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Effects of Thermomigration on the Washfastness of Disperse Dyes Having Different Molecular Size

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Abstract: Effects of chemical structure of disperse dyes applied to conventional and microdenier polyesters on the dyeing property and washfastness were studied. It was found that washfastness of dyed polyester fabric is closely related to the degree of thermomigration of disperse dye during heatsetting. The bulky disperse dye, which was synthesized by substituting two acetoxy groups of C.I. Disperse Red 82 with two benzoxy groups, showed almost the same amount of absorbed dye by the microdenier polyester as C.I. Disperse Red 82, but the degree of thermomigration was low and subsequent washfastness was excellent. The high grade of washfastness of the bulky disperse dye might be caused by the increased dye-fiber interaction and the reduced mobility.

Keywords: Microdenier polyester, Disperse dye, Dyeing property, Washfastness, Thermomigration

Introduction

Polyester and its blends have been widely used for sportswear and leisurewear which need to have high level of washfastness to endure frequent washing. Recently there is a worldwide growth in the microdenier polyester because of the soft hand and comfort. It is well known that as the diameter of the fiber becomes smaller, the total surface area of the fiber increases considerably. A greater amount of dye is needed for the microdenier polyester to reach the same depth of shade as the conventional polyester. These two factors often result in deteriorating washfastness of the microdenier polyester [1].

Even though loosely bound dyes on the fiber surface are completely removed through reduction clearing after dyeing, subsequent heat setting promotes dye migration from the fiber interior to the fiber surface, leading to lower washfastness. This phenomenon is known as thermomigration which is the diffusion of dye as a result of the breakage of the interaction between dye and fiber by the increased thermal motion of both the dye molecule and the polymer chain at elevated temperatures. This thermomigration becomes more severe as the denier of fiber is smaller, and it is regarded as the origin of low washfastness of the microdenier polyester. Factors affecting thermomigration are known to be the fiber thickness, the chemical structure of the disperse dye, the amount of absorbed dye in the fiber, and heatsetting conditions [2].

Two methods to reduce the undesirable effect of thermomigration are considered as follows:

1) one is to lower the staining ability of disperse dyes toward other fibers in washing liquor. Although the thermomigrated dyes are dissolved or dispersed in the washing liquor, if the dyes are easily hydrolyzed and turned into colorless compounds, they do not cause any problem of staining other fibers at all. The example of this type of dye is benzodifuranone disperse dye which is easily hydrolyzed in weak alkaline aqueous solution.

2) the other is to minimize the degree of thermomigration by enhancing the interaction between the fiber and the dye. Polyester fiber does not have any functional groups to form covalent bond with dyes, and also does not have ionic groups to interact electrostatically with dyes. Hence, the introduction of bulky substituents or polar groups is considered to be useful method enhancing the fiber-dye interaction through van der Waals force or hydrogen bonding. It is well known that as the size of the disperse dye becomes big, the washfastness improves. Therefore, the development of disperse dyes with a low degree of thermomigration by increasing molecular size can be considered plausible. In this case the expected weak points are the unlevel dyeing owing to the increased fiber-dye interaction and the low dye uptake due to the reduced mobility [3].

The purpose of this study is to investigate the dyeing and fastness properties of disperse dyes having different molecular size for the design of new dyes having good dyeing properties and excellent washfastness on the microdenier polyester.

Experimental

Materials

Two disperse dyes, 2-cyano-4-nitro-4'-(N,N-diacetoxyethyl) amino-azobenzene (C.I. Disperse Red 82, Dye I) and 2-cyano-4-nitro-4'-(N,N-dibenzoxyethyl)amino-azobenzene (Dye II) were used and their synthetic methods were described elsewhere [4]. Their structures are shown in Figure 1.

Desized, scoured conventional polyester fabric (75d/36f, 2d monofilament, plain weave, 100 × 89/inch) and microdenier

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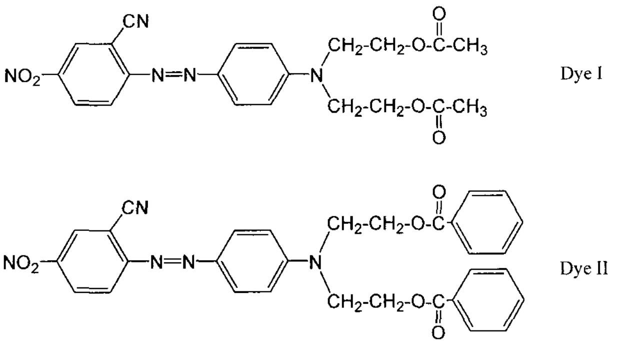

Figure 1. Chemical structure of disperse dyes used in this study.

polyester fabric (50d/96f, 0.5d monofilament, plain weave, 147 x 84/inch) were used.

Dyeing Process

Purified dye and dispersing agent (weight ratio 1:2) were milled to dye dispersions whose particle size were in the range of 0.3-0.4 μm, using glass beads and mechanical stirrer.

Dyeing was carried out in the sealed dyepot (Labomat, Mathis), pH was adjusted to 4.5 by adding acetic acid, and a liquor ratio was 30:1. Temperature was raised from 50 °C to 130 °C at the rate of 1 °C/min, and dyeing was continued at 130 °C for 60 minutes, then the temperature was reduced to 80 °C. Dyed polyester fabric was reduction cleared in an aqueous solution containing sodium hydroxide (2 g/*l*) and sodium hydrosulphite (2 g/*l*) at 80 °C using a liquor ratio 50:1 for 20 minutes, and rinsed. The dyed fabric was heatsetted at 180 °C for 30 seconds.

Determination of Dye Uptake

The dye absorbed by the fiber was extracted using N,N-dimethylformamide (DMF) at 100 °C. The optical density of the extract was determined on UV-VIS spectrophotometer (UV-160A, Shimadzu). Calibration curves plotted with pure dyes were used to calculate the amount of absorbed dye from the optical density values and expressed in terms of mg of dye/g of fiber.

Fastness Test

Fastness to washing, light, heat, and abrasion were measured using AATCC 61 IIA, AATCC 16E, AATCC 117 III, and AATCC 8 methods respectively.

Degree of Thermomigration [2]

The amount of thermomigrated dye on the fiber surface was determined by extracting dye from the dyed fabric after heatsetting in DMF at 25 °C for 120 minutes and by measuring the optical density of the DMF solution. The amount of dye in the fiber was determined by extracting in DMF at 100 °C. The degree of thermomigration was calculated by the following equation (1):

$$\text{Degree of Thermomigration(\%)} = \frac{D_{surface}}{D_{surface} + D_{fiber}} \times 100 \quad (1)$$

Where, $D_{surface}$: the amount of thermomigrated dye on the fiber surface.

D_{fiber}: the amount of dye in the fiber.

Results and Discussion

Dye Uptake

Two polyester fabrics were dyed with several concentrations of Dye I and Dye II to compare their build-up profiles, the amounts of absorbed dye were calculated and listed in Table 1. The dye uptake generally increases as the concentration of dye increases, exhibiting reasonably good build-up property.

For both dyes, 0.5d fiber absorbs greater amount of dye than 2d fiber. In other words, the lower the denier of the fiber is, the higher the dye uptake is. This trend is common and attributable to the greater total surface area, through which the dye molecules are diffused into the fiber, of the microdenier polyester. For both fibers, Dye II is less absorbed than Dye I probably because the diffusion of Dye II is hindered by its bigger size. But the difference in the dye uptake between two dyes is smaller than expected, especially for 0.5d fiber, the amounts of absorbed Dye II are quite close to those of Dye I. The reason may be that the increased substantivity caused by the π-π interaction between the benzene ring in the polyester polymer chain and the benzene ring in the dye molecule compensates the decrease of the dye uptake due to the increased molecular size.

Rate of Dyeing

The rate of exhaustion of two dyes on both fibers is shown in Figure 2. The rate curve was plotted by measuring the dye

Table 1. The amounts of absorbed dye (mg of dye/g of fiber) by conventional and microdenier polyesters at several dye concentrations

Dye	Fiber	Dye concentration (% owf)							
		0.25	0.5	1	2	3	4	5	6
I	2d	1.25	2.36	2.94	5.63	8.30	10.90	13.19	15.00
	0.5d	1.29	2.09	3.59	6.16	8.95	11.43	13.78	15.74
II	2d	0.88	1.59	2.76	5.34	7.82	9.51	10.92	12.34
	0.5d	0.92	1.80	2.99	5.90	8.62	11.12	12.59	14.19

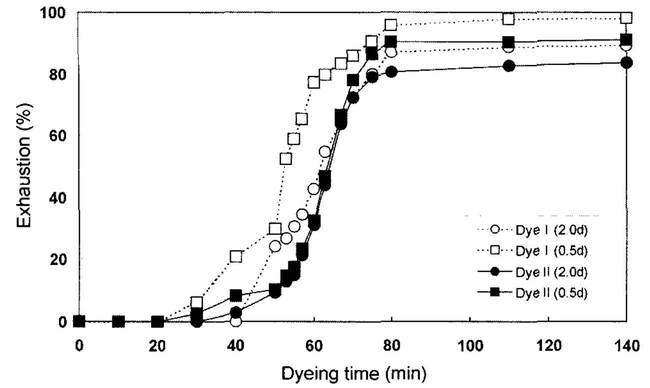

Figure 2. The rate of exhaustion curves of disperse dyes applied to conventional and microdenier polyesters at 1 % owf.

uptake of dyed fabric which was taken out from the dyepot at predetermined dyeing times.

Microdenier polyester starts to absorb Dye I at lower temperature and gets dyed at a rapid rate as compared with the conventional polyester. The faster rate might be attributed to the large surface area of the microdenier polyester. The rate of exhaustion of Dye I is very dependent on the thickness of the fiber, but that of Dye II appears to be almost independent on the thickness of the fiber except the early stage of dyeing, suggesting that the increased surface area do not affect markedly the rate of dyeing of the bulky dye which diffuses slowly. It can be also noted that the rate of dyeing of Dye I on 0.5d fiber is very fast than that of Dye II on the same fiber. The results clearly show that the relatively big dye is difficult to penetrate into the fiber. However, the difference between the rate of dyeing of two dyes becomes less apparent on 2d fiber.

Since the disperse dyeing process is diffusion controlled, the diffusion coefficient of the dye and the surface area of the fiber would obviously be the rate determining factors in dyeing [5], but it can be considered that the contribution of these two factors vary according to the size of the dye and the denier of the fiber. Based on the results of this study, it can be said that the rate of exhaustion of Dye II is less sensitive to the surface area of the fiber than Dye I.

Fastness

Grades of fastness of polyester fabrics dyed at 2 % owf are shown in Table 2. As far as light, heat and abrasion fastnesses are concerned, their grades are good to excellent, and there are no significant differences between two dyes.

Washfastness of the microdenier polyester dyed with Dye I lowers by 2 grades as compared with that of the conventional polyester. On the other hand, washfastness of the microdenier polyester dyed with Dye II is very close to that of the conventional polyester because of the increased interaction and the enhanced hydrophobicity originated from the presence of two benzene rings in Dye II [6]. The results imply that the dye having bigger molecular size is effective for the microdenier polyester to maintain the high level of washfastness. This fact seems to be very important from the viewpoint of improving washfastness of the microdenier or the ultramicrodenier polyester.

In order to investigate precisely the difference in washfastness between two dyes, we measured color difference (ΔE) of the attached white nylon fabric before and after washfastness test for fabrics dyed at 1-4 % owf. Figure 3 shows ΔE values measured from the heatsetted and the non-heatsetted 2d polyester. The higher value of ΔE means the lower grade of washfastness. In the case of Dye I, ΔE for the non-heatsetted polyester on which the loosely bound dyes were removed by reduction clearing changes little according to the dye concentration, but ΔE for the heatsetted polyester increases with the dye concentration, indicating that there is the dye

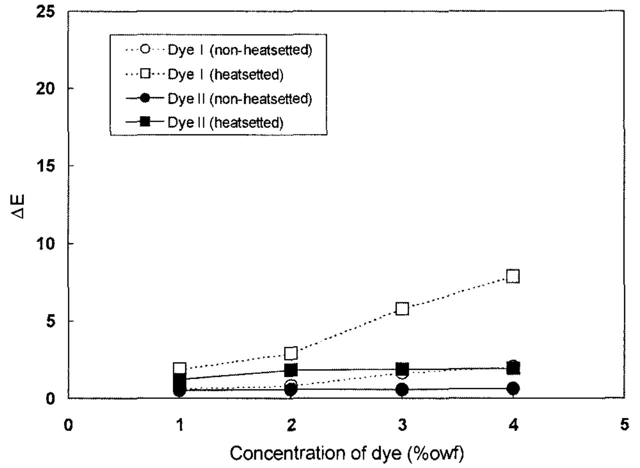

Figure 3. ΔE values of the stained nylon fabric attached to the conventional polyester for washfastness test.

Table 2. Grades of fastness for conventional and microdenier polyesters dyed at 2 % owf

Dye	Fiber	Washing	Light	Heat		Abrasion	
		Nylon staining	Color change	PET staining	Nylon staining	Dry	Wet
I	2d	4-5	4-5	4	4	5	4-5
	0.5d	2-3	4	4	4	5	4-5
II	2d	4-5	4-5	4-5	4-5	5	4-5
	0.5d	4	4	4-5	4-5	5	5

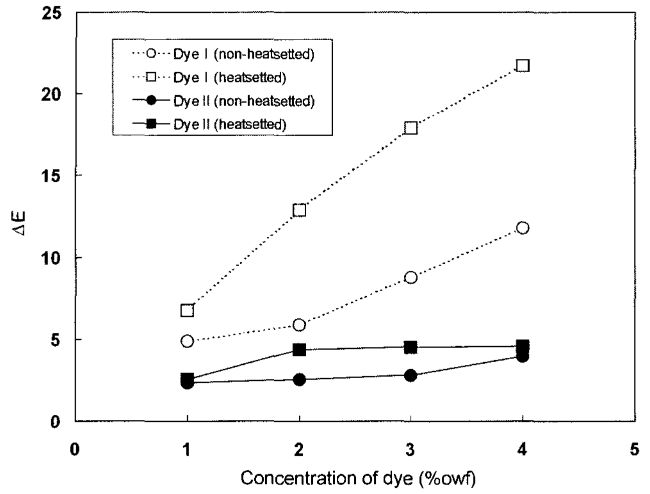

Figure 4. ΔE values of the stained nylon fabric attached to the microdenier polyester for washfastness test.

migration to the fiber surface during heatsetting and the amount of thermomigrated dye is directly proportional to the dye concentration in the fiber. In the case of Dye II, ΔE for the heatsetted polyester is slightly higher than that for the non-heatsetted polyester, and the differences in ΔE do not change with the dye concentration, suggesting that the big molecular size of Dye II suppresses thermomigration effectively. Figure 4 demonstrates ΔE values measured from the heatsetted and the non-heatsetted 0.5d polyester. In the case of Dye I, ΔE of the heatsetted 0.5d polyester increases much more than that of the non-heatsetted 0.5d polyester and the difference between them is getting large as the dye concentration increases, which means that thermomigration in the 0.5d polyester occurs more intensely due to the large surface area. However, Dye II behaves differently from Dye I. ΔE for the heatsetted 0.5d polyester change a little as compared with that for the non-heatsetted 0.5d polyester over the 1-4 % owf dyeings. It indicates that Dye II is very resistant to thermomigration and the extent of thermomigration of Dye II is hardly affected by the dye concentration in the fiber.

Degree of Thermomigration

The amount of thermomigrated dye, the degree of and the grade of washfastness for 2d and 0.5d fibers dyed with Dye I and Dye II at the four dyeing depths were examined to study the relationship between the tendency of thermomigration and the grade of washfastness quantitatively, and are shown in Tables 3 and 4. As the amount of thermomigrated dye, or the degree of thermomigration, increases, the grade of washfastness is getting low. Therefore, it can be said that washfastness is dependent on the degree of thermomigration.

In the case of Dye I in 2d polyester, as the dye concentration increases the amount of thermomigrated dye increases, and the grade of washfastness drops from 4-5 at the 1 % owf dyeing to 3 at the 4 % owf dyeing. This phenomenon becomes more evident for Dye I in 0.5d polyester as shown in Table 3, the amount of thermomigrated dye at the 4 % owf dyeing is

Table 3. The amount of thermomigrated dye, the degree of thermomigration and the grade of washfastness of Dye I on conventional and microdenier polyesters at different dyeing depth

Fiber	Measurements	Dye concentration (% owf)			
		1	2	3	4
2d	Amount of thermomigrated dye (mg of dye/g of fiber)	0.005	0.020	0.063	0.094
	Degree of thermomigration (%)	0.156	0.406	0.778	0.887
	Grade of washfastness	4-5	4-5	3-4	3
0.5d	Amount of thermomigrated dye (mg of dye/g of fiber)	0.030	0.119	0.247	0.518
	Degree of thermomigration (%)	0.915	1.932	2.814	4.479
	Grade of washfastness	3-4	2-3	2	1-2

Table 4. The amount of thermomigrated dye, the degree of thermomigration and the grade of washfastness of Dye II on conventional and microdenier polyesters at different dyeing depth

Fiber	Measurements	Dye concentration (% owf)			
		1	2	3	4
2d	Amount of thermomigrated dye (mg of dye/g of fiber)	0.004	0.020	0.032	0.039
	Degree of thermomigration (%)	0.144	0.387	0.398	0.403
	Grade of washfastness	4-5	4-5	4-5	4-5
0.5d	Amount of thermomigrated dye (mg of dye/g of fiber)	0.014	0.048	0.072	0.096
	Degree of thermomigration (%)	0.465	0.807	0.835	0.842
	Grade of washfastness	4-5	4	4	4

almost five times as many as that at the 1 % owf dyeing, as a result, the grade of washfastness at the 4 % owf dyeing deteriorates to 1-2. These results mean that the increase of the total surface area accelerates thermomigration of the dye. In the case of Dye II in 2d polyester, the degree of thermomigration at the 4 % owf dyeing is similar to that at the 2 % owf dyeing, and the amounts of thermomigrated dye are smaller than those of Dye I in 2d polyester, suggesting that for the dye with bigger molecular size, the tendency of thermomigration to the fiber surface reduces. Resistance to thermomigration is more evident for Dye II in 0.5d polyester as shown in Table 4, the amounts of the thermomigrated dye are much smaller than those for Dye I in 0.5d polyester, the grade of washfastness of Dye II in 0.5d polyester at the 4 % owf dyeing maintains at 4. The reason might be that the increased interaction between Dye II and fiber and the reduced mobility of the dye owing to its bigger molecular size. The higher degree of heatfastness for Dye II can be regarded as an other evidence.

Conclusions

It is found that washfastness of the polyester fabrics is closely related to the degree of thermomigration of disperse dye during heatsetting. The degree of thermomigration of the regular size disperse dye such as Dye I increases with the concentration of dye in the fiber and decreases as the denier of the fiber increases, on the other hand that of the bigger sized disperse dye like Dye II does not change markedly according to the dye concentration and the denier of the fiber. Since the interaction between the polyester fiber and disperse dye are mainly van der Waals forces and hydrogen bonding, it is difficult to inhibit the dye migration completely during heatsetting, but the introduction of two benzene rings into the dye molecule turns out to be quite effective to reduce the degree of thermomigration especially for the microdenier polyester. Hence, it can be concluded that the dye having bigger molecular size and higher substantivity is suitable for microdenier polyester to maintain the high level of washfastness without a notable diminution in the dye uptake.

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