[Technical Paper]

Development and Application of Polyester/Cotton Blended Fabric Dyes

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Abstract : Reactive disperse dye was synthesized using 2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate as diazo component, and 2-hydroxy-1, 4-naphthoquinone for coupling component. The molecular structure of reactive disperse dye was confirmed by infrared spectrum, ultraviolet spectrum, ¹H NMR, ¹³C NMR and mass spectrographic analysis, molecular formula of the dye is C₁₈H₁₅N₂O₉S₂. Through the contrast experiments, the study analyzes the dyeing performance of the polyester/cotton blended fabrics dyed with reactive dye and disperse dye (using traditional dyeing methods) and reactive disperse dye. The fabrics dyed with reactive disperse dye, its rubbing fastness was up to 4–5, washable color fastness was up to 4–5. Both of them are superior compared with the traditional dyeing methods.

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1. Introduction

Blended products of chemical and natural fibers have been deeply welcomed by consumers, because chemical fibers are wear and wrinkle resistance and natural fibers have high potential to absorb moisture and high permeability^[1–3]. Because different fibers have significantly different properties, blended textiles are usually dyed using reactive dyes or acid dyes and disperse dyes by sub-bath or sub-step dyeing methods. But these methods can cause some problems. The different types of dyes on different fibers will produce different color depth and brightness, and the appearance of the dyed product is affected. Dyes will stain fibers, which reduces the rate of dyeing. Greater energy consumption is required and more waste water is generated^[4–8]. One of the important ways to solve the above problems is to develop a unitary type of reactive disperse dyes. The reason is that the natural fibers combined with reactive groups by covalent bonds, which can improve washing fastness^[9]. Meanwhile one bath dyeing is achieved, a better dyeing effect is obtained, and energy can be saved^[10–11].

Reactive disperse dye was synthesized using the laboratory synthesis of natural dye 2-hydroxy-1,4-

naphthoquinone as the coupling component, 2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate (para-ester) as diazo component. The dye was used for dyeing polyester/cotton blended fabrics. The structure of the dye was characterized, and dyeing properties were studied.

2. Experiment

2.1 Materials

50:50 polyester/cotton fabric with plain weave was desized, scoured and bleached. Reactive yellow 145 and disperse yellow 134:2; All other chemicals were chemically pure.

2.2 Synthesize

2.2.1 Diazotization of Para-ester

experimental procedure :

(1) 3.2 g of para-ester was added into ice-water bath beaker (150 ml), beating using a magnetic stirrer.

(2) 1.6 ml of concentrated hydrochloric acid (advance refrigerated) was added into the beaker.

(3) 0.7 g of sodium nitrite was weighted and prepared a solution using deionized water. the solution was added dropwise at a constant speed (constant temperature was maintained throughout the process).

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(4) A yellow viscous liquid was yielded.

(5) A small amount of amino acid was added to destroy excess sodium nitrite. (KI starch test paper was not changed to blue at the end point)

2.2.2 Coupling reaction of diazonium salt of the para-ester and lawsone.

Experimental phenomenon: The mixture of para-ester and water was gray turbid liquid while stirring in ice field. After the addition of concentrated hydrochloric acid solution, the liquid was turned into yellow-green. The liquid gradually became viscous and yellow after dropping the sodium nitrite solution.

Experimental procedure :

(1) 0.84 g sodium bicarbonate was dissolved in 50 ml distilled water. 1.742 g 2-hydroxy-1,4-naphthoquinone was added. The mixture was cooled to 0~5°C.

(2) The pH of diazonium salt solution of the para-ester was adjusted to lightly acidic condition (pH = 6~6.5) using sodium bicarbonate solution. The temperature was maintained constant.

(3) The lawsone solution which had been dissolved in sodium bicarbonate solution was slowly poured on diazonium salt solution of para-ester. The mixture was stirred constantly under weak acidic condition, and the temperature was maintained below 15°C. The product was filtered after 3 hours.

2.3 Dyeing

2.3.1 Pretreatment

The cotton/polyester blended fabrics was pretreated to minimize the impact of external factors in dyeing process. The recipe of polyester/cotton blended fabrics dyeing pretreatment process was as follows: sodium carbonate 1 g/L, Net lotion 1 g/L, bath ratio 1 : 50, treated the fabrics at 60°C for 30~40 min, with warm water wash at least 5 min, then dry.

2.3.2 Dyeing

(1) Dyeing process of reactive disperse dye: Putting wet fabric in the dye bath, adjusting the pH of dye solution to 6~6.5. Initial temperature for dyeing was 40°C, incremental temperature was 1°C /min, final was 120°C and was maintained for 30~60 min. Soda ash was added, dye solution pH was adjusted to 8~9, and the temperature was fixed at 95°C. The mixture was soaped to remove floating color after dyeing.

(2) Reactive dye and disperse dye one-bath, two-step dyeing process: The dye bath contained disperse dye, reactive dye, and alkali agent. After steamed, reactive dye penetrating into cotton fibers,

for the steam content of 25%, 120°C, 2 min; then dyeing polyester fibers at 195°C, 2 min. Then remove the floating color.

(3) Reactive dye and disperse dye two-bath dyeing process: Disperse dye and reactive dye solutions were prepared respectively, OWF: 2%, MLR: 1 : 30. First with hot-melt method disperse dye dyeing on polyester fibers at 195°C, 2 min. By impregnation method reactive dye dyeing on cotton fibers, at 50°C, 2 min, fixating at 70°C, 40 min. Then remove the floating color.

2.4 Performance testing

2.4.1 Determination of color difference

Color difference is that the differences between the L*, a* and b* values of the sample and standard in CIE-Lab color system. According to the Equation 1^[12], ΔE value were calculated. In this study, each sample was measured in a measurement (Datacolor 7000 A, X-rite, USA) using D₆₅ illuminant and 10° observer. Setting the undyed fabric as standard, other dyed fabrics were as samples.

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

2.4.2 Color levelness test

The ΔE value was measured at six different sites on the each dyed fabric sample. The average was calculated as benchmark. The difference between the ΔE value and the average value of the discreteness was as dispersion. The higher the dispersion, the worse the levelness. On the contrary, the better levelness^[13].

2.4.3 Color fastness test

According to the standards of ISO 105-C06:1994 (2010), the washing fastness of the dyed fabrics samples was evaluated by IIIA of the AATCC Test Method 124-2001 using a Launder-o-meter. The fastness to rubbing was evaluated as per ISO 105-X 12:2001 standards using a crock meter.

3. Discussion

3.1 Synthesis

The protonation of nitrous acid was first dehydrated, and then nitrous acid anhydride generated with nitrite. The nitrous acid anhydride is a weak electrophilic reagent. N-nitroso amine can be generated by its amino with para-ester. Para-ester diazonium salts were generated by N-nitroso amine ketone type - enol tautomerism, then through the protonation and dehydration (Figure 1).

Fig. 1 Diazotization of para-ester

A coupling reaction was investigated in this study. The coupling reaction involved using an aromatic diazonium salt with phenols and aromatic amines forming an azo compound. Phenols and aromatic amines are called coupling components. The coupling reaction is an electrophilic substitution of an aromatic ring. firstly, coupling components and the cationic diazonium salt generated an intermediate product; Secondly, protons were released from the intermediate product to released protons for proton acceptor, and then azo compound was generated. Lawsone should belong to the phenols due to hydroxyl on the quinone ring of lawsone. However, lawsone was similar with 2-amino-1,4-naphthoquinone proven by many experiments. Diazonium salt can only couple with it under the condition of weak acid (Figure 2).

Fig. 2 The synthetic mechanism of reactive disperse dye based on lawsone.

3.2 Molecular Structural Characterization

3.2.1 Ultraviolet spectrum analysis

Figure 3. shows the ultraviolet spectrum diagram

Fig. 3 UV spectra of reactive disperse dye based on lawsone.

of the target dye was detected by uv-vis spectrophotometer (Lambda35, PerkinElmer, USA).

Maximum absorption wavelength of the target dye is 418 nm (Figure 3) It was a blue shift phenomenon when it compared to the maximum absorption wavelength of lawsone dye.

3.2.2 Infrared spectrum detection

The FTIR spectra of reactive disperse dye based on lawsone was detected by infrared spectrometer (Spectrum10, PerkinElmer, USA), the results are shown in Figure 4. The infrared absorption peaks of the target product are as follows: 3397 cm^{-1} , 2688 cm^{-1} , 1690 cm^{-1} , 1773 cm^{-1} , 1540 cm^{-1} , 1446 cm^{-1} . Hydroxyl group stretching vibration absorption peak is at 3397 cm^{-1} . Peak at 2688 cm^{-1} is the stretching vibration absorption of carbon-hydrogen bond of the aromatic ring. The carbonyl stretching vibration absorption peak is at 1690 cm^{-1} . Peak at 1773 cm^{-1} is the carbon-carbon double bond stretching vibration absorption of the quinone ring. Peak at 1540 cm^{-1} is the aromatic ring's absorption. The nitrogen and nitrogen double bond absorption peak of the coupling product is at 1406 cm^{-1} .

Fig. 4 FTIR spectra of reactive disperse dye based on lawsone.

3.2.3 Nuclear magnetic resonance detection

The molecular structure of the target product was characterized by nuclear magnetic resonance

Fig. 5 ^1H NMR analysis of the para-ester diazonium salt with lawsone coupling product.

(NMR) spectrometer (AdvanceIII, Bruker, Germany). The results are shown in Figure 5 and Figure 6, respectively :

^1H NMR (400 MHz, DMSO- d_6) δ 14.78 (s, 1 H, OH), 14.57 (s, 1 H, OH), 8.23 and 8.12 (d, $J = 7.4$ Hz, 1 : 1 H, CH in benzene ring), 7.95 (m, 6 H, CH in benzene ring), 3.97 (t, $J = 6.6$ Hz, 2 H, CH_2), 3.66 (t, $J = 6.6$ Hz, 2 H, CH_2)

Fig. 6 ^{13}C NMR analysis of the para-ester diazonium salt with lawsone coupling product.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6) δ 178.8 (Cq, C=O), 175.5 (Cq, C=O), 146.0, 134.3, 133.4 and 127.5 (Cq each), 136.2, 135.0, 129.8, 127.2 and 117.7 (CH in benzene ring), 59.3 (CH_2), 54.9 (CH_2).

3.2.4 Mass spectrometry

A mass spectrometer (Q-TOF 6540, Agilent, USA) was used to detect the structure of the target product. The results are shown in Figure 7 :

Fig. 7 HRMS spectra of reactive disperse dye based on lawsone.

Molecular formula of the target product is $\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}_9\text{S}_2$. The theoretical value of $[\text{M} + \text{H}]^+$ is 467.0219. The actual molecular mass by efficient mass spectrometer analysis of the product was 467.0228 (Figure 7). The structure of the product is reasonable based on the results from mass spectrometry and nuclear magnetic resonance analysis.

3.3 Dyeing property

Reactive dye and disperse dye were used by one-

bath two-step and two-bath processes for 50/50 polyester/cotton blended fabrics dyeing. The color difference and color fastness of the dyed products were tested. The results are shown in Table 1. The color difference of reactive dye and disperse dye in one-bath dyeing was the minimum and the color fastness was the worst. When the reactive dye and disperse dye in one-bath were dyed, the dyeing conditions of two different types of dyes are different. One-bath dyeing cannot satisfy with the optimum dyeing conditions of two kinds of dyes. The two dyes in the dyeing process will affect each other and thus can not achieve good dyeing effect. While traditional reactive dye and disperse dye two-bath dyeing method also can achieve good dyeing effect, but it needs long dyeing process and high energy consumption. The color difference of dyed products of reactive disperse dye is the highest, and the color fastness is the best. The reasons are that the reactive disperse dye provided the characteristics of reactive dye and disperse dye, and dyes are fixed on the fabrics by molecular inter-atomic forces and hydrogen bonding in the process of dyeing. It can make reactive groups and hydroxyl of the cotton fiber to form covalent bonding, so the color fastness of dyed products can be improved.

Table 1 The performance of the dyed polyester-cotton fabric

Dyeing	Color difference	Rubbing fastness		Washing fastness	
		Dry staining	Wet staining	Shade change	Stain change
A	69.58	3	2-3	3	3
B	78.29	4	3-4	3	4
C	80.05	5	4-5	3-4	4-5

A : Reactive dye and disperse dye (one-bath process).

B : Reactive dye and disperse dye (two-bath process).

C : Reactive disperse dye.

3.3.1 Levelness test

The results of levelness determination of three kinds of dyeing samples are shown in Table 2. The ΔE value of reactive disperse dye is the minimum, and levelness is the best. It is followed by reactive dye and disperse dye two-bath process, and finally is the reactive dye and disperse dye in one-bath, two-step process. Because of using one-bath or two-bath dyeing process to dyeing polyester/cotton blended fabrics, disperse dye and reactive dye stained on cotton and polyester fibers, so the dyed products have poor levelness. And unitary type of disperse dyes on polyester/cotton blended fabrics dyeing process,

Table 2 The level-dyeing property

Dyeing	Color difference						Average	MSE
	Comp.1	Comp.2	Comp.3	Comp.4	Comp.5	Comp.6		
A	68.62	68.94	73.32	72.47	69.05	71.74	70.69	2.0603
B	74.95	74.82	75.19	76.23	77.16	77.37	75.95	1.3633
C	81.05	78.89	80.56	80.14	80.22	79.42	80.05	0.7461

A : Reactive dye and disperse dye (one-bath process).

B : Reactive dye and disperse dye (two-bath process).

C : Reactive disperse dye.

MSE : Mean squared error of the ΔE .

vinyl sulfone sulfate was transformed into vinyl sulfone absorbing onto the fabrics. Some of them bonding with cotton by chemical combination, and a small amount exists in cotton by lake type. While other ethylene biting into polyester, the process of metastasis may occur from cotton to polyester. The dyes migration and levelness of the dyeing products are improved.

4. Conclusions

(1) A kind of vinyl sulfone reactive disperse dye was designed and synthesized using 2-hydroxyl-1,4-naphthoquinone as coupling component, with para-ester as diazo component. The target product was characterized, and the structure is presented.

(2) Dyeing polyester/cotton blended fabrics with reactive disperse dye, firstly dyeing fabrics under acidic condition as dispersible form, which have better migration, levelness and hiding power for fiber defects. Then under the condition of alkaline to fixating, it can promote the color saturation, levelness and fastness of the fabrics.

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