

# The structure of azo disperse dyes and its distribution on polyurethane fiber blend with polyester, or polyamide fiber<sup>☆,☆☆</sup>

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Received 9 December 2005; received in revised form 18 February 2006; accepted 24 April 2006

Available online 12 June 2006

## Abstract

Using a range of monoazo disperse dyes, the distributions between PU fiber and polyester, and polyamide fibers were studied. It was found that at lower temperature, the disperse dyes exhausted more on polyurethane fiber than on polyester or polyamide, and then less exhausted as the temperature was increased. The distributions on polyurethane fiber blends varied with the structure of disperse dyes. The presence of halogen groups on diazo component at the ortho position to the azo link made dye uptake on polyurethane component higher, but the cyano derivative and the dye from diazo component of 5-nitro-benzothiazole tended to lower the adsorption on polyurethane fiber. The addition of two terminal cyano groups on coupling component showed lower dye uptake on polyurethane. The dyes with two terminal hydroxyl groups had high exhaustion on polyurethane fiber when blended with polyester fiber but low exhaustion when blended with polyamide.

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**Keywords:** Disperse dyes; Structure; Distribution; PU fiber blends

## 1. Introduction

Polyurethane fiber (abbreviated as PU fiber) is a segment polymer containing at least 85% segmented polyurethane. They are built from alternating rigid and flexible segments. The chemical structure is illustrated in Fig. 1.

The rigid segments, which contain polar groups including ureylene (–NHCONH–) and urethane (–NHCOO–), can form intermolecular hydrogen bond. The intermolecular hydrogen bond makes the molecular chains pack orderly to form hard domain, which increases the polymer's tensile

strength and thermal resistance. On the other hand, owing to the absence of polar group, there is no strong intermolecular force formed among the soft segments, and the molecular chains can move easily, pack disorderly to become the amorphous region, which renders the PU fiber flexible. The glass transition temperature of soft segment is very low. The PTMG-based PU fibers have a  $T_g$  ranging from –60 °C to –30 °C [1]. The model of the physical structure of PU fibers is described in Fig. 2 [2].

Recently, with the development of applied technology, elastic polyurethane fibers possessing remarkable stretchability combined with a low elastic modulus and high recovery have been widely used. However, the fabric containing PU fiber usually has lower degree of colorfastness because of the stain of dye on PU fiber [3]. In order to keep the properties of PU fiber from damage, the fabric such as polyurethane–polyester blend is usually dyed at lower temperature. As a result, the dyes do not dye the polyester fiber very well. One of the solutions to these problems is to look for the disperse dyes which exhaust less on PU fiber or have excellent dyeing

<sup>☆</sup> Contract Grant Sponsor: Natural Science Foundation of Zhejiang Province; contract grant number: Y404314.

<sup>☆☆</sup> Contract Grant Sponsor: Doctor Creative Foundation of Donghua University.

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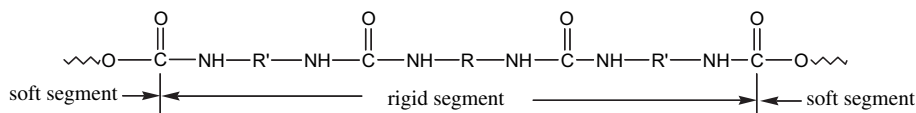


Fig. 1. Chemical structure of polyurethane fiber, where R' is the diisocyanate residue, R is the extender residue, and soft segment is a long chain diol (high molecular weight), i.e. polyester chain or polyether chain.

behaviors on both PU fibers and polyester at lower temperature, so the relationship between structure of disperse dyes and its distribution between PU fiber and its blended fibers is worth studying.

## 2. Experimental

### 2.1. Materials

The PU fiber (44.4 dtex, PTMG-based type) used in this study was produced by Dupont. Its trade name is Lycra. DSC (Differential Scanning Calorimetry) for this fiber, as

shown in Fig. 3, was carried out using DSC Q100, America TA Instrument. The samples were scanned at a heat rate of 10 °C/min and protected by 50 mL/min Ar. The woven polyester fabric (density, 220 × 210; weight, 168 g/m<sup>2</sup>) was obtained from Nanfang Company. The knitted fabric made of 40D/12f polyamide filament (weight, 85 g/m<sup>2</sup>) was obtained from Hongda Company.

Two series of disperse dyes (shown in Fig. 4), were applied in this study. One has the same coupling component but vary in diazo component. Another has the same diazo component but vary in coupling component. Each of the dyes was obtained in the form of commercially available presscake of

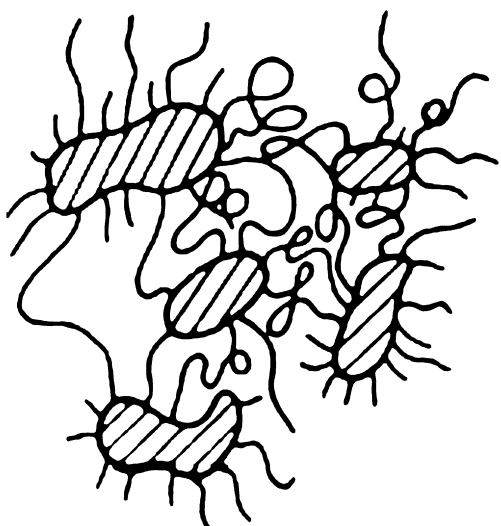


Fig. 2. Structure of domains in segmented PU: hatched area is hard domain, — rigid segments, and ~ flexible segments.

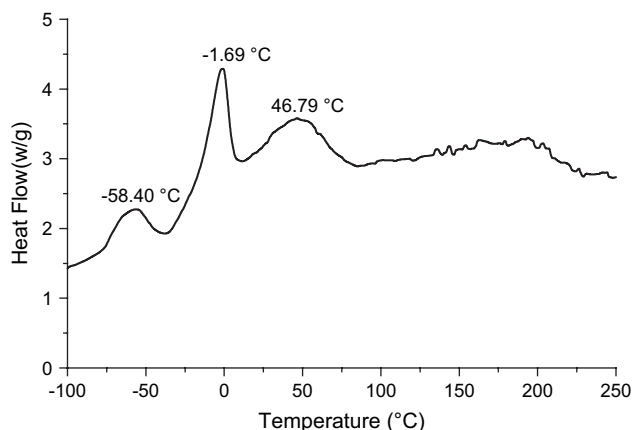
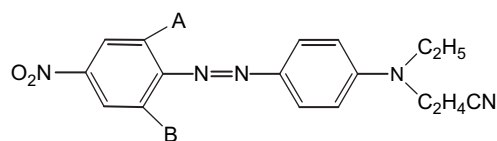
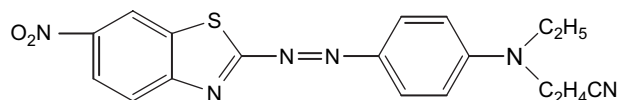


Fig. 3. DSC scanning of the PU fibers.

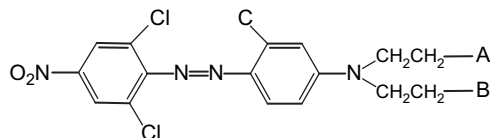


		A	B
1a	C. I. Disperse Orange 25	H	H
1b	C. I. Disperse Red 50	Cl	H
1c	C. I. Disperse Orange 76	Cl	Cl
1d	C. I. Disperse Orange 61	Br	Br
1e	C. I. Disperse Red 73	CN	H



If C. I. Disperse Red 145

(Series 1)



		A	B	C
2a	C. I. Disperse Brown 1	OH	OH	Cl
2b	C. I. Disperse Brown 19	COOCH <sub>3</sub>	COOCH <sub>3</sub>	H
2c	C. I. Disperse Orange 30	OCOCH <sub>3</sub>	CN	H
2d(1c)	C. I. Disperse Orange 76	H	CN	H
2e	C. I. Disperse Yellow 163	CN	CN	H

(Series 2)

Fig. 4. The molecular structures of disperse dyes.

greater than 98% purity (HPLC %area at  $\lambda_{\max}$ ). For this experiment, all these dyes were milled and spray-dried by the same method. The milling was performed in the presence of dispersing agent (XP-9 from Norway) of a mass equal to that of dye.

## 2.2. Dye application

All the dyes were applied to a mixed sample with polyester woven fabric and PU fiber (9:1), and to a mixed sample with polyamide knitted fabric and PU fiber (9:1), respectively. The liquor ratio was 50:1. The dye concentration was 2% (o.w.f). Dyeing was carried out with a laboratory dyeing machine (Rapid) at a constant temperature for an hour. For the polyester–PU blend, various temperatures ranging from 40 °C to 130 °C were applied. For the polyamide–PU blend, the applied temperature ranges from 30 °C to 120 °C. After dyeing, the samples were washed with hot water of 85–90 °C to remove the loosely bound dyes.

## 2.3. Measurement

The amount of disperse dyes in PU fiber is obtained by measuring absorption of dye solution extracted from dyed sample with acetone at the maximum wavelength using a UV–vis spectrophotometer (Shimadzu UV-2450). The exhaustion of disperse dyes on polyester component or polyamide component is calculated by subtracting the exhaustion on PU fiber from the total one which can be obtained by

measuring the absorption of dye solution before and after dyeing. The equation used to calculate the total exhaustion is as follows:

$$\text{Exhaustion}(\%) = \left(1 - \frac{D_2 \times V_2}{D_1 \times V_1}\right) \times 100\%$$

Where  $D_1$  and  $D_2$  represent the light absorptions of original dye solution and residual dyebath, respectively.  $V_1$  and  $V_2$  are the volumes of original dye solution and residual dyebath, respectively.

## 3. Results and discussion

### 3.1. Distribution on polyester–PU blend

The exhaustion on PU component for two sets of dyes is illustrated in Fig. 5.

Fig. 5 indicates that for all the disperse dyes except **2e**, the curves reflecting the relationship between the exhaustion on PU fiber and dyeing temperature are similar. At lower temperature, the disperse dyes exhausted more on PU fiber than polyester fiber because the PU fibers have lower glass transition temperature. DSC scanning of the PU fibers, as shown in Fig. 3, in which three heat-absorbing peaks can be observed at  $-58.40$  °C,  $-1.69$  °C, and  $46.79$  °C, respectively, had demonstrated this fact. For some dyes such as **1b**, **2a** and

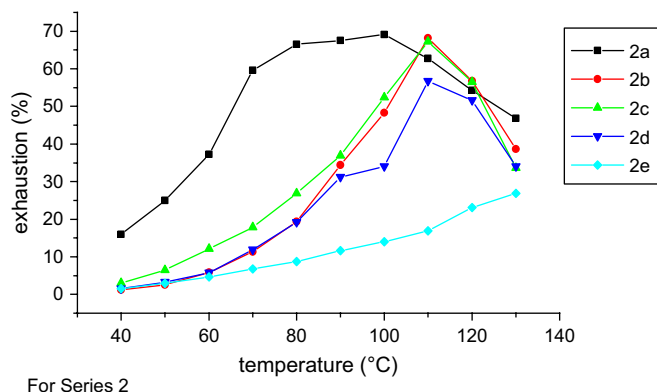
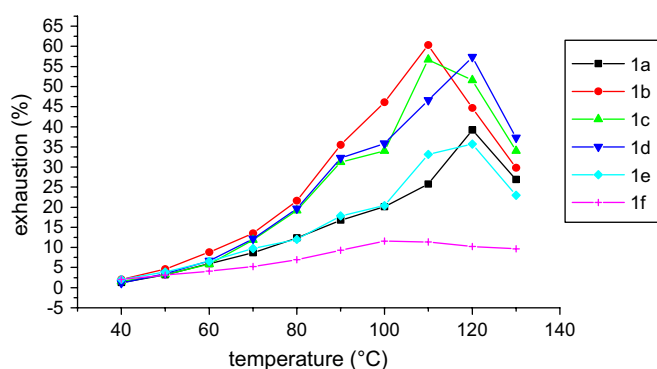


Fig. 5. Exhaustion of disperse dyes on PU component in polyester–PU blend at different temperatures.

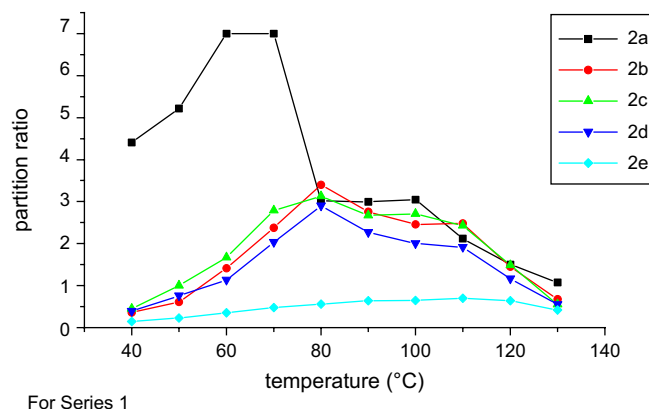
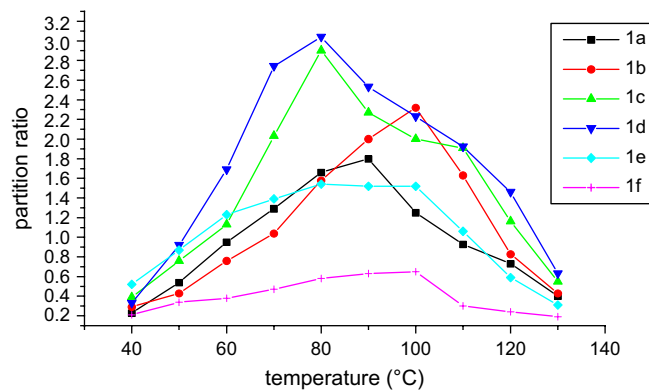


Fig. 6. Partition ratio of disperse dyes on PU fiber and polyester fiber at different temperatures.

**2c**, the dye uptakes on PU fiber reached more than 20% at 80 °C, even though the weight proportion of PU fiber was only 10%. As the dyeing temperature was increased to 100 °C, 110 °C or 120 °C, the amounts of disperse dyes on PU fiber began to decrease while part of disperse dyes which had adsorbed on PU fiber would be transferred to polyester. The relative amounts of dyes on two fibers depend on their affinity for two fibers. It was found that most of the disperse dyes adsorbed on PU fiber to a great degree. Many kinds of dyes had the highest dye uptake of more than 50% on PU fiber, and had partition ratios of more than 2 between PU fibers and polyester fibers at a certain dyeing temperature. At 130 °C, the ratios of the amounts of dyes on these two fibers were more than the corresponding weight ratio of the two fibers (1:9).

Both Figs. 5 and 6 show that the distributions varied with disperse dyes. For Series 1, the order of exhaustion on PU fiber was **1d** > **1c** > **1b** > **1a**. It may be concluded that the incorporation of the groups such as chlorine, bromine on diazo component at the ortho position to the azo link leads to great adsorption on PU fiber. Dichlorine derivative adsorbed more than monochlorine derivative, and dibromine derivative adsorbed more than dichlorine derivative. It can be explained by the increasing van der Waals force between dye molecules and polymer molecule in PU fiber resulting from the increase in polarity or volume of dye molecules. However, the cyano substitute, **1e** had lower adsorption on PU fiber, the reason is not understood. Dye **1f**, which has heterocyclic diazo

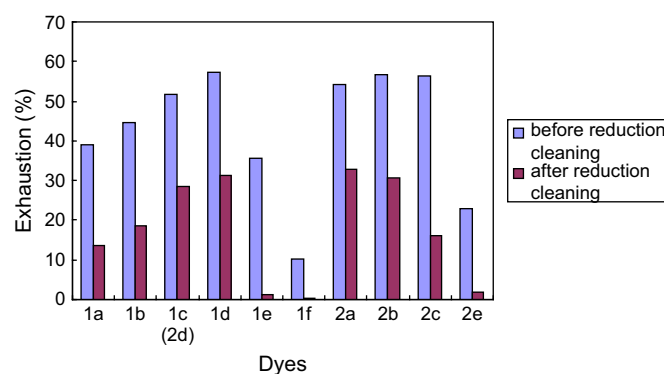


Fig. 7. Exhaustion of disperse dyes on PU fiber before and after reduction cleaning at 120 °C.

component, 5-nitro-benzothiazole showed the lowest adsorption on PU fiber.

For Series 2, although all disperse dyes have the same diazo component, the dyeing behavior for every individual on PU–polyester blend was different from each other. At 130 °C, the order of adsorption on PU fiber was **2a** > **2b** > **2c** ≈ **2d** > **2e**. What needs to be mentioned is that dye **2a** had unique dyeing behaviors on PU–polyester blend. At the low dyeing temperature, dye **2a** had relatively high dye uptake on PU fiber. When the dyeing temperature was 40 °C, its dye uptake had reached about 15%, and its

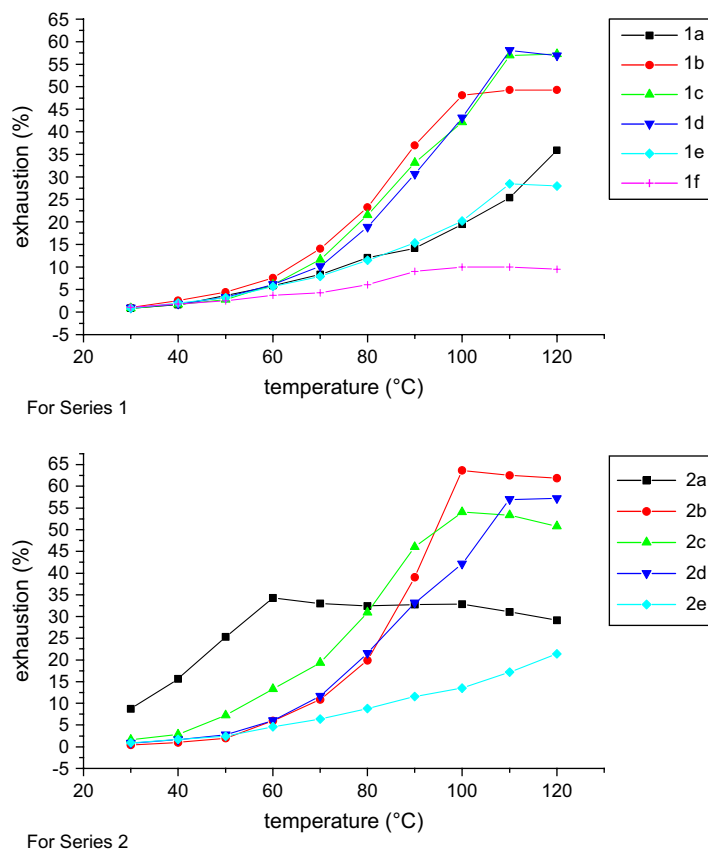


Fig. 8. Exhaustion of disperse dyes on PU component in PU–polyamide blend at different temperatures.

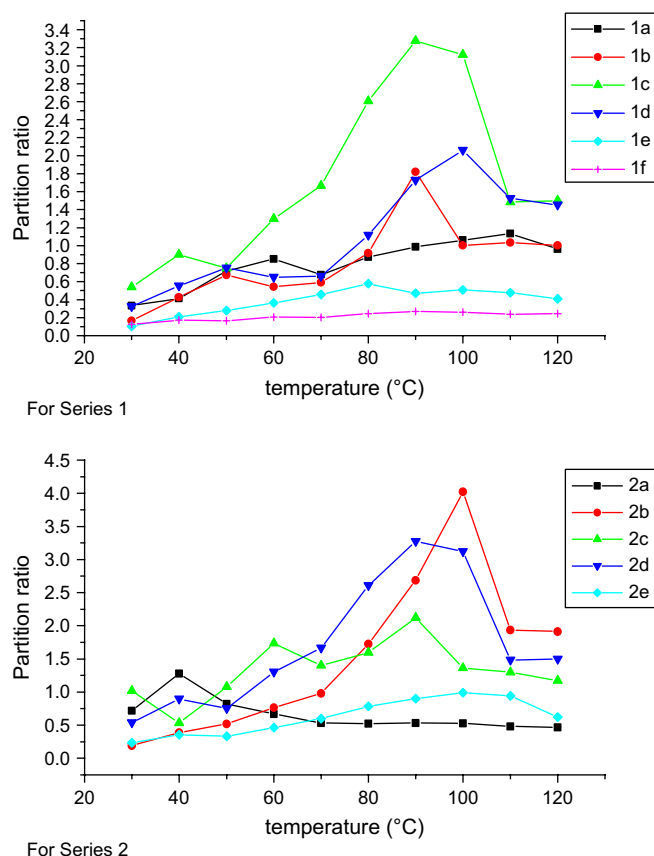


Fig. 9. Partition ratios of disperse dyes on PU fiber and polyamide fiber at different temperatures.

distribution was about 4.5. At the highest point, the ratio was 7. When the dyeing temperature was 130 °C, this dye showed the greatest adsorption on PU fiber. This observation may be related to the existence of two hydroxyl groups in dye molecule, which can make the dyes bound with ureylene ( $-\text{NH}-\text{CONH}-$ ) and urethane ( $-\text{NHCOO}-$ ) in the polymer molecule of PU fiber, thus producing high affinity for PU fiber. Because of lower glass transition temperature, the PU fibers have slack in physical structure. As long as the solubility of dyes in water is high enough, the dyes would have the considerable dyeing rate. For dye **2a**, the two hydroxyl groups bring better solubility as well as higher affinity for PU fiber so that it has great exhaustion on PU fiber at low dyeing temperature. Regarding other dyes in Series 2, it follows that for dye **2b** which contains terminal methoxycarbonyl groups has greater distribution on PU fiber, while dyes **2c** and **2d** containing terminal acetoxy and cyano groups, or a hydrogen and a cyano group, respectively, had the similar dyeability on PU component. Dye **2e**, which brings two terminal cyano groups on coupling component, gave the lowest distribution on PU fiber.

In order to investigate the influences of reduction cleaning on the adsorption of disperse dyes on PU fiber, this research also measured the amounts of dyes on PU fiber dyed at 120 °C after being reduction cleaned. The result is shown in Fig. 7 from which it is observed that the amount of every dye in PU fibers would be obviously decreased after reduction cleaning. Some dyes such as **1e**, **1f** and **2e**, which have low distribution on PU

fibers, almost had no stain on PU fiber after reduction cleaning. The final order of amount of dyes on PU fiber was almost consistent with that at 130 °C without reduction cleaning except that dye **2c** was less than dye **2d** after reduction cleaning.

### 3.2. Distribution on polyamide–PU blend

Polyamide fiber have more polar groups such as amino and amide in polymer chain. When these two series of disperse dyes were applied to PU–polyamide blend, except dye **2a**, the rest performed similar to that in the case of PU–polyester blend, as shown in Figs. 8 and 9. The orders of dye uptake and distribution on PU fiber were consistent well with that observed during dyeing of PU–polyester blend.

One of the differences was that when the temperature was 110 °C, for most disperse dyes, the dyeing of PU–polyamide blend tended to reach equilibrium, and the distribution was maintained constant. In addition, in the range of Series 2, it is noticed that dye **2a**, which contains terminal hydroxyl groups, had lowest partition ratio on PU fiber in the case of PU–polyamide blend but highest for PU–polyester blend. It is deduced that polyamide fibers have relatively greater capability of forming hydrogen bonds with dye molecules so that part of dyes can be adsorbed by this force producing increased dye uptake on polyamide, whereas polyester fibers have lower capability of forming hydrogen bonds with dye molecules and so the dyes tended to adsorb on PU fiber by hydrogen bonds to produce the higher dye uptake on them.

## 4. Conclusion

Disperse dyes have considerable adsorption on PU fiber during dyeing of PU–polyester or PU–polyamide blend even though the content of PU component is only 10%.

The partition ratio varies with different dyes; the existence of hydroxyl groups in dye molecules is beneficial to adsorption on PU component when combined with polyester fiber but produce lower dye uptake on PU component in a blend with polyamide fiber. Incorporation of halogen on diazo component seems to enhance the distribution on PU fiber whether blended with polyester or polyamide. The cyano derivatives either on diazo component or on terminal groups of coupling component tend to have lower adsorption on PU fiber. The azo dye from 5-nitro-benzothiazole exhausts less on PU fiber.

Reduction cleaning would obviously decrease the dye uptake on PU component so that this is the commonly used method to decrease the stain on PU fiber to improve the fastness properties during the application of disperse dyes for PU fiber blends.

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