Surface Coloration of Silk Dyed by Aniline Based on Different Process

Zong-qian WANG, Hai-wei YANG, Hu-lin ZHANG and Jing-jing XU
School of Textile and Garment, Anhui Polytechnic University, Wuhu 241000, China
*Corresponding author

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Abstract. In order to improve surface coloration of dyed silk fabric, especially for high color fastness and low damage to silk protein, several new techniques have been developed recently. Aniline was treated as the dye mimetic, and two chemical modification dyeing techniques including the coupling reaction and three-component mannich-type reaction dyeing process of silk fabric were developed in this study. Meanwhile, the surface coloration indexes such as reflectance, K/S value, color fastness and other properties of dyed silk based on the above two dyeing techniques have been studied and compared with the traditional adsorption dyeing process of aniline under weak acid condition. The results showed that good surface coloration of silk including the K/S value and color fastness can be gotten in the two chemical modification dyeing techniques which developed in this experiment compared to traditional adsorption dyeing technique. The improvement of surface coloration and color fastness was confirmed to be caused by covalent bond which will be formed in these chemical modification dyeing between aniline or its diazonium salt and characteristic active groups of silk protein.

Introduction

Silk is one of the most common natural protein fiber with excellent performances [1]. The dyed silk fabrics are widely used in the production of high-end home textiles, clothing and ladies’ ornaments and other upmarket products, which are welcomed deeply by the market [2,3]. Silk was commonly dyed with acid or reactive dyes, wherein a low color fastness especially the wet fastness will be gotten easily in acid dyeing process. Another, a low fixation will be gotten easily in reactive dyeing process, besides that, more dyestuff wastewater will be produced and the silk protein will be damaged easily from the alkaline fixing condition in reactive dyeing process [4,5]. In addition, although color stain can be eliminated effectively in silk yarn heavy-shade dyeing with some selected acid mordant dyes, the acid mordant dyeing was restricted because of its impact on environment [6]. Therefore, new dyeing technique of silk is still the researchers interested in. In recent years, a series of works about dyeing technique of silk and other fibers have been published, and the published new dyeing techniques or processes including eco-friendly dyeing [7], low temperature ultrasonic dyeing [8], plasma treatment prior to dyeing [9], enzymatic natural dyeing [10], dyeing with reactive and crosslinking dyes [11] and so on.

Prior to this study, we have done our research on the chemical modification of silk protein, and a benzotriazole structure has been in-situ synthesized on tyrosine residues of silk protein which can improve the light stability of the modified silk effectively [12]. Meanwhile, coloration of dyed silk fabric based on coupling reaction with a series of diazonium compounds has been researched in our previous work [13]. Characteristic spectra generated by three-component mannich-type reaction for selective tyrosine bioconjugation of silk protein was used as a probe to label protein [14]. So tyrosine residue was confirmed as one site of chemical modification of silk protein as the modification site are still limited.

Aniline was treated as dye mimics in this study, comparative analysis of surface coloration and other properties of dyed silk based on traditional adsorption dyeing and two chemical modification dyeing were carried out, which gets the research on silk and other protein dyeing more abundant. Meanwhile, the research result of the above two chemical modification dyeing techniques can be...
provided experimental and theoretical basis to obtain high color fastness dyeing technique. At the same time, the research results have great significance for the exploitation of new structure dyes, as well as the preparation of functional silk protein based on chemical modification method.

**Experimental**

**Materials**

Degummed silk plain woven fabric (78g/m²) was used. Chemicals used in this experiment were analytical reagent grade.

**Traditional Adsorption Dyeing Process of Aniline as Dye Mimics**

Silk was dyed with aniline under weak acid dyeing bath in laboratory dyeing machine. Different aniline concentrations (0.5%~20% owf) were evaluated. The liquor ratio of solution to fabric was 50:1 and the pH was adjusted to 5.0 using acetic acid. Sodium sulfate (2 g/L) was added to the dye solution to improve the dyeing evenness. Dyeing was started at room temperature and using a 2°C/min gradient, the temperature was raised to 95°C and at this temperature dyeing was performed for 60 min. The temperature was reduced to around 40°C and the samples were removed, rinsed with cold water for 3 min, and finally dried at room temperature.

**Dyeing Process Based on Coupling Reaction with Aniline Diazonium Salt**

The diazonium salt of aniline was prepared at first. Aniline diazonium salt preparation was as follows, aniline (0.1mol) was dissolved in a mixture of hydrochloric acid (0.3mol) and water (30ml). The solution was then cooled to 0°C and a 50% aqueous solution of sodium nitrite (0.102mol) was added to the aniline solution and stirred for 30 min at 0°C. Further stirring for next 5 min resulted in a clear diazonium salt solution of aniline, which was kept under 0°C and dark condition to inhibit decomposition of the diazonium salt. Before dyeing with the anilinediazonium salt, silk should be subjected to an alkali treatment in advance. Alkali treatment was as follows, NaHCO₃ (10g/l) solution and water were added with stirring until a transparent solution was formed, then silk fabric was immersed in this NaHCO₃ solution for 10 min and then padded twice. The pickup of liquid on the fabric was 100%. It needs to mention that the alkali treatment of silk fabric should be operated within 60 minutes in advance of dyeing to inhibit the damage of alkali to silk. Then the aniline diazonium salt solution was adjusted to pH 4.5 with acetic acid/sodium acetate buffer solution. The silk fabric padded with NaHCO₃ was immersed into the diazonium salt solution while shaking sightly to begin the dyeing in various temperatures for 60 min. The aniline diazonium salt concentration was evaluated as 2% owf in this dyeing and the liquor ratio of solution to fabric was also 50:1. Finally, the fabric sample was rinsed with cold water for 3 min and finally dried at room temperature.

**Dyeing Process Based on Three-Component Mannich-Type Reaction with Aniline**

Aniline and formaldehyde with the same molar amount were added into distilled water to made an aqueous reaction solution. The reaction solution was shaken in an incubator shaker all this whole process. Concentrations of the two reagents both were 0.02mol/L in this experiment. Then, a piece of silk fabric (2g) was immersed into the reaction solution and began dyeing. Aniline, formaldehyde and tyrosine residues of silk protein will form a three-component mannich reaction to achieve dyeing of silk fabric. The liquor ratio of solution to fabric was also 30:1. A series of silk fabrics was dyed with different dyeing temperature under different dyeing time. After dyeing the samples were removed, rinsed with cold water for 3 min, and finally dried at room temperature.

**Stripping Process of Dyed SILK fabric**

The dyed silk fabric was stripped by DMF solvent [15] in a laboratory dyeing machine. The triple stripping process was used in this experiment and each stripping was started at 40°C and performed for 30 min. After that, the stripped silk fabric was removed, rinsed with cold water for 3 min, and finally dried at room temperature.
Coloration Measurement
Coloration including reflectance spectra, $K/S_{400nm}$ were measured using a Datacolor 650 spectrophotometer with Colortools software. The optical parameter was set at D65 with a 10° collection angle, specular reflection included, and its spectral range was between 400 to 700 nm. The sampling aperture size was 10*10 mm.

Ultraviolet-Visible (UV-vis) Absorption Spectra
UV-vis spectra was recorded on a UV 2600 spectrophotometer (Tianmei Inc., USA).

Color Fastness Test
The wash fastness of dyed fabric was measured according to ISO 105-C03:1989, and the rub fastness was measured according to ISO 105- X12: 1993.

Breaking Strength Test
The breaking strength of silk samples was tested according to ASTM D5035-1995 (2003) standard. All samples were tested 3 times and the average value was recorded.

Results and Discussion
Coloration of Silk Based on Traditional Adsorption Dyeing Process of Aniline
From Figure 1, reflectance of the dyed silk fabric was not declined obviously compared to original silk fabric. Upon further analysis, the reflectance will be decreased slightly as the dyeing temperature raising under the same dosage of aniline with the same dyeing time conditions. Even though the surface coloration of dyed silk was very weak, still it can be concluded dyeing temperature raising can favor the penetration of aniline into the silk fiber and increase its pickup. At the same time, the surface coloration and color depth $K/S$ value of dyed silk fabric will be enhanced and deepened as the dosage of aniline increasing under the same dyeing temperature and time conditions. However, color of the each dyed silk fabric based on traditional adsorption dyeing process of aniline under weak acid condition was very slight, and the result can be confirmed from Figure 2. Sample 1 was the original silk fabric, sample 2 was the dyed silk fabric with 10% (owf) aniline under 90°C*60 min dyeing conditions, sample 3 was the stripped silk fabric of sample 2. Aniline will be absorbed onto silk fiber with ionic bond and hydrogen bond in the weak acid dyeing condition, and which will be removed by the stripped process of DMF. The color fastness of this dyed silk fabric including wash and rub fastness were at a low level.

![Figure 1. Reflectance curve of dyed silk fabric with aniline based on traditional adsorption dyeing process.](image1)

| Sample | $K/S_{400nm}$ |
|--------|---------------|
| 1      | 0.1097        |
| 2      | 0.2003        |
| 3      | 0.1456        |

![Figure 2. Color photos of dyed silk with aniline based on traditional adsorption dyeing process.](image2)
Coloration of Silk Based on Coupling Dyeing with Aniline Diazonium Salt

Aniline diazonium salt was prepared by the above diazotization process described in the experimental. Meanwhile, UV-vis spectrums were tested before and after diazotization of aniline, and the result was shown in Figure 3. For diazonium salt is sensitive to temperature, aniline diazonium salt will be deteriorated as the temperature raising and its reaction activity will be decreased [16].

From Figure 4, reflectance of the dyed silk fabric based on coupling reaction with aniline diazonium salt was declined obviously compared to original silk fabric. In other words, silk fabric can be gotten good surface coloration even at low dyeing temperature based on this chemical modification dyeing method. Further analyses showed that temperature raising has no obvious effect on reflectance of dyed silk.

In this figure, sample 1 was the original silk fabric, sample 2, 3, 4 was the dyed silk fabric with 2% (owf) aniline diazonium salt under 10°C*60 min, 15°C*60 min and 20°C*60 min dyeing condition respectively.

From this figure, K/S value of silk which dyed based on coupling reaction dyeing with aniline diazonium salt was improved greatly. And the silk fabric’s K/S value was reached the maximum value at the dyeing temperature of 15°C. If continue raising the dyeing temperature to 20°C, K/S value of the dyed silk will be falling instead of rising. The reason of this result was also explored as follows, firstly, more large conjugated system will be formed in the coupling reaction of aniline diazonium salt to amino acid residues especially tyrosine residue of silk protein, at the same time, characteristic absorption spectrum will be generated for this conjugated system, so the dyed silk will be gotten good surface coloration. Secondly, the coupling reaction can be carried out at low temperature, on the contrary, higher coupling temperature will also affect the stability of the diazonium salt, which is of no advantage to this coupling dyeing. The coupling reaction dyeing mechanism of aniline diazonium salt onto silk fabric was also analyzed in this paper. The reflectance of stripped silk fabric by DMF was tested and the result was showed in Figure 6.
By comparing the reflectance of dyed silk fabric before and after DMF stripping from the Figure 6, reflectance of dyed silk fabric was increased after stripping, however, the stripped silk fabric was still with a high K/S value. It is generally known that ionic bond and hydrogen bond which was once formed between the protein and the diazonium salt of aniline will be stripped by DMF and the surface coloration will be disappeared. So it can be concluded that the remained coloration or K/S value of the stripped silk should be resulted from covalent bond formed between aniline diazonium salt and amino acid residues of silk protein. It is the presence of this covalent bond that has caused good surface coloration and deeper K/S value of dyed silk. The coloration contrast of dyed silk fabric samples before and after stripping was showed in Figure 7.

In this figure, sample 1,3 was the dyed silk fabric with 2% (owf) aniline diazonium salt under 10°C*60 min, 15°C*60 min respectively. Meanwhile, sample 2, 4 was the stripped silk fabric from sample 1 and 3 respectively. From Figure 7, dyed silk fabrics still had deep K/S values even the stripping had occurred, in other words, the dyed silk fabric based on coupling reaction with aniline diazonium salt will have a good stripping color fastness.

**Coloration of Silk Based on Three-Component Mannich-Type Reaction Dyeing with Aniline**

Silk was dyed based on three-component mannich-type reaction dyeing with aniline in this paper and its operating conditions have been described in experimental section. The reflectance curves of dyed silk fabrics with difference dyeing conditions were shown in Figure 8 and Figure 9.
As seen in Figure 8, with dyeing time remaining unchanged, the reflectance of dyed silk was declined with increasing of dyeing temperature, therefore, the surface coloration was gradually deepen with increasing of dyeing temperature. Moreover, as seen in Figure 9, under the same dyeing temperature of 80°C, the reflectance of dyed silk was declined with prolonging of dyeing time, therefore, the surface coloration was gradually deepen with prolonging of dyeing time. In conclusion, surface coloration of dyed silk was positively related to dyeing temperature and time. The color photos of dyed silk were shown in Figure 10.

Figure 10. Color photos of dyed silk based on three-component mannich-type reaction dyeing with aniline.

In this figure, sample 1, 2, 3, 4 was the dyed silk fabric based on three-component mannich-type reaction dyeing with aniline under 30°C*5h, 40°C*5h, 60°C*5h and 80°C*5h dyeing condition respectively, with other dyeing conditions remaining unchanged. The conclusion that surface coloration of dyed silk was positively related to dyeing temperature and time has been confirmed from the color photos in Figure 10. The stripping color fastness of dyed silk based on this process was also discussed, and color photos of the dyed silk fabrics before and after stripping were measured and shown in Figure 11.

Figure 11. Color comparison of dyed silk fabric before and after DMF stripping.

In Fig11, sample 1,3 was the dyed silk fabric under 60°C*5h and 80°C*5h respectively. Meanwhile, sample 2, 4 was the stripped silk fabric from sample 1 and 3 respectively. From Figure 11, similarly as silk fabric dyed based on coupling reaction with aniline diazonium salt, dyed silk
fabrics based on three-component mannich-type reaction dyeing with aniline still had deep K/S values even the stripping had occurred, in other words, dyed silk fabric with this process also have a good stripping color fastness. However, color difference of dyed silk such as L, a, b values were existed between the two different kinds of dyeing process.

**Color Fastness and Other Properties of Dyed Silk Based on Difference Process**

Three essential performance indexes including color fastness, strength loss and shrinkage were usually used to evaluate silk fabric’s dyeing process. So, these properties of dyed silk fabric with different process were tested and showed in Table 1 and Table 2.

| Sample | Strength/N | Strength loss /% | Shrinkage percentage /% |
|--------|------------|------------------|-------------------------|
| 1      | 392.50     | --               | --                      |
| 2      | 308.75     | 21.34            | 2.23                    |
| 3      | 359.50     | 8.41             | 1.65                    |
| 4      | 340.05     | 13.36            | 1.80                    |

In this table, sample 1 was the original silk fabric without any treating. Sample 2 was silk fabric dyed with 10% (owf) aniline under 90°C*60 min dyeing conditions based on traditional adsorption dyeing process of aniline. Sample 3 was silk fabric dyed with 2% (owf) aniline diazonium salt under 15°C*60 min conditions based on coupling reaction dyeing with aniline diazonium salt. Sample 4 was silk fabric dyed based on three-component mannich-type reaction dyeing with aniline under 80°C*15h conditions.

The result showed that dyed silk fabric based on coupling reaction dyeing with aniline diazonium salt has the smallest strength loss from Tab 1, followed by dyed silk based on three-component mannich-type reaction dyeing with aniline. The largest strength losses was occurred at the dyed silk fabric with dyeing conditions based on traditional adsorption dyeing process and the loss ratio was highly reached to 21.34%. So, the two chemical modification dyeing processes studied in this paper have a great advantage compared with traditional absorption dyeing in fabrics’ strength protection. Meanwhile, good dimensional stability can be reached of dyed silk fabric with these two chemical modification dyeing processes.

| Sample | Wash | Rub |
|--------|------|-----|
|        | Color change | Color staining | dry | wet |
|        | silk | cotton |     |     |
| 1      | 3    | 2-3   | 3   | 4   |
| 2      | 5    | 4-5   | 4-5 | 4-5 |
| 3      | 5    | 4-5   | 5   | 4-5 |

In this table, sample 1 was silk fabric dyed with 10% (owf) aniline under 90°C*60 min conditions based on traditional adsorption dyeing process of aniline. Sample 2 was silk fabric dyed with 2% (owf) aniline diazonium salt under 15°C*60 min conditions based on coupling reaction dyeing with aniline diazonium salt. Sample 3 was silk fabric dyed based on three-component mannich-type reaction dyeing with aniline under 80°C*15h conditions.

From the table 2, color fastness especially for the wet rubbing and silk staining of dyed silk fabric with traditional adsorption dyeing process of aniline was low, even cannot attain the basic standard of dyed fabric. Instead, each color fastness of dyed silk fabrics with these two chemical modification dyeing processes was improved obviously and each reached higher than or equal to 4-5 grade. So, the two chemical modification dyeing processes studied in this paper have a great advantage compared with traditional adsorption dyeing in color fastness of dyed silk.
**Summary**

As a dye, aniline was used in silk fabric dyeing experiments based on three different processes, one was the traditional adsorption dyeing process, and two chemical modification dyeing processes including coupling reaction dyeing with aniline diazonium salt and three-component mannich-type reaction dyeing with aniline. The results showed that good surface coloration of silk fabric can be obtained only based on chemical modification dyeing process. And chemical modification dyeing processes studied in this paper have great advantage compared with traditional adsorption dyeing in DMF stripping color fastness, strength protection, good dimensional stability, color fastness of dyed silk fabric. The definite mechanism of each chemical modification dyeing was one important focus for future research.

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