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Dyeing Properties of 4-Amino-4'-fluorosulfonylazobenzene Disperse Dyes on Poly(ethylene terephthalate)

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Abstract: Dyeing properties of a series of 4-amino-4'-fluorosulfonylazobenzene disperse dyes on poly(ethylene terephthalate) (PET) were investigated. Build-up properties and color properties on PET were examined. In particular, the 4-aminoazobenzene dyes containing a nitro group instead of a fluorosulfonyl group at 4'-position were also synthesized in order to compare their dyeing properties on PET with that of 4'-fluorosulfonyl analogues.

Keywords: Poly(ethylene terephthalate), 4-Amino-4'-fluorosulfonylazobenzene disperse dyes, Build-up properties, Color properties

Introduction

In the disperse dyeing of poly(ethylene terephthalate) (PET), the usual aftertreatment carried out is reduction clearing, where the dyed fabric is treated in a strong reduction bath, usually made up of sodium hydrosulfite and caustic soda. However, when the conventional reduction clearing process is applied to azo disperse dyes, azo linkage is broken. If this occurs toxic amines may be liberated into the effluent, which also has high BOD values due to the presence of sodium hydrosulfite [1,2]. Alkali-clearable disperse dyes offer a means of tackling both of these challenges simultaneously. These so-called alkali-clearable disperse dyes obviated the need for sodium hydrosulfite and significantly reduced the cost of effluent treatment [3-10]. Furthermore, it is thought that minimizing the need for reduction clearing can lead to substantial productivity improvements and water and chemical savings as well as a reduction on the effluent load and should be a key objective in implementation of a “Rapid Dyeing” approach for polyester [2].

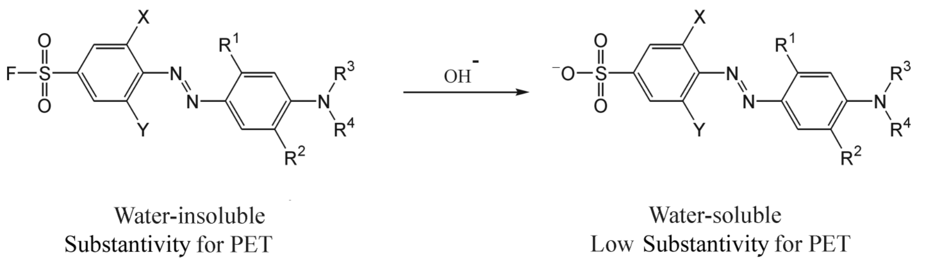
In previous work [6-10], we suggested novel alkali-clearable azo disperse dyes containing a sulfonyl fluoride group. The azo disperse dyes containing a fluorosulfonyl group were hydrolyzed under alkaline condition by S_N2 mechanism (Scheme 1), and pseudo first-order kinetics were determined by analysis of the dye hydrolysis under alkaline conditions using HPLC [7,8]. Their spectral properties were also examined with respect to the effects of substituents in absorption spectra, halochromism and solvatochromism [9]. However, since the introduction of new alkali-clearable azo disperse dyes containing a fluorosulfonyl group [6], only very little information is available on the dyeing properties on PET. Therefore, it would be worth comparing their dyeing properties on PET compared with the conventional azo disperse dyes.

In this study, dyeing properties of 4-(*N*,*N*-diethylamino)-4'-fluorosulfonyl azobenzene disperse dyes and their 4'-nitro analogues on PET were investigated in a comparative manner.

Experimental

Materials

PET fabrics (KS K 0905, 70 ± 5 g/m^2, plain weave, warp yarn: 75 denier, weft yarn: 75 denier) were used for dyeing throughout the study. All the chemicals used in the synthesis and dyeing were of laboratory-reagent grade. Diwatex (Borregaard Lignotech, anionic) was used as a dispersing



Scheme 1. Alkali-hydrolysis of 4-amino-4'-fluorosulfonylazobenzene disperse dyes (X,Y=H, Cl, Br, NO_2, CN, R^1, R^2=H, CH_3, OCH_3, $NHCOCH_3$, R^3, R^4=substituted alkyls).

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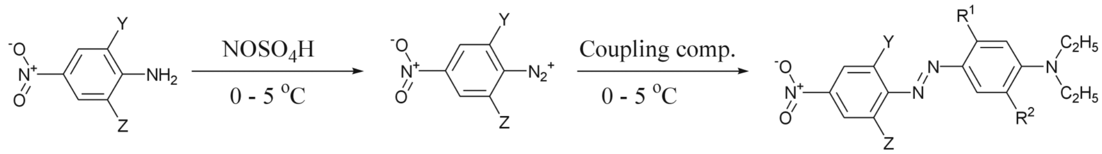
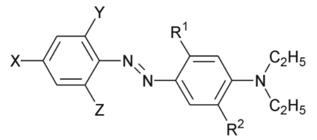


Scheme 2. Diazotization of 4-nitroaniline and its coupling reaction.

Table 1. 4-(*N*,*N*-Diethylamino)-4'-fluorosulfonylazobenzene dyes **1-6** used in the present study



Dye	X	Y	Z	R^1	R^2
1a	FO_2S	H	H	H	H
1b	NO_2	H	H	H	H
2a	FO_2S	H	H	H	CH_3
2b	NO_2	H	H	H	CH_3
3a	FO_2S	NO_2	H	H	H
3b	NO_2	NO_2	H	H	H
4a	FO_2S	NO_2	H	H	CH_3
4b	NO_2	NO_2	H	H	CH_3
5a	FO_2S	NO_2	Cl	H	H
5b	NO_2	NO_2	Cl	H	H
6a	FO_2S	NO_2	Cl	H	CH_3
6b	NO_2	NO_2	Cl	H	CH_3

agent for milling and Lyocol RDN Liquid (Clariant, anionic) was used as a dispersing agent for the dyeing of polyester fabric. Sandozin NIE (Clariant, nonionic) was used as a wetting agent.

Dye Synthesis

The synthesis of 4-(*N*,*N*-diethylamino)-4'-fluorosulfonylazobenzene disperse dyes has been described in the previous work [7,9]. In order to synthesize 4-(*N*,*N*-diethylamino)-4'-nitroazobenzene disperse dyes, the same procedure was repeated except that in place of substituted amines containing fluorosulfonyl group, and the substituted amines containing a nitro group as diazo components were used (Scheme 2) [7]. The dyes **1-6** that were used throughout the study were given in Table 1.

Preparation of Dye Dispersions

Synthesized dyes were formulated to be applied to PET. The composition comprises dispersing agent (Diwatex, 40 % on the weight of the dye), wetting agent (Sandozin NIE Liquid, 1 drop) and dye (1.0 % on the weight of water) in 100 m*l* of water that is buffered at pH 4.0 to 4.5. Dye dispersions were prepared by milling the composition mixture with glass beads in an aqueous medium for 1 week until the mean particle size was ~1 μm.

Dyeing

PET fabrics were dyed in a laboratory using a dyeing machine (Ahiba, Datacolour International) at a liquor ratio of 30:1. 60 m*l* of dyebath was prepared with the formulated dyes and a dispersing agent (Lyocol RDN Liquid 1.0 m*l*/*l*) and adjusted to pH 4.5. Then, PET fabric (2.0 g) was immersed in the dyebath for 60 min at 130 °C.

The percentage of dyebath exhaustion on PET was estimated colorimetrically by extracting the dyed fabric with DMF under reflux at boiling point for 5 min and measuring the absorbance value of extracted dye using a UV/Visible-spectrophotometer (Kontron uvikon).

Color Measurement

The color properties (CIE L*, a*, b*, C*, and h_{ab}) of the PET samples dyed with the synthesized dyes (dyes **1-6**) were measured using a spectrophotometer (Spectra flash 500, Datacolor, standard light D65, 10 ° standard observer, SPIN) interfaced with a personal computer.

The build-up property of dye was also investigated by measuring f_k values of dyed fabrics at various dye concentrations. f_k is color strength value which is the sum of the weighted K/S values in the visible region of the spectrum; it is calculated using equation (1) [11].

$$f_k = \sum_{\lambda=400}^{700} (K/S)_\lambda(\bar{x}_{10,\lambda} + \bar{y}_{10,\lambda} + \bar{z}_{10,\lambda}) \qquad (1)$$

where, $x_{10,\lambda}$, $y_{10,\lambda}$, and $z_{10,\lambda}$ are color matching functions for the 10 ° standard observer at each wavelength (ISO 7724/1-1984).

Results and Discussion

Exhaustion Properties on PET

Table 2 shows the exhaustion (%) of the synthesized dyes at 1.0 %owf. The dyes which have only one or no substituents in their diazo components or coupling components (i.e. **1a** and **2a**) showed relatively lower exhaustion (%) compared to those of di- or tri-substituents.

4'-Nitro derivatives showed higher exhaustion (%) than 4'-fluorosulfonyl analogues. Thus, in the dyeing of PET fiber, the substantivity of 4'-fluorosulfonyl derivatives which contain the *p*-fluorosulfonyl group in the diazo component must be lower than that of 4'-nitro analogues, due to their relatively lower hydrophobicity [12].

Color Properties on PET

Depending on the substituents of the diazo and coupling components, the color of dyeings was changed from reddish orange to reddish purple as indicated in Figures 1 and 2. The colorimetric properties of the dyeings, as expressed in terms of the CIELab system, are listed in Table 3; CIE L*, a*, b*, chroma (C*) and hue angle (*h*) values are tabulated along with λ_{max} values of K/S. Trends in the hues of the dyeings were generally consistent with those observed for absorption maxima of the dyes in ethanol solution [7,9]. Dyes **4** and **5** are relatively dull compared to dyes **1**, **2**, and **3** as shown in Figures 1 and 2. The results are due to the steric hindrance at the azo link to broaden visible absorption peaks.

As expected, the 4-(*N*,*N*-diethylamino)-4'-nitroazobenzene dye was bathochromic on PET relative to its 4'-fluorosulfonyl analogues, owing to greater electron withdrawing power of nitro group [13]. However, the 4'-nitro derivatives are relatively dull compared to the 4'-fluorosulfonyl analogues as shown in

Table 2. Exhaustion (%) of 4-(*N*,*N*-diethylamino)-4'-fluoroazobenzene dyes and their 4'-nitro analogues on PET fabric at 1.0 %owf dye concentration

Dye	Exhaustion (%)	Dye	Exhaustion (%)
1a	73.5	**1b**	96.3
2a	77.7	**2b**	95.1
3a	81.3	**3b**	97.8
4a	84.2	**4b**	98.2
5a	85.3	**5b**	98.9
6a	89.1	**6b**	99.2

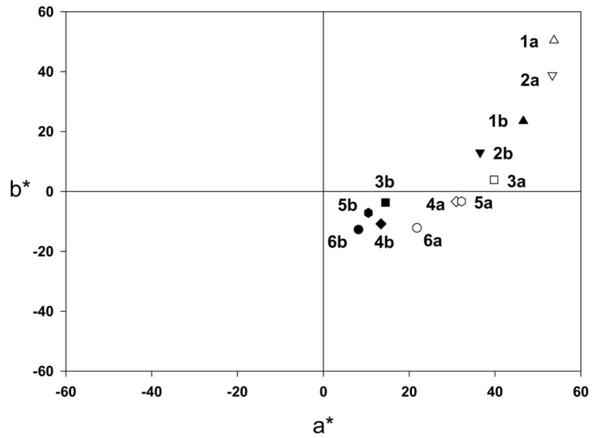


Figure 1. Comparison of CIE a* and b* values of the dyed PET fabrics with 4'-fluorosulfonyl derivatives and 4'-nitro derivatives at 1.0 %owf dye concentration.

Table 3. Colorimetric data and visual appearance of the dyed PET fabrics with 4'-fluorosulfonyl derivatives and 4'-nitro derivatives at 1.0 %owf dye concentration

Dye	L*	a*	b*	C*	h_{ab}	λ_{max}	Color on PET
1a	52.54	53.75	50.43	73.00	43.17	480	Vivid Reddish Orange
1b	37.02	46.59	23.51	52.19	26.77	500	Moderate Red
2a	45.49	53.36	38.79	65.97	36.02	500	Vivid Red
2b	30.82	36.52	13.00	38.76	19.60	500	Dark Red
3a	32.60	39.79	3.89	39.98	5.59	520	Dark Purplish Red
3b	22.83	14.48	−3.71	14.95	345.63	520	Dark Purplish Red
4a	27.87	30.98	−3.38	31.16	353.78	540	Dark Purplish Red
4b	22.62	13.46	−10.80	17.26	321.26	540	Dark Purple
5a	29.51	32.20	−3.32	32.37	354.12	540	Dark Purplish Red
5b	22.79	10.50	−7.15	12.70	325.74	560	Dark Purple
6a	24.79	21.82	−12.20	25.00	330.78	560	Dark Reddish Purple
6b	22.10	8.19	−12.73	15.14	302.77	580	Dark Violet

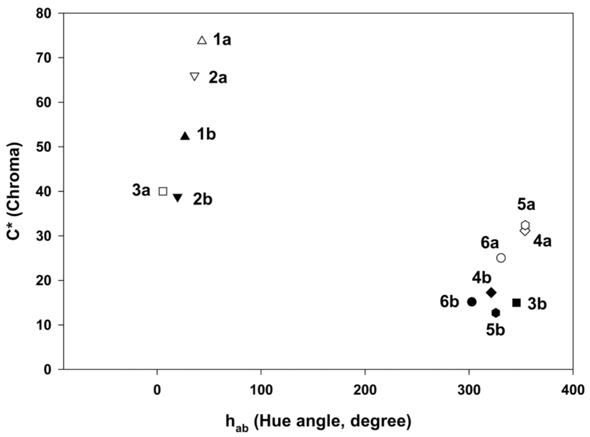


Figure 2. Comparison of Hue (*h*) and Chroma (C*) values of the dyed PET fabrics with 4'-fluorosulfonyl derivatives and 4'-nitro derivatives at 1.0 %owf dye concentration.

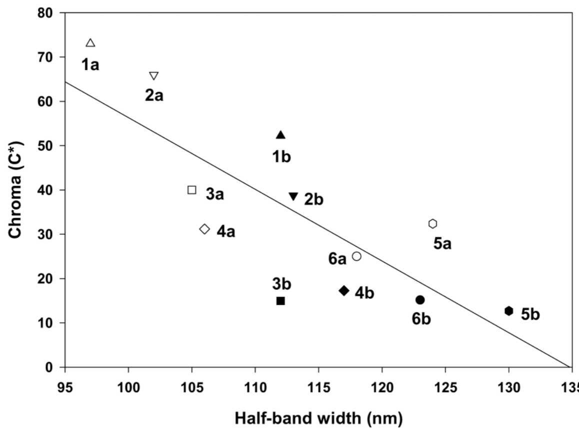


Figure 3. Comparison of half-band width and Chroma (C*) values of the dyed PET fabrics with 4'-fluorosulfonyl derivatives and 4'-nitro derivatives at 1.0 %owf dye concentration.

Figures 1 and 2. These trends in the colorimetric properties are consistent with their spectral properties in solvent. Also, as seen in Figure 3, the reasonable linear correlations can be found between chroma values of the dyed samples and the half-band width (in EtOH) of the synthesized dyes [9]; the sharper the half-band width of the dyes, the brighter was the color of dyed PET.

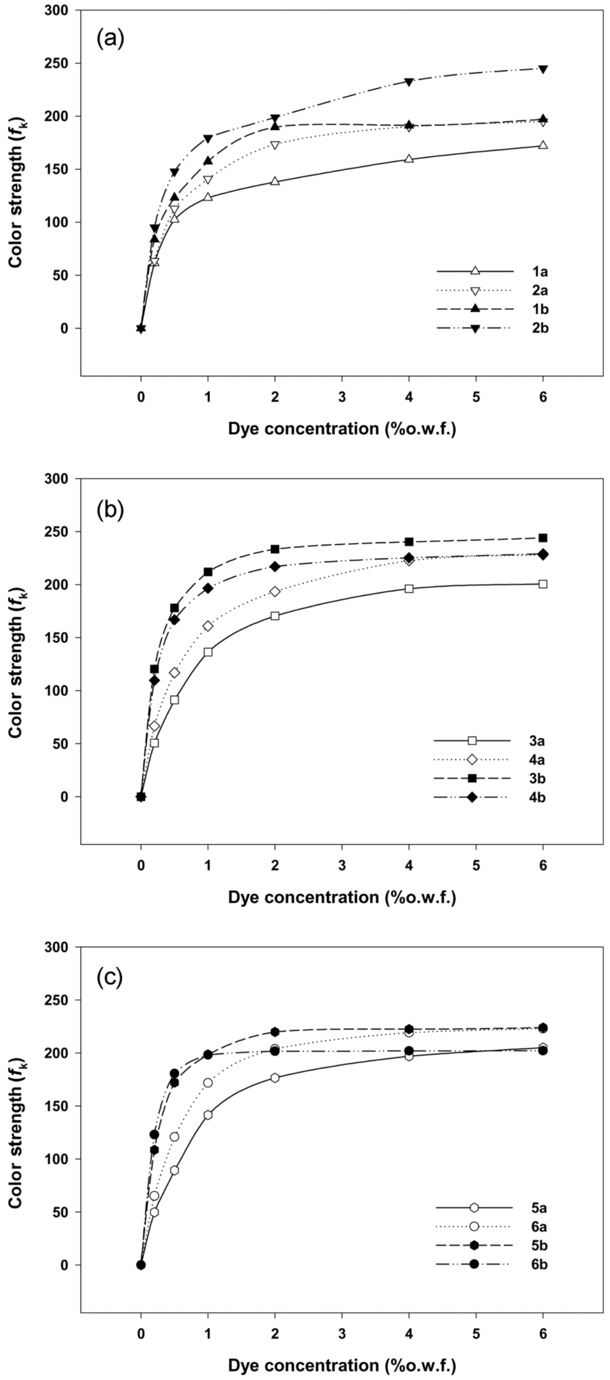


Figure 4. Build-up properties on PET; 4'-fluorosulfonyl derivatives vs 4'-nitro derivatives.

Build-up Properties on PET

Figure 4 illustrates the relative color strength (f_k) of dyed PET fabrics depending on the amounts of dye applied (%owf). f_k value is a visually-weighted function of K/S, which indicates the strength of the dyeing. Most synthesized dyes showed reasonable build-up properties on PET and saturation was reached at application levels of 2.0-4.0 %owf. The exhaustion of the synthesized dyes on PET increased with the increase of the number of substitution groups in diazo component or coupling component, presumably because the substituents give more hydrophobicity and resulting substantivity to hydrophobic PET fabric [12].

4'-Nitro derivatives exhibited more rapid build-up and, especially in the case of dyes **1**-**4**, higher color yield at saturation points compared with 4'-fluorosulfonyl analogues (Figure 4). Thus, in the dyeing of PET fiber, the substantivity of 4'-nitro derivatives which contain a *p*-nitro group in the diazo component was shown to be higher than that of 4'-fluorosulfonyl derivatives which contain a *p*-fluorosulfonyl group. For example, dye **1b** produced a greater depth at 1.0 %owf (f_k 157.42) than its fluorosulfonyl analogue (dye **1**a, f_k 123.03). Similarly, dye **2b** yielded a marginally higher value of 211.99 compared with the fluorosulfonyl derivatives (dye **2a**, f_k 136.35): indeed, many commercial azo disperse dyes for PET fiber contain the *p*-nitro group in the diazo component to enhance build-up.

Conclusions

Dyeing properties of 4-(*N*,*N*-diethylamino)-4'-fluorosulfonyl-azobenzene disperse dyes and their 4'-nitro analogues on PET were investigated in a comparative manner.

In the dyeing of PET fiber, 4'-fluorosulfonyl derivatives which contain the *p*-fluorosulfonyl group in the diazo component showed lower exhaustion (%) values and higher build-up properties than that of 4'-nitro analogues, probably due to their lower hydrophobicity.

The 4-(*N*,*N*-diethylamino)-4'-fluorosulfonylazobenzene dyes was hypsochromic on PET relative to their 4-nitro analogues, owing to lower electron withdrawing power of fluorosulfonyl group. However, the 4'-fluorosulfonyl derivatives exhibited relatively bright color on PET compared to the 4'-nitrosulfonyl analogues.

Acknowledgements

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