

NAPHTHALIMIDE BASED DISPERSE DYES FOR NYLON 6 AND POLYESTER (PET) FIBERS: SYNTHESIS AND EVALUATION OF TECHNICAL PROPERTIES IN THE PRESENCE OF UREA

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Abstract Technical properties of two naphthalimide based disperse dyes on nylon 6 and polyester fibers were investigated in the presence of urea. The two naphthalimide based disperse dyes were synthesized. The dyes were purified and then fully characterized using ¹H-NMR, FTIR and melting point analysis. Dispersion of the dyes was prepared in water and applied on nylon 6 and PET fibers. The dyes offered good build-up properties on the substrates. In order to increase dye adsorption of the substrates, urea was added into the dyebath. By adding urea, the dye adsorption of polyester was increased significantly, while the increase of that of nylon 6 was not marked. The dyes showed good fastness properties on the substrates.

Keywords: Naphthalimide; Nylon 6; Polyester; Urea; Disperse dye.

INTRODUCTION

The early disperse dyes for the dyeing of cellulose acetate fibers were developed in 1923's and subsequently used for the dyeing of nylon 6 and polyethylene terephthalate (PET) fibers. Over 90% of disperse dye is used for the coloration of PET (polyester) fibers and its blends. Due to high crystallinity and hydrophobicity of polyester, the dyeing of polyester fibers is performed using high temperatures (130°C), thermosol (180–220°C) or carrier dyeing methods. Therefore, the disperse dyes must be stable towards heat and sublimation^[1–5].

Azo dyes are the class of dyes which are widely used in textile industries. They contain over 50% of total world dyes production^[2]. The usage of azo dyes can be attributed to the possession of several advantages such as intensive color, ease of preparing in a multi-purpose chemical plant from cheap, readily available starting materials, the whole color gamut, and desirable fastness properties. Derivatives of azo naphthalimides are well known as dyes for dyeing of synthetic and natural fibers^[1–5]. Most of these materials have been made as disperse dyes for dyeing of polyester (PET) fabrics. Monoazo disperse dyes containing naphthalimide residues have acceptable dyeing properties on polyester fibers. They present excellent thermal stability and good dyeing fastness properties. However, they suffer from their very poor water solubility. This poor water solubility makes them to have low diffusion coefficients and Nernst distribution constant^[6]. In order to increase solubility of the dyes, the use of wetting agent is of great importance. Urea is one of the wetting agents, which is used in tie dyeing and other forms of direct application of dyes^[7]. It increases the dye adsorption of many fibers such as cotton^[8] and wool^[7, 9, 10].

The goal of this study was to apply naphthalimide based dyes on nylon 6 and polyester fibers and optimize their application on the fibers by means of employing urea. For this purpose, two naphthalimide based disperse dyes are employed. Dye 1 has already been synthesized and characterized using UV-Vis spectroscopy, ¹H-NMR

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and FTIR^[11]. Dye 2 is synthesized and characterized using UV-Vis spectroscopy, ¹H-NMR and FTIR in this study. Technical properties of the dyes are evaluated on nylon 6 and polyester fibers. The effects of urea on the adsorption of the dyes on nylon 6 and polyester fibers are also investigated.

EXPERIMENTAL

Materials and Apparatus

Acenaphthene, ethyl glycinate, salicylic acid and thiosalicylic acid were purchased from the Aldrich Company (UK) and used without further purification. All other used materials were reagent grade. Nylon 6 and polyester fibers were obtained from two local suppliers (Alyaf Co. and Polyacryl Co. Iran), respectively.

Thin layer chromatography (TLC) was carried out with silica gel plates using dimethylformamide (DMF) as solvent. Melting points were determined using a Barnstead Electrothermal 9200 instrument (UK). The proton nuclear magnetic resonance (¹H-NMR) spectra were obtained with a Bruker AVANCE-500 MHZ (USA) using the appropriate deuterated solvent. Fourier transform-infrared (FTIR) spectra were recorded on a Nicolet magna-IR 560 (USA). Ultraviolet-visible (UV-Vis) absorption spectra were measured with a Cintra 10 spectrophotometer (GBC Co., Australia). The colorimetric properties of the dyes (D65 illumination, 10° observer) were obtained using a Texflash spectrophotometer (Datacolor, Germany).

Synthesis of Intermediates

The synthesis of the required intermediates has been explained in previous works^[11] and is briefly shown in Fig. 1.

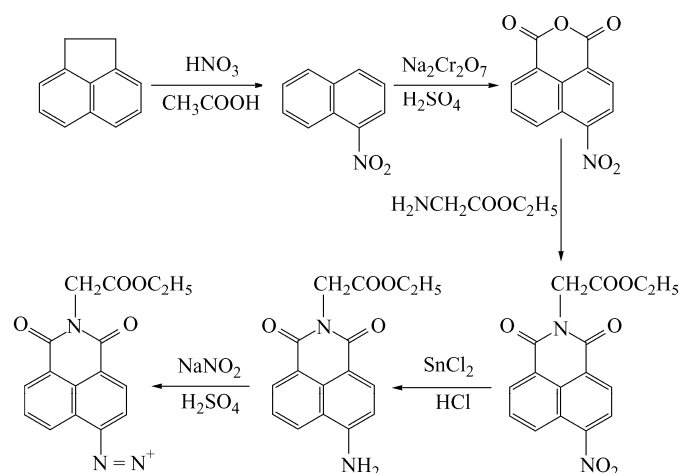


Fig. 1 Synthesis route for intermediates

Synthesis of Dyes

Dye 1

Dye 1 was synthesized *via* diazotisation of 4-amino-*N*-ethylglycinate-1,8-naphthalimide and then coupling of the produced diazonium salt to salicylic acid. The diazotization and the coupling procedures for the synthesis of dye 1 have been described previously^[11] and are briefly shown in Fig. 2. The yield was 85%.

Dye 2: diazotisation of 4-amino-*N*-ethylglycinate-1,8-naphthalimide

This stage is similar to that of dye 1.

Coupling

The coupling reaction for dye 2 is the same as that for dye 1, except the stage after completion of the coupling reaction, which is as follow:

After the termination of the reaction, the pH of the mixture was adjusted to 6–7 with the aid of acetic acid.

The reaction mixture container was removed from the ice and water bath and heated slowly. As stirring continued, 6 mL of 200 g/L aqueous copper sulphate (II) was added slowly. The temperature of the reaction mixture was raised to 50–60°C and the stirring continued for 30 min at the same temperature in order to complete the reaction. Then, the reaction mixture was cooled down and the crude dye was collected using vacuum filtration and purified with preparative TLC using DMF as solvent (Fig. 2). The dyes were characterized using analytical methods ($^1\text{H-NMR}$, FTIR, melting point and UV-Vis spectroscopy). The yield was 87%.

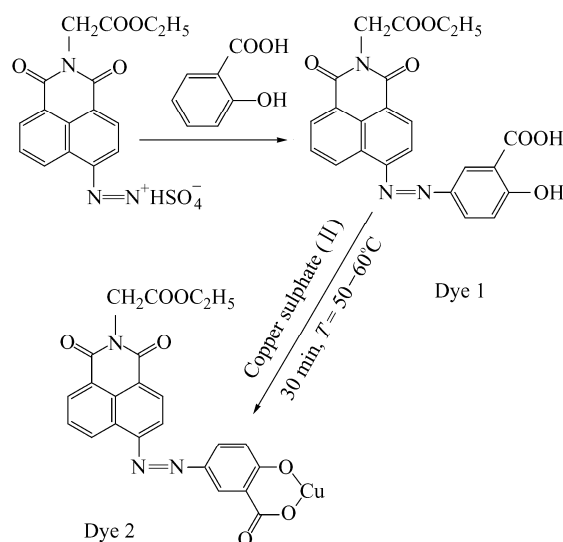


Fig. 2 Synthesis route for dyes 1 and 2

Preparation of Dye Dispersions

Because the synthesized dyes have low water solubility, the dispersions of them were prepared before being applied to the substrate. For this purpose, 0.5 g of dye, 1 g of dispersing agent (Lyoprint EV; Ciba Co., Switzerland) and 2 mL water were added to a mortar and mixed up. Then, 20 mL water was added to this mixture and the resulting mixture transferred to a ball mill and treated for 20 h. The mixture was diluted to 100 mL and then filtered off using Micro-Prazisions Sieb Fritsch (5 μm ; Fritsch, Germany).

Dyeing Procedure

The fabric samples (2 g) were pretreated with a nonionic detergent (Dyatex NW, Dyer Chimie Co., Iran) (5 g/L) for 20 min at 50°C and 80°C for nylon 6 and polyester, respectively. The dyeing of polyester fabric was carried out using HT method (Nasaj Sanat Yazd Ltd, Iran) and a liquor to goods ratio of 50:1, pH 5–7 (acetic acid). The concentrations of the dye dispersions were 0.1%, 0.5%, 0.7%, 1%, 1.5%, 2% and 4% o.w.f. (on weight of fiber). Dyeing of nylon 6 was started at 45°C and the temperature was then raised to boiling point over 45 min and continued at the same temperature for 60 min. For polyester, dyeing process was started at 30°C. The temperature was raised to 90°C over 30 min, then raised to 130°C with the rate of 1 K/min and continued at the same temperature for 60 min. Afterward, temperature was cooled down to 70°C and the substrate was rinsed. Finally, the unwashed, reduction cleared and alkali cleared substrates were submitted to fastness tests. The dyed sample was reduction cleared in a solution of 3 g/L sodium dithionite, 1 g/L sodium hydroxide and 1 g/L nonionic detergent at 50°C for 20 min. Alkali clearing of the samples was performed using 2.5 g/L sodium hydroxide at a constant temperature of 80°C and then rinsed.

Determination of Fastness Properties

Wash fastness of all dyed fabrics (samples dyed at a concentration of 2% o.w.f.) was determined according to the standard ISO 105 B01 C2S. Rubbing fastness was carried out using a crockmeter in accordance with ISO 105-X 12:1993(E). The dry heat fastness and light fastness were measured according to standards ISO 105-P01:

1993(E) and ISO105-B02:1994(E), respectively.

Spectrophotometric Properties of the Synthesized Dyes

The maximum absorption wavelength ($\lambda_{\max}$), molar absorption coefficient ($\epsilon_{\max}$) and half band width ($\Delta\lambda_{1/2}$) are the spectrophotometric properties. For determination of these properties, the absorption band profiles of the dyes were obtained using dimethylformamide (DMF) as solvent and then the molar absorption coefficients of the dyes were calculated by means of the beer-lambert law (Table 1). Measurements of maximum absorption wavelength of the synthesized dyes showed that dye 1 is red in colour and dye 2 is reddish yellow.

Table 1. Spectrophotometric properties of the dyes

Dye	$\lambda_{\max}$ (nm) in DMF	$\epsilon_{\max}$ (L mol ⁻¹ cm ⁻¹)	$\Delta\lambda_{1/2}$
1	609	26638	93
2	543	21648	124

Influence of Urea

In order to investigate the effect of urea on increasing build-up of the dyes on nylon 6 and polyester fabrics, dyeing with dye concentrations of 0.1%, 0.5%, 0.7%, 1%, 1.5%, 2% and 4% o.w.f. was performed in the presence of 10 g/L urea.

RESULTS AND DISCUSSION

Synthesis of Dyes

Dyes 1 and 2 were successfully synthesized and characterized by ¹H-NMR, FTIR, melting point and elemental analysis. The results are shown as follows:

Dye 1: ¹H-NMR (CDCl₃): δ 1.27–1.34 (3H, CH₂CH₃), 4.24–4.31 (2H, COOCH₂CH₃), 4.98 (2H, NCH₂), 4.87 (1H, OH), 6.79–6.82 (1H, 5'-H), 7.83–7.89 (1H, 6-H), 7.97–8.06 (3H, 2'-H, 6'-H, 5-H), 8.66–8.70 (2H, 2-H, 7-H), 9.28–9.31 (1H, 3-H), 10.08 (1H, COOH); FTIR (KBr): ν 3441 cm⁻¹ (OH str.), 2965 cm⁻¹ (C–H str. ar.), 2924 cm⁻¹ (C–H str. aliphatic), 1748 cm⁻¹ (C=O str. ester), 1698, 1622 cm⁻¹ (C=O str. carbonyl), 1588 cm⁻¹ (N=N str.); melting point: 320°C; $\lambda_{\max}$ (DMF) 609 nm. Elemental Calculated for C₂₃H₁₇N₃O₇: C, 61.75%; H, 3.83%; N, 9.39%; Found: C, 61.68%; H, 3.75%; N, 9.35%.

Dye 2: ¹H-NMR (CDCl₃): δ 1.27–1.34 (3H, CH₂CH₃), 4.24–4.31 (2H, COOCH₂CH₃), 4.98 (2H, NCH₂), 6.79–6.82 (1H, 5'-H), 7.83–7.89 (1H, 6-H), 7.97–8.06 (3H, 2'-H, 6'-H, 3-H), 8.66–8.70 (2H, 2-H, 7-H), 9.28–9.31 (1H, 3-H); FTIR (KBr): ν 3441 cm⁻¹, 2961 cm⁻¹ (C–H str. ar.), 2925 cm⁻¹ (C–H str. aliphatic), 1748 cm⁻¹ (C=O str. ester), 1699, 1662 cm⁻¹ (C=O str. carbonyl), 1596 cm⁻¹ (N=N str.); melting point: 350°C; $\lambda_{\max}$ (DMF) 543 nm.

Dyeing Properties

For evaluating the adsorbed dye on nylon 6 and polyester fabrics, dyebaths with dye concentrations of 0.1%, 0.5%, 0.7%, 1%, 1.5%, 2% and 4% o.w.f. were provided and the concentrations of the dyes were determined on the substrates and in wastewater. The results for nylon 6 and polyester fabrics are shown in Fig. 3.

From the figure, it is clear that dyes 1 and 2 have the higher and lower adsorption on nylon 6, respectively. Considering the chemical structure of dye 1, there are hydroxyl and carboxyl groups present in the molecule. These polar groups bond chemically with polar groups in nylon 6 structure, resulting in increased adsorption of dye 1. On the other hand, dye 2 has a bigger structure without free polar groups available and therefore, penetration of the dye molecule into the fiber is difficult so that the adsorption of dye 2 on the fiber is reduced. As shown in Fig. 3, similar results are obtained for polyester. Figure 3 also reveals that both of the dyes have higher adsorption on nylon 6 fiber which is attributed to the physical structures of nylon 6 and polyester fibers. Because of less crystalline structure of nylon 6 (crystallinity values of 50% and 65%–85% for nylon 6^[12] and polyester^[13], respectively), the adsorption of the dyes on nylon 6 is more than that on polyester.

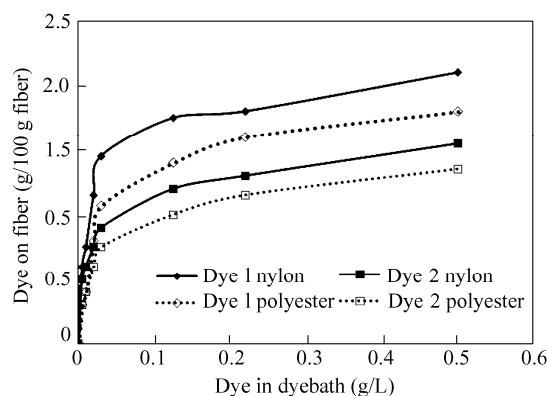


Fig. 3 Dye adsorption properties of dyes 1 and 2 on nylon 6 and polyester fibers

Figures 4 and 5 show the effect of urea on the dyeing properties of the synthesized dyes.

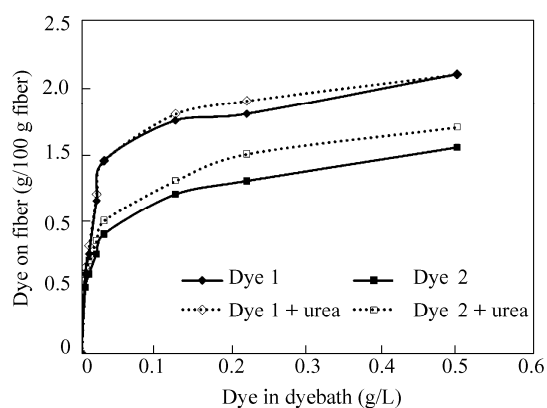


Fig. 4 Effect of urea on dye adsorption of nylon 6 fiber

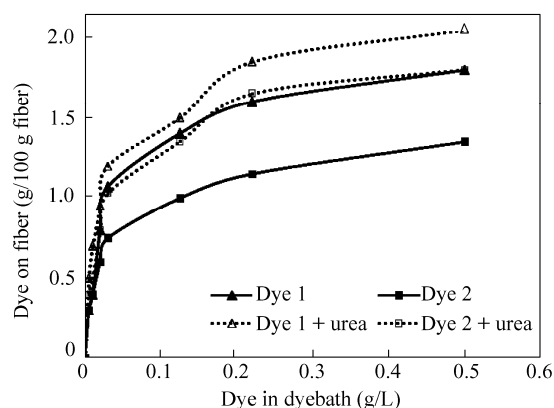


Fig. 5 Effect of urea on dye adsorption of polyester fiber

These figures show that by adding urea in the dyebath, the adsorption values are increased. This increase in dye adsorption is more obvious for dye 2 which may be due to the lower solubility of dye 2. Poor water solubility of the dye molecules makes them to have low diffusion coefficients^[6] and low adsorption on the textile fibers. In order to increase solubility of the dyes, the use of wetting agent such as urea is of great importance. This mechanism suggests more increase in dye adsorption of hydrophobic dye molecules such as dye 2 in the presence of urea as shown in Figs. 4 and 5.

Figures 4 and 5 also reveal that, in the presence of urea, increase in dye adsorption on polyester fiber is more than that on nylon 6 fiber. This observation could be explained by the effect of urea on the physical structure of the polyester fiber. Urea, *via* making hydrogen bonding with carbonyl groups in the polymer chains of polyester fiber, provides less crystalline fiber and accelerates dye adsorption at high temperatures (Fig. 6). In the case of nylon 6 fiber, because the polymer chains of nylon 6 fiber is less compact than that of polyester fiber so the effect of urea on the adsorption of the dyes on the fiber is not significant.

Wash fastness properties of samples dyed with 2% o.w.f. of dyes 1 and 2 expressed as the color change of the samples, *i.e.* staining on cotton and polyester fabrics, are summarized in Table 2.

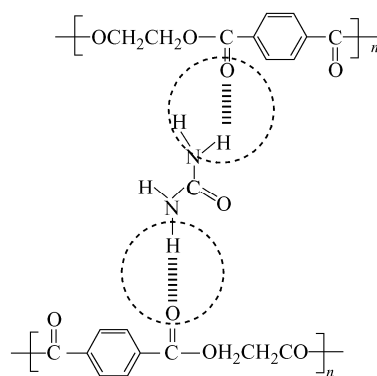


Fig. 6 Interaction of urea with polyester fiber

Table 2. Washing fastness of dyed polyester fabric

Dye	Unwashed			Reduction cleared			Alkali hydrolysed		
	Color change	Staining on cotton	Staining on polyester	Color change	Staining on cotton	Staining on polyester	Color change	Staining on cotton	Staining on polyester
1	3–4	4–5	5	5	5	5	5	5	5
2	4–5	5	5	5	5	5	5	5	5

In order to compare the hydrolysis ability of synthesized dyes, the colored substrates were provided in the form of unwashed, reduction cleared and alkali hydrolysed. Table 2 reveals that reduction cleared and alkali hydrolysed samples show excellent washing fastness for both dyes. Although wash fastness of the dyes is not good for unwashed samples, dye 2 shows better wash fastness (4–5) in comparison with dye 1 (3–4) which may be due to the lower solubility and larger molecular size of dye 2.

Rubbing fastness of dyed polyester and nylon 6 fabrics was measured in dry and wet states and summarized in Tables 3a, 3b and 4.

Table 3a. Rubbing fastness of polyester in dry state

Dye	Unwashed		Reduction cleared		Alkali hydrolysed	
	Color change	Staining	Color change	Staining	Color change	Staining
1	4	4–5	5	5	5	5
2	3–4	3	5	5	5	5

Table 3b. Rubbing fastness of polyester in wet state

Dye	Unwashed		Reduction cleared		Alkali hydrolysed	
	Color change	Staining	Color change	Staining	Color change	Staining
1	4	4	4–5	4–5	4–5	4–5
2	3	3	4–5	5	5	4

As can be seen from these tables, the rubbing fastness of the dyes on nylon 6 is very good whereas their rubbing fastness on polyester fibers is acceptable after reduction clearing or alkali hydrolysis.

Table 4. Color fastness of dyed nylon 6

Dye	Rubbing fastness						Heat fastness at 180°C	Light fastness	K/S
	Wet		Dry						
	Color change	Staining	Color change	Staining	Color change	Staining			
1	5	5	5	5	4–5	4	4–5	32.1	
2	5	4–5	5	5	5	4–5	4–5	22.6	

Table 5. Heat and light fastness of dyed polyester

Dye	Heat fastness at 180°C		Light fastness	K/S
	Color change	Staining		
1	4–5	4	5	20.6
2	5	5	5	8.3

Dye 2 has higher heat fastness as compared with dye 1 as shown in Tables 4 and 5. It could be attributed to the larger molecular size of dye 2. Furthermore, heat (sublimation) fastness of the dyes on polyester is higher than that of nylon 6, because of the compact structure of polyester fibers. By considering the K/S (K is absorption coefficient and S is scattering coefficient) values, it is clear that dye 1 has higher adsorption on the fibers as compared with dye 2.

CONCLUSIONS

The synthesis of two naphthalimide based disperse dyes was explained. The application properties of the dyes were successfully evaluated on the dyeing of nylon 6 and polyester fabrics. The effect of urea on dyeing the fabrics was also investigated. Dye adsorption on polyester fibers was increased in presence of urea. Urea has more effect on dyeing properties of the less water soluble dye (dye 2) and the more hydrophobic fiber (polyester fiber). The dyes were successfully used for the dyeing of nylon 6 and polyester fabrics with acceptable fastness properties.

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