Coloring fabrication of self-assembly multilayers on the synthetic fabrics with polyelectrolyte and various dyes

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Abstract

Recently developed electrostatic layer-by-layer deposition has been shown to be a simple and versatile method for assembling thin layer films. This technique provides a way to control the construction of ultrathin films at nano-scale ranges and can be easily obtained. However, there have been few studies on applying it to textile processing. In this context, alternate multilayer films of diazonium resin and coupling compound are prepared by self-assembly electrostatic attractions between oppositely charged ions. In addition to multilayer fabrication, the diazo coupling reaction proceeded at the same time to form nano-scale azo dye layer. The build up of the multilayer films has been discussed on the level of color strength (K/S) achieved. The growth of multi-layers formed by the sequential alternative adsorption and coupling reaction of diazonium resin and coupling compound was observed and determined.

Keywords: Layer-by-layer; diazonium resin; coupling reaction; multi-layer

1. Introduction

Ultrathin organic films are of considerable interest due to their potential technological applications in the fields of surface coatings, sensors and optoelectronics. These films are commonly formed using Langmuir-Blodgette (LB) deposition or self-assembly techniques based on chemisorptions [1]. Generally, it is well known that multi-levels of polyelectrolyte layers are prepared using alternate electrostatic layer-by-layer adsorption or electrostatic self-assembly interaction. Self-assembly electrostatic layer-by-layer film deposition has been presented to be a simple method for assembling thin films. Commonly, alternate adsorption of charged polyions is readily achieved to the oppositely charged surfaces. The electrostatic attraction between oppositely charged molecules seems to be a good driving force for multi-layer build-up. The overall thickness of the fabrication films can be simply controlled and monitored using the deposition numbers [2, 3]. This technique has been actively investigated in recent years from Nakamra and Tani [4]. However, there have been few studies on applying it to textile processing. In this context, the preliminary approaches, namely alternate layer-by-layer self-assembly attraction onto fiber substrates might be a useful skill to produce coloration and functional fibers.

Azo dyes, the largest chemical class of dyes with the greatest variety of colors, have been used extensively in the latest years for the textile dyeing and paper printing [5]. Almost without exception, azo chromospheres 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 known as phenol and amine coupling, respectively. Consequently, hydroxyl compounds such as phenols and naphthols coupled in an alkaline condition, whereas amine compounds are coupled in a slightly acidic medium [6].

In this study, the diazonium resin compounds [2,7] using the polycondensation of 4-diazodiphenylamine sulfate with paraformaldehyde were prepared to manufacture multi-layer fabrication films on the textile fabrics. In addition to layer-by-layer adsorption, coupling reaction between diazonium resin and coupling compound was also expected and its resulting multilayer of the azo dye was obtained on the textile fabrics. This layer assembling process of individual diazonium resin and coupling compound was performed on polyester fabrics. Dyed fabrics have been discussed on the level of color strength (K/S).

2. Experimental

2.1 Preparation of the diazonium resin

The diazonium resin compounds using the polycondensation of 4-diazodiphenylamine sulfate with paraformaldehyde were prepared to device multilayer fabrication films on polyester fabrics.

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 ^oC. 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 [2,6]. The preparation of

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diazonium resin was carried out and kept in the dark.

2.2 Coupling reaction with coupling compound

The coupling reaction of diazonium resin and coupling compound was carried out. Prior to coupling reaction between diazonium resin and coupling compound, PDDA-PSS layers were prepared by immersing the fiber substrates in PDDA and PSS solution alternatively with intermediate washing in Milli-Q-water. After that, the coupling reaction between diazonium resin and coupling compound was prepared on the precursor film with the conditions similar to those in the precursor assembly. 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 schematically illustrated in Fig. 1. Self-assemblyed multi layers on the fabrics were deposited sequentially between the diazonium resin and coupling compound solutions until the desired number of multi-layers was achieved.

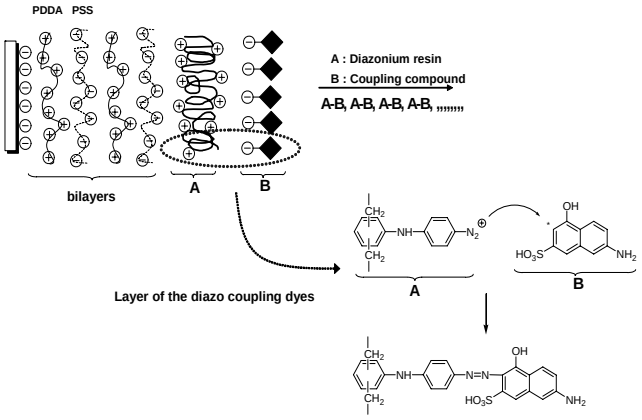

Fig. 1. Scheme of the self-assembled alternating multilayer films

2.3 Color measurement

Reflectance measurements on the dyed fabrics 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^{o} standard observer. The average of three reflectance measurements, taken at different positions on the dyed fabrics, was used. Color strength (K/S) was calculated by the Kubelka-Munk formula:

3. Results and discussion

Fig. 1 shows a schematic illustration of self-assembled and diazo coupled films which are fabricated with alternating layers of the diazonium resin and coupling compound. A substrate with a negative charged surface is immersed into the solution of the positively charged diazonium resin. A self-assembled diazonium resin layer on the fiber surface firstly occurred at this step. In the next step, the substrate was dipped into the solution containing the negatively charged coupling compound.

In this study, the self-assembled multi-dye layer underwent diazo coupling reaction at the same time to form a layer of the azo dyes. The growth of the dye layers formed by the sequential coupling reaction of diazonium resin and coupling compound was examined by using K/S spectra. Fig. 2 shows the K/S spectra of the diazonium resin/J-acid assemblies in a polyester fabric with 1-5 layers, $(PDDA/PSS)_2(Diazonium\ resin/J\text{-}acid)_n$, n = 1~5. In this case, it shows that the K/S spectra increase almost on proportion on the number of attraction cycles, indicating constant growth of diazonium resin and coupling compound layers on the fabrics.

From the results in this figure, it can be proposed that the fabrication of multi-layer was successfully achieved due to the electrostatic attraction forces between positive charges on the diazonium resin and negative charges on the coupling compound and its corresponding phenol type coupling reaction was also conducted. It shows the linear increase in K/S values at 520nm with the number of layers, indicating a progressive deposition with almost equal amount of deposition of the coupling compound in the each cycle. The coupling reaction of diazonium resin and J-acid can produce thin dye layers on the polyester fabrics with electrostatic layer-by-layer attraction.

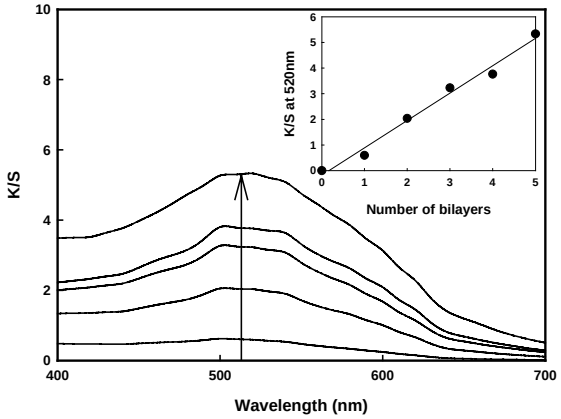

Fig. 2. K/S spectra of the diazonium resin/J-acid alternate assemblies on polyester fabrics.

Conclusions

The present works show the feasibility of the self-assembly layer-by-layer attraction and coupling reaction between the diazonium resin and J-acid coupler onto the textile fabrics. The diazonium resin-coupling compound layers were well prepared on the polyester fabrics. Multi-dye layer thin films consisting of diazonium resin and coupling compound have been successfully fabricated by electrostatic layer-by-layer self assembly attraction. The growth of the dye layers formed by the sequential coupling reaction of diazonium resin and coupler was examined by K/S spectra. The K/S spectra of the fabricated layers showed gradual increase behaviors caused by the electrostatic attraction forces.

Acknowledgements

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