Color Analysis on Natural Polyphenolic Dyed Cotton Cellulose Fibers

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Abstract: Natural polyphenolic dye extracted from green tea is used to dye cotton cellulose fibers. FTIR for the microstructure analysis of fibers, and SEM for the surface morphology observation have been used to characterize the changes induced by tea dyeing. Color shade, thermal stability and mechanical property of dyed fibers are tested. The results show that hydroxyl group of tea polyphenolic and cotton cellulose forms hydrogen bond in dyed fibers without mordant agent, while both coordinate bond and hydrogen bond are coexisted in meta-mordant dyed fibers. The deep shade is obtained in acid media of pH 4 for meta-mordant dyed fibers due to the mordant effect. The coordinate bond contributes to the thermal stability of meta-mordant dyed fibers. The formation of fiber-Fe complexation decreases tensile strength and increases elongation at break for fibers.

Keywords: Cotton cellulose fiber, natural polyphenolic dyestuff, green tea, iron ion, thermal stability, tensile property.

1. Introduction

Cotton cellulose fibers are popular materials used for apparel and home furnishing due to their natural and comfortable properties. There are increasingly used in dyeing of cotton fabrics with natural plant dyes on account of environmental compatibility, low toxicity and allergic reaction [1-4]. Green tea extraction is a natural dyestuff containing several polyphenolic catechins [5], and has been extensively used in medical fields [6] and beverages [7]. The green tea extraction is also reported to be a colorant for cellulose dyeing [8,9].

The above-mentioned researches on dyeing with green tea extraction mainly focus on quantitative aspects of dyed samples. Furthermore, most textile products are dyed after the fabrics have been constructed. The piece dyeing is always quite satisfactory for many users. There are, however, some disadvantages associated with piece-dyed fabrics such as incomplete penetration of dyestuff into fabric, single in fabric color and complicated dyeing control on fabrics made of different fiber types. One of the solutions is to dye fibers and then spin fibers with different colors into yarns.

One of the primary considerations in dyeing fibers with natural dyestuff before spinning is to ensure thermal stability of color and mechanical stability of dyed fibers. This study is to explore the dyeing of cotton cellulose fibers with green tea extraction as the natural dyestuff. The iron ion is selected as a mordant agent due to the least toxicity among the other commonly used mordant agents [10]. The changes in chemical structure and surface morphology induced by tea dyeing are investigated with FTIR and SEM. The thermal durability and tensile properties of dyed fibers are tested to study the color stability and fiber mechanical strength.

2. Experimental

2.1. Materials

Commercial green tea powder was from Hangzhou, China. The combed 100% cotton fibers were provided by Huafu Holding Pte. Ltd., China. $FeSO_4 \cdot 7H_2O$ was used as a mordant agent in this study. Acetate acid and sodium hydroxide were of the analytical reagents.

2.2. Dyeing cotton fibers with green tea

2.2.1 Extraction of green tea

Green tea powder of 2 g was added to distilled water of 100 mL. The mixture was boiled at 100 ºC for 60 min, allowed to be statically cooled at room temperature and then filtered. The filtrate was used as green tea extraction for dyeing.

2.2.2 Dyeing without a mordant agent

Cotton fibers were immersed into green tea extraction at a liquor ratio of 1:50, and dyed with a shaking dyeing machine (L24B-1, Taiwan) at 100 ºC for 60 min. The dyeing bath was cooled down to room temperature.

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After which, the dyed cotton fibers were removed from the dyeing bath and rinsed thoroughly with tap water, followed by squeezing and air drying under shade.

2.2.3 Meta-mordant dyeing of cotton fibers

In the case of meta-mordant dyeing, cotton fibers were immersed into a dyeing bath containing mordant agent and green tea extraction. The liquor ratio was set as 1:50. The other procedure was the same as described in Section 2.2.2.

2.3 Color measurement

Color values were evaluated by *K/S*, ΔE, ΔL, Δa and Δb tested with Spectraflash SF600 spectrophotometer (illuminated D65/10º observer). Each value was averaged from three samples.

2.4 Thermal stability

The meta-mordant dyed cotton fibers were dipped into boiled water for a certain time and rinsed thoroughly with tap water. After squeezing and air drying, the color values of fibers were tested to evaluate color thermal stability.

2.5 Characterization

Scanning electron microscope (SEM, JSM-5600LV) was used to study morphology of the cotton fiber samples before and after dyeing. The samples were sputter-coated with gold prior to examination. Secondary electron images were acquired using an accelerating voltage of 10 kV. Fourier transform infrared spectra were collected using a TENSOR37 FTIR Spectrometer (Bruker Company). The samples were analyzed in 800 ~ 4000 cm^{-1} range with a 4 cm^{-1} resolution.

2.6 Tensile property of cotton fibers

A model YG001A fiber tensile tester (Taicang, Jiangsu, China) was used to test tensile property of cotton fibers. The pretension was 10 cN. The gauge length was 1 cm and the loading speed was 10 mm/min. The test was carried out at room temperature with relative humidity of (65±5) %. Each value was averaged from 50 tests.

3. Results and discussion

3.1 FTIR analysis

The interaction between cotton cellulose fibers and dyestuff plays important role on stability of dyed fibers. The molecular structure change induced by tea dyeing could be identified by FTIR due to the vibration mode modification of the molecules involved [11].

Figure 1 shows the FTIR spectra of cotton fibers before and after dyeing. The band near 3368 cm^{-1} in the raw cotton fibers is the characteristic hydroxyl group peaks of cellulose. After dyeing, the peak intensity increases and shifts towards high wavenumber, indicating the change of hydrogen bond. This could be attributed to the damage of intramolecular hydrogen bond and formation of intermolecular hydrogen bond between oxygen of tea polyphenolic compounds and hydroxyl group of cellulose fiber [12]. New peaks representing the aromatic ring vibrations of tea polyphenolic are found around 1600~1450 cm^{-1}, especially in the spectrum of dyed fibers without mordant agent. For the meta-mordant dyed fibers, there appeared some peaks around 2400~2000 cm^{-1} which are attributed to the transition-metal carbonyls [13]. This indicates that both coordinate bond and hydrogen bond exists in the meta-mordant dyed fibers. The formation of coordinate bond between cellulose and iron ion is expected to improve color fastness.

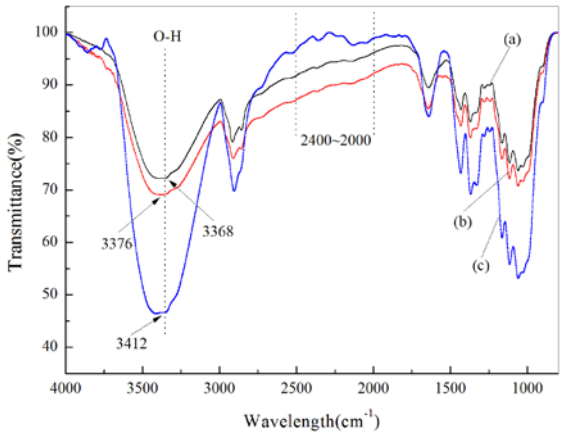
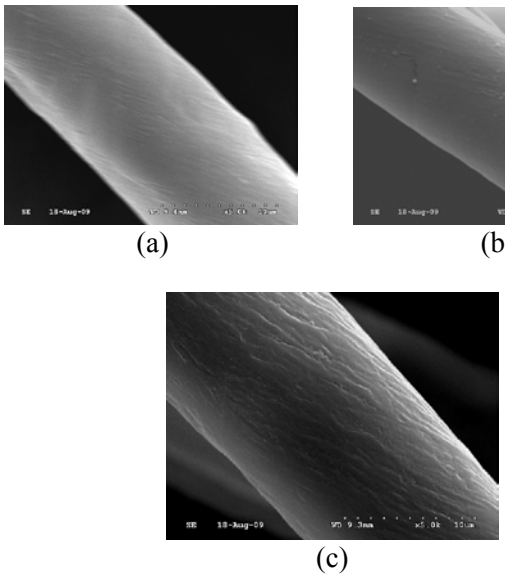


Figure 1 FTIR of cotton fibers. (a) Before dyeing. (b) Dyeing without mordant agent. (c) Meta-mordant dyeing.

3.2 Morphology analysis by SEM

The surface morphology of raw cotton fibers and dyed fibers is observed by SEM as shown in Figure 2. It is concluded from Figure 2 that the SEM micrograph of

raw cotton fibers is different from that of the dyed fibers. The surface of raw cotton fiber is smooth with characteristic groove structure of cotton fibers [Figure 2(a)]. A little microripple, however, is clearly seen in Figure 2(b), indicating that very fine particles of tea organic compounds are coated on the fiber surface [13]. The surface of meta-mordant dyed fibers [Figure 2(c)] is the roughest among the three samples. This could be due to the deposition of Fe (II) complexation, leading to significant changes in the surface of cotton fibers.



(a) (b) (c)

Figure 2 SEM morphology of cotton fibers. (a) Raw cotton fiber. (b) Directly dyed cotton fiber. (c) Meta-mordant dyed cotton fiber.

3.3 Color analysis of cotton fibers

3.3.1 Effect of dyestuff concentration on dyeing characteristic of cotton fibers

Table 1 shows the effect of dyestuff concentration on dyeing characteristics of cotton fibers. Undiluted 100% green tea extraction was diluted to 50%, 33% and 25% with distilled water. To carry out the experiments, pH of dye bath was adjusted to 4 with acetate acid, and the mordant agent concentration was kept 2% o.w.f.

It is seen from Table 1 that *K/S* of all dyed samples decreases with the dilution of green tea extraction. Dark and dull shades are obtained for cotton fibers dyed with aqueous green tea solution ($\Delta L<0$). Some differences, however, could be found for fibers dyed with and without mordant agent. In comparison with the meta-mordant dyed fibers, the *K/S* of dyed fibers without mordant agent is significantly decreased. This could be due to the low affinity of cellulose fibers to green tea colorants [9]. The meta-mordant dyed cotton fibers show a reddish blue color ($\Delta a>0$, $\Delta b<0$), while the dyed fibers without mordant agent show reddish yellow color ($\Delta a>0$, $\Delta b>0$). Furthermore, the color of meta-mordant dyed fibers becomes dark. This is attributed to the formation of insoluble complexation of Fe (II) as analyzed by FTIR and SEM.

Table 1 Effect of dyestuff concentration on dyeing characteristics of cotton fibers

Dye conc. (%)	Mordant agent conc. (% o.w.f)	*K/S*	ΔL	Δa	Δb
100	0	1.74	-9.712	5.866	9.754
	2	16.33	-36.09	1.18	-9.09
50	0	1.14	-7.150	4.491	6.414
	2	15.37	-39.68	1.46	-5.89
33	0	0.79	-5.393	3.147	4.465
	2	14.31	-36.81	1.27	-5.92
25	0	0.69	-5.004	2.852	3.505
	2	14.34	-37.25	1.28	-5.50

3.3.2 Effect of pH on dyeing characteristic of cotton fibers

The *K/S* of dyed fibers as a function of pH is shown in Figure 3. The pH of dye bath was adjusted with acetate and sodium hydroxide. The undiluted 100 % green tea extraction and the mordant agent concentration of 2% o.w.f. were kept in the experiments.

For the meta-mordant dyed fibers, high color depth is observed at strong acidic conditions, and then decreased with increase of pH from neutral to alkaline. The maximum *K/S* is found at pH 4. It is reported that the adsorption capacity of tea solution to metal ion rapidly increases at pH>4 [14]. Therefore, the insoluble complexation formed between tea and metal ion is easy to be deposited in dye bath, which reduces the dye adsorption on cotton fibers. On the other hand, the oxidation of tea polyphenolic at neutral and alkaline pH generates much more negative ions in the surface of tea solution [15], while the cellulose is easy to be anionised at alkaline condition. The ionic repulsion between dye and anionised cotton fibers decreases the adsorption of tea polyphenolic.

It may also be noticed that the influence of pH on dyeing characteristics of the two dyed fiber samples is different. The *K/S* of dyed fibers without mordant agent shows a gradual increase from pH 3 to 8, although the change is not significant. This is due to the occurrence of some change in color shade due to the oxidation of

tea polyphenolic. The change, however, shows little effect on color shade of meta-mordant dyed fibers. The results also suggest that the pH-independent stability has to be taken into consideration due to the following post-finishing and washing treatments when commercial color-spun yarn with tea extraction is produced.

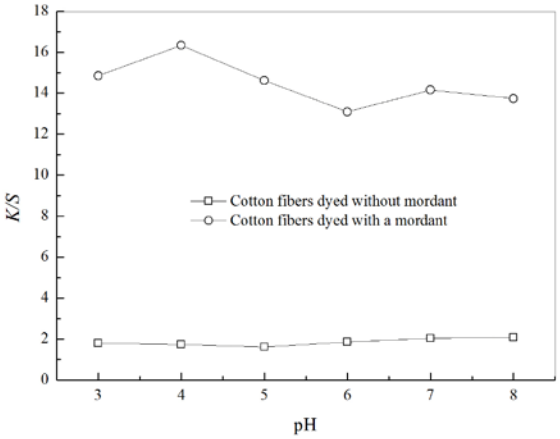


Figure 3 Effect of pH on *K/S* of dyed fibers.

3.3.3 Effect of mordant agent concentration on dyeing characteristic of cotton fibers

The effect of mordant agent concentration on dyeing characteristics of fibers was studied as illustrated in Figure 4. The dye bath was undiluted 100 % green tea extraction adjusted to pH 4 with acetate acid.

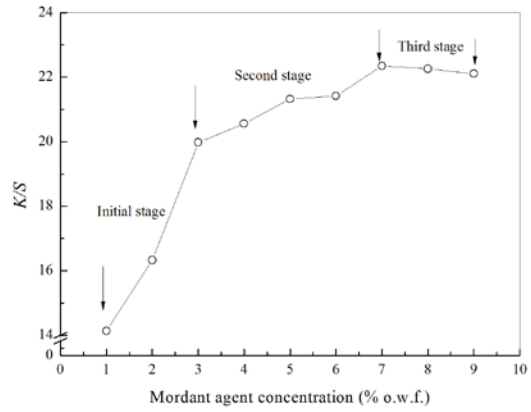


Figure 4 Effect of mordant agent concentration on *K/S* of dyed fibers.

It is seen from Figure 4 that the color depth increases with the mordant agent concentration. This could be as a result of the darkening and dulling of shades due to the mordant effect. The difference, however, become small when the mordant agent concentration is above 7% o.w.f. The increase of mordant agent concentration is beneficial to the complex formation of Fe (II) with dye molecules and fibers during the initial stage. As seen in Figure 4, the *K/S* value increases sharply and reaches 19.98 at the concentration of 3 % o.w.f. A further increase in mordant agent concentration shows slight increase in *K/S* (see the second stage in Figure 4) and gradually levels off at the third stage.

3.4 Thermal stability of meta-mordant dyed cotton fibers

It is different from dyeing fabrics that the color-spun yarns used as warp should also be slashed to ensure the minimum end breakage during weaving. The sizing temperature of cotton yarns is generally at or above 90 ºC [16]. Thermal stability of color, therefore, is one of the most important properties that should be considered for dyed fibers. A simple method to evaluate thermal stability as described in Section 2.4 is applied, and the *K/S* of meta-mordant dyed fibers after a number of boiling cycles is illustrated in Figure 5.

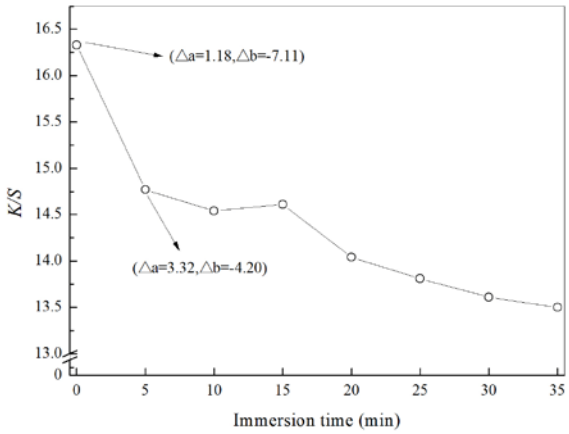


Figure 5 Thermal stability of meta-mordant dyed fibers.

A fast decrease of *K/S* is observed at the first 5 min of boiling. Furthermore, the Δ*a* value increases from 1.18 to 3.32 and Δ*b* value decreases from -7.11 to -4.20. These results show that part of complexation formed between Fe (II) and tea has been stripped from fiber surface due to the simple deposition on fiber surface. After boiling for 5 min, the decrease of *K/S* slows down. The tea-dyed cotton cellulose fibers with Fe^{2+} as a mordant agent acquire a relatively stable thermal stability.

3.5 Tensile properties of cotton fibers

In case of dyeing fibers before spinning, the mechanical performance of fibers should be considered

to ensure a normal drawing, roving and spinning process. Since the shade and thermal stability of meta-mordant dyed fibers is better than that of dyed ones without mordant agent, it is reasonable to assume that the research on tensile properties of meta-mordant dyed fibers is necessary. The effect of dyeing parameters on tensile properties is illustrated in Figure 6.

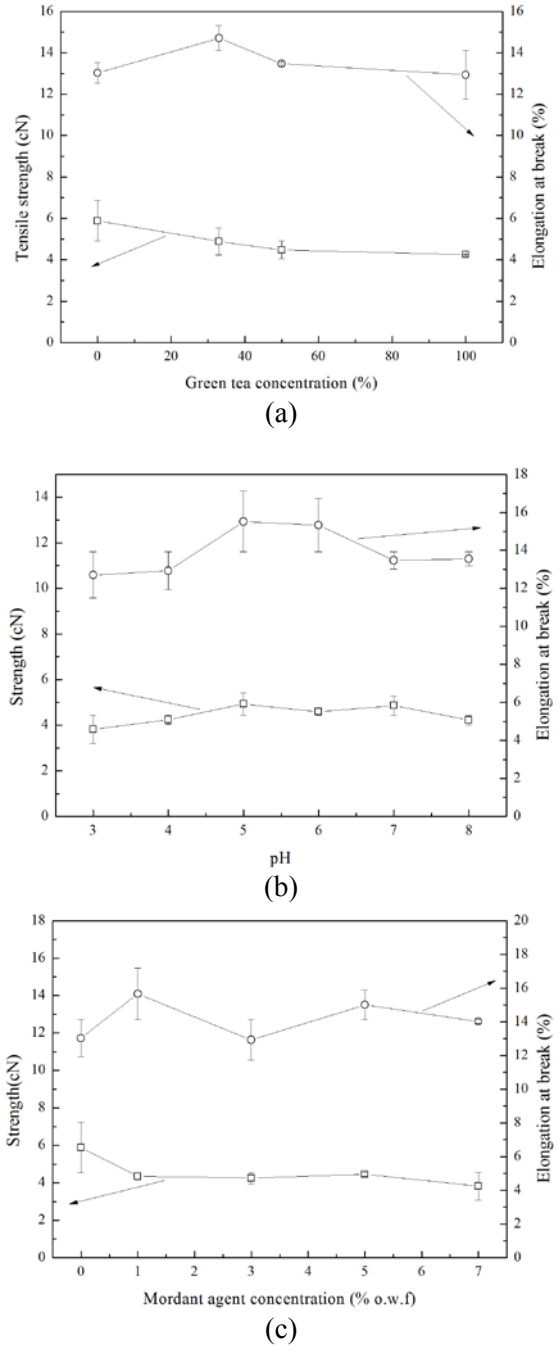


Figure 6 Effect of dyeing parameters on tensile strength and elongation at break of meta-mordant dyed cotton fibers. (a) Dyestuff concentration. (b) pH. (c) Mordant agent concentration.

It can be seen from Figure 6 that the strength of dyed fibers slightly decreases especially in acidic environment. This could be attributed to the increase in the packing density after formation of fiber-Fe complexation [17]. On the other hand, the elongation at break of the dyed fibers increases due to the bridged effect of iron ions [18].

4. Conclusion

The interaction of cotton cellulose fibers with green tea molecules and Fe (II) were studied with FTIR and SEM. The dyeing of green tea on cotton fibers is mainly as a result of hydrogen bond interaction. For the fibers dyed with Fe (II) as a mordant agent, there exists a coordinate bond formed between Fe (II) and hydroxyl group of tea polyphenolic molecules and cotton cellulose fibers except hydrogen bond. The coordinate bond contributes to the thermal stability of color and increase of deep shade. Furthermore, the strength decreases and elongation at break increases for dyed fibers due to the mordant effect.

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