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〈Research Communication〉

Direct Coloration using Self-assembly Fabrication Method on PET Fibers -Surface diazo coupling reaction-

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Abstract— The electrostatic layer-by-layer technique provides a convenient way to control the construction of ultrathin films at nano-scale ranges and can be easily obtained. It can be also applicable to fiber substrate with dye compounds. We have fabricated multilayer dye films using diazonium resin and three couplers, which are prepared by self-assembly approach. This method is based on layer-by-layer deposition using electrostatic attraction between oppositely charged ions. Beside, the diazo coupling reaction proceeded to form azo dye layer on the PET fibers the same time. The corresponding results of the multilayer films have been discussed on the level of color strength (K/S).

Keywords: *layer-by-layer, coupling reaction, diazonium resin, coupling compound*

1. Introduction

Preparations and characteristics of ultra-thin layers are of considerable interests due to their potential technological applications in the fields of coatings, sensors and optoelectronics. These films are commonly formed using Langmuir-Blodgette (LB) deposition or self-assembly techniques based on chemisorptions[1]. Self-assembly electrostatic layer-by-layer film deposition has been presented to be a simple method for fabricating thin films.

The electrostatic attraction between oppositely charged molecules seems to be a good driving force for multi-layer build-up property.

The general thickness of the fabrication films can be simply controlled and monitored using the deposition numbers[2-4] This technique has been actively investigated in recent years from Tani and Nakamura[5]. However, there have been few studies on applying it to textile dyeing and finishing process. In this context, the preliminary approaches, namely alternate layer-by-layer self-assembly attraction with dye moieties onto fiber substrates might be a useful skill to produce coloration and functional effect.

Azo dyes, the largest chemical class of dyes with a variety of color ranges, have been used in textile dyeing[6-8]. Almost without exception, azo colorants are prepared by diazotization of a primary aromatic amine followed by coupling reaction of the resultant diazonium salt with an electron-rich nucleophile. This coupling reaction is commonly known as phenol and amine coupling, respectively. Hydroxyl compounds such as phenols and naphthols are coupled in an alkaline condition, whereas amine compounds are coupled in a slightly acidic medium[9].

In this study, the diazonium resin[2,10] and three couplers were prepared to manufacture multi-layer dye films on the PET fibers. Beside, the diazo coupling reaction proceeded to form multi dye layers on the PET fibers at the same time. Dyed fibers have been measured the level of color strength (K/S) and the charateristics were discussed in detail.

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2. Experimental

Diazonium resin[2,10] was prepared by polycondensation between 4-diazodiphenylamine sulfate with paraformaldehyde in concentrated sulfuric acid are shown Fig. 1.

4-diazodiphenylamine sulfate (5g, 0.017 mole) was added to 50 ml flask and concentrated H_2SO_4 (8 ml) was added dropwise with stirring. Using an ice-water bath, the flask was cooled and paraformaldehyde (0.6 g, 0.02 mole) was added slowly into batches at 0-5 °C. The reaction continues for 3 hrs in the dark and then the reaction mixture was poured carefully into 30 ml of ice water. Five grams of zinc chloride was added to precipitate the diazonium resin as a 1/2 $ZnCl_2$ complex. After filtration with $ZnCl_2$ aqueous solution (saturated) and drying in vacuum, a yellow-green powder was obtained[2,10].

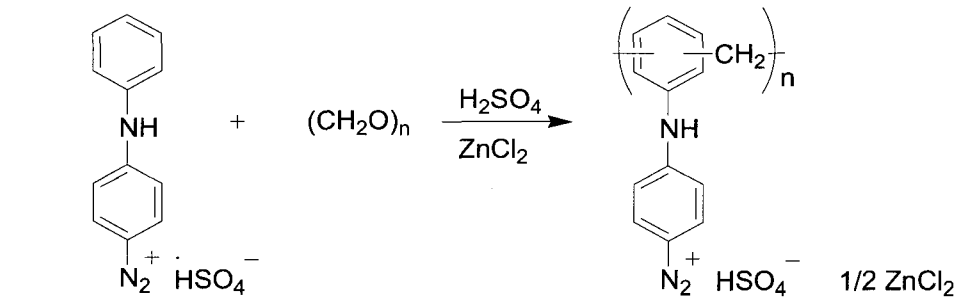
The preparation of diazonium resin was carried out and kept in the dark.

Prior to azo dye coupling reaction between diazonium resin and coupling compounds three layers of poly (diallyldimethylammonium chloride) (PDDA) and poly (sodium-4-styrene) sulfonate (PSS) precursors (PDDA/PSS) were firstly prepared by immersing the PET fibers in PDDA and PSS solution alternatively and intermediate washing in distilled water was followed. After that, the coupling reaction between diazonium resin and coupling compound was carried out on the treated fiber substrates with the conditions similar to those in the precursor assembly. The structure of the three coupling compounds shown in Fig. 2.

In the coupling solution, 0.5g of NaOH was added to provide alkaline condition for phenol type coupling reaction. The fabrications of diazonium resin and coupling compound are shown in Fig. 3.

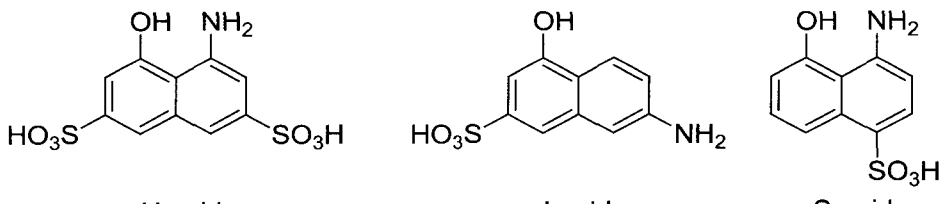
Self-assembly multi dye layers on the fiber substrates were deposited sequentially until the desired number of dye layer deposition was achieved.

Dyed fabrics have been discussed on the level of color strength (K/S) in detail. Reflectance measurements on the dyed fibers were carried out using a Datacolor SF 600 plus spectrophotometer interfaced to a PC. Measurements were taken with the specula component of the light excluded and the UV component included, using illuminant D65 and 10° standard observer. The average of three reflectance measurements, taken at different positions on the dyed fiber substrates, was carried out. Color strength (K/S) was calculated by the Kubelka-Munk formula.



4-diazodiphenylamide sulfate **Diazonium resin**

Fig. 1. Preparation of the diazonium resin.



H-acid J-acid S-acid

Fig. 2. The coupler structures.

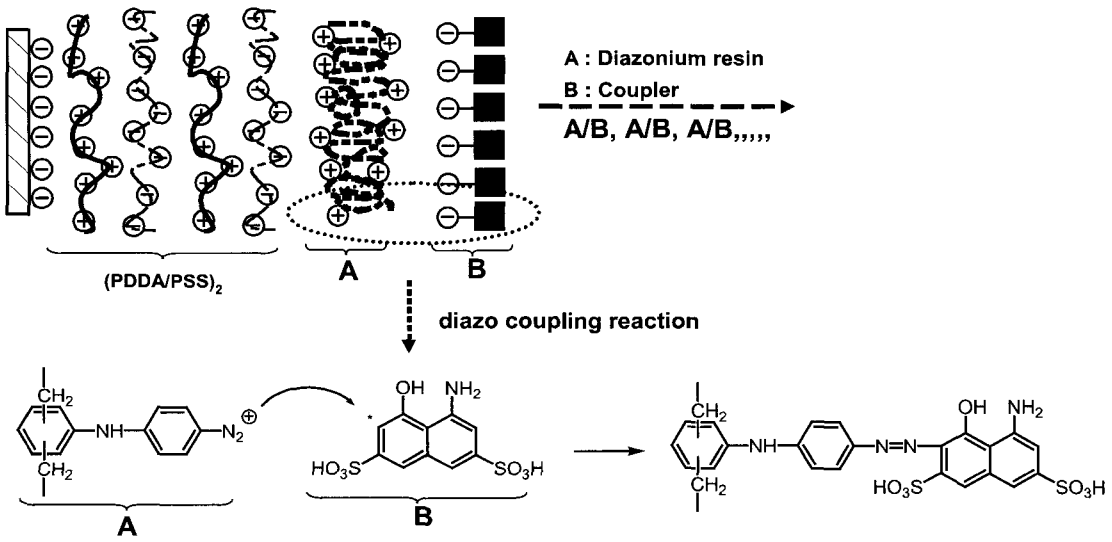


Fig. 3. Scheme of the self-assembly dye layer coloration.

3. Results and Discussion

Fig. 3 shows a schematic illustration of self-assembled and diazo coupled dye layer deposition with alternating layers of the diazonium resin and three couplers. In step A, a substrate with a negative charged surface is immersed in the solution of the positively charged diazonium resin. A diazonium resin layer firstly occurred at this step. In step B, the substrate is dipped into the solution containing the negatively charged coupling compound. The self-assembled layer and coupling reaction were simultaneously formed on the PET fiber surface.

In this study, the growth of the azo dye layers on the PET fiber surface formed by the continuous coupling reaction was examined using K/S spectra determination. Fig. 4 shows the K/S spectra of the diazonium resin/H-acid coupling dye layers on PET substrates by 1~5 layers. From the results in this figure, it can be proposed that the fabrication of multi dye layer was successfully achieved. It shows the linear increase in K/S values at 580nm with the number of layers, indicating a progressive deposition with almost equal amount of deposition of the dyes in the each cycle. Similar adsorption behavior was observed in other two couplers (Table 1).

In this context, the aim of this preliminary work is to attempt and investigate the direct multi-dye

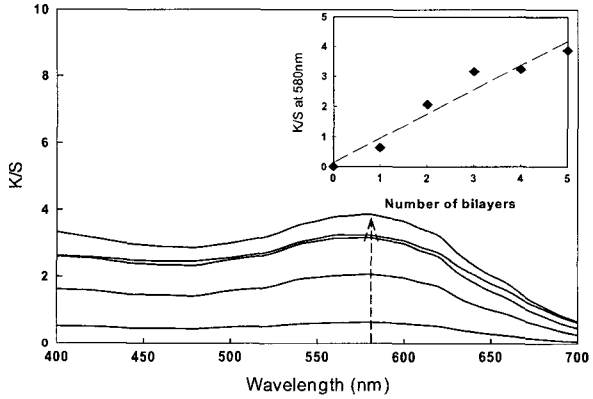


Fig. 4. K/S spectra of the diazonium resin/H-acid dye couplings on the PET substrates.

Table 1. Comparison of K/S spectra with three couplers

Coupler	K/S spectra	K/S values of layers				
		1	2	3	4	5
H-acid	580nm	0.63	2.07	3.17	3.24	3.87
J-acid	520nm	0.60	2.03	3.23	3.76	5.33
S-acid	580nm	1.19	4.16	7.19	9.91	10.93

layer deposition on PET fiber surface using the diazonium resin and three couplers. This is an interesting dyeing concept using electrostatic self-assembly deposition method. The diazonium resin/coupling compound layers were well prepared on the PET substrates. The K/S spectra of the fabricated dye layers showed gradual increase behaviors. However, it should be considered the wash fastness properties of the dye layers for

commercial interests. This consideration will be further examined.

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References

1. T. Radeva, K. Kamburova, Polypeptide multilayer films on colloidal particles: An in situ electro-optical study, *Journal of Colloid and Interface Science*, **308**, 309-317(2007).
2. X. Li, S. Zhao, M. Yang, C. Sun, L. Guo, Covalently attached multilayer assemblies of diazo-resins and binuclear cobalt phthalocyanines, *Thin Solid films*, **478**, 310-317(2005).
3. S. H. Kim, C. H. Ahn, S. Y. Park C. J. Shin, H. J. Suh, Electrostatic layer-by-layer self-assembly of anionic squarylium and cationic polyelectrolyte, *Dyes and Pigments*, **69**, 108-110(2006).
4. C. Wang, S. Ye, L. Dai, X. Liu, Z. Tong, Enzymatic desorption of layer-by-layer assembled multilayer films and effects on the release of encapsulated indomethacin microcrystals, *Carbohydrate Research*, **342**, 2237-2243(2007).
5. T. Katsuhiko, N. Takashi, Preparation of dye thin films on fibers by electrostatic layer-by-layer adsorption, *ISDF proceeding*, 149-150(2006).
6. S. Pricelius, C. Held, S. Sollner, S. Deller, M. Murkovic, R. Ullrich, M. Hofrichter, A. Cavaco-Paulo, P. Macheroux, G. M. Guebitz, Enzymatic reduction and oxidation of fiber-bound azo-dyes, *Enzyme and Microbial Technology*, **40**, 1732-1738(2007).
7. S. Y. Kim, J. Y. An, B. W. Kim, The effects of reductant and carbon source on the microbial decolorization of azo dyes in an anaerobic sludge process, *Dyes and Pigments*, **76**, 256-263(2008).
8. M. S. Lucas, A. A. Dias, A. Sampaio, C. Amaral, J. A. Peres, Degradation of textile reactive Azo dye by a combined chemical-biological process: Fenton's reagent-yeast, *Water Research*, **41**, 1103-1109(2007).
9. Y. A. Son, Y. M. Park, C. J. Shin, S. H. Kim, Self-assembly multi-layer of diazonium resin and its coupling reaction with J-acid and H-acid, *Dyes and Pigments*, **72**, 345-348(2007).
10. Z. Yang, T. Cao, J. Chem, W. Cao, Self-assembly of homopolymer and copolymers of N-4-hydroxyphenyl-acrylamide with diazoresin via H-bonding attraction, *European Polymer Journal*, **38**, 2077-2082(2002).