N/P mixture fabric.

Table 4. Fastness to washing, light, and rubbing of Dye 1 and 2 on N/P mixture fabric

Dye	%o.w.f.	Washing							Light	Rubbing	
		Color change	Staining							Dry	Wet
			Wool	Acryl	PET	Nylon	Cotton	Acetate			
Dye 1	0.25	4-5	5	5	5	5	5	4-5	4	5	5
	0.5	4-5	4-5	5	5	5	5	4-5	4	5	5
	1	5	4-5	5	5	4-5	5	4	3-4	5	5
	2	4-5	4	4	4	3	4	3	3-4	4-5	5
Dye 2	0.25	4-5	5	5	5	5	5	4-5	3	4-5	4
	0.5	4-5	4-5	5	5	5	5	4-5	3	4-5	4
	1	5	4-5	5	5	4-5	5	4	3-4	4-5	4
	2	4-5	4	4	4	3-4	4-5	3-4	3-4	4	3-4

high temperature to relax its structure, the other is weak attraction force of PET toward SES form of the reactive-disperse dye. Dye 2 which is more hydrophobic shows a little higher *K/S* values of PET than Dye 1 in the simultaneous dyeing.

N/P mixture fabric is dyed with Dye 1 and 2 by one-bath, one-step method at pH 5 and 120 °C. As the concentration of dye increases, color strength of dyed N/P mixture fabric, shown in Figure 10, increases linearly up to 1 %owf. Both dyes show the similar build-up profiles. Even though there is difference in color strength between two component fibers, the surface, either front side or back side, of N/P mixture fabric looks almost solid color due to fabric structure. Color fastness to washing, light and rubbing of the dyed N/P mixture fabric, listed in Table 4, show very similar tendency to those of 100 % nylon and 100 % PET. Although the one-bath, one-step dyeing gives pseudo one-tone effect, it is more desirable to make even distribution of dyes between two component fibers.

Conclusion

The dyeing and color fastness properties of the reactive-disperse dyes containing a sulfatoethylsulfone group on nylon, PET and N/P mixture fabrics have been investigated. Nylon is successfully dyed with both Dye 1 and 2 at pH 4-8, the rate of dyeing at early stage is largely affected by dye bath pH, however, the final dye uptakes at all dye bath pH are over 97 %. Different dyeing rates at pH 4-8 are probably caused by the combination of two main interactions such as electrostatic force and covalent bonding between dye molecule and nylon with different ratios. Color strength of the dyed nylon increases up to 0.5 %owf and then slows down over 1 %owf dyeing. Washing and rubbing fastness of the dyed nylon are excellent, but grade of light fastness is moderate. Dyeability of the reactive-disperse dyes on PET is not much influenced by dye bath pH. *K/S* values of PET fabric dyed at pH 5-8 are lower than those of nylon at all pH examined. Build-up and color fastnesses properties of PET show the same tendency with nylon. The rate of dyeing of the reactive-disperse dyes on nylon fabric is faster than on PET fabric when both fabrics are dyed simultaneously in a dye pot. Subsequently color strength of nylon is much higher than PET. N/P mixture fabric is dyed well with the reactive-disperse dyes when applied at pH 5 and 120 °C, and their build-up property are better than 100 % nylon and PET fabrics. Further study on the structure of a reactive-disperse dye is necessary to obtain true one-tone effect by improving the dye uptake on PET.

Acknowledgements

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