Dyeing for Silk Fabrics by Utilising Chemical Oxidation of (+)-Catechin

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Abstract

The silk dyeing utilising chemical oxidation of (+)-catechin was attempted in order to establish the deep dyeing at low temperature in a short time for inventing novel human- and eco-friendly dyeing. In the study, the dyeability of the new oxidation technique was compared with the mordanting method. The compounds giving Al3+, Cu2+, Fe2+, or Fe3+ ion in aqueous solution were used as mordants for the mordanting dyeing. The oxidation by the use of O2, H2O2 or NaIO4 was tried for the oxidation dyeing. The two-step treatment was performed as the oxidation dyeing, in which the first treatment is adsorption of (+)-catechin onto the silk fabric and the second one is oxidation of the adsorbed (+)-catechin by the oxidant. The results show that O2 and H2O2 are not available as oxidants for the oxidation dyeing. The silk fibre is dyed brown colours by the mordanting dyeing and deep reddish brown by the oxidation dyeing with NaIO4 at 30 °C and pH = 7.0 for 80 min of total treatment time. The dyeability of the oxidation dyeing with NaIO4 is much higher than that of mordanting dyeing. Colour fastness obtained by the oxidation dyeing to washing is high enough in practical use.

Key Words: (+)-Catechin, Oxidation dyeing, Mordanting dyeing, Periodate, Bio-catechols

1. Introduction

In the dyeing industry of fibre products, some of the chemicals used in treating solution are not safe, and a large amount of waste water is discharged. Additionally, massive energy and water are consumed in the dyeing process, and factory operatives must work under too hot and humid conditions. Thus, it is important and desired that a novel dyeing using safer, sustainably-obtainable and naturally-degradable materials is invented and deep dyeing at low temperature (~ room temperature) in a short time (within a few hours) is achieved. Recently, the use of natural dyes and biobased materials in dyeing and finishing has been attracting attention.

The mordanting dyeing with metal salts is the traditional technique in order to stabilise and deepen the dyed colour. The dyeing method is commonly employed for improving colour fastness to light and washing, in the case of dyeing with biobased materials. Mordants are agents applied to fibre before, during or after the colouration step. Metal compounds are mostly used as mordants, when biobased materials such as polyphenols having a plurality of phenolic OH groups are used in dyeing [1]. A complex formation between the catechol OH groups of (+)-catechin and a metal cation is exampled in Fig. 1(a).

Laccases that are copper-containing oxidases catalysing the oxidation of catechols to form corresponding o-benzoquinones, were used with catechins for dyeing cellulose fibre [2] or keratin

![Fig. 1 Pigmentation schemes of (+)-catechin through metal complex formation (a) and oxidation by O2 (b) at the catechol part.](image-url)

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hair [3]. Unoxidised catechins are colourless and they are coloured in reddish brown after oxidised. However, the dying with laccases requires long time as 2~24 h.

The research group of the authors has studied human hair colouring using (+)-catechin and the tyrosinase which is an enzyme oxidising naturalcatechol substances with higher efficiency than laccase [4]. The hair dyeing was accomplished with the enzymatic treatment of them and hair for 40 min at 30 °C. It was also found that hair is dyed by the chemical oxidation of bio-catechols, which are biobased materials having catechol as in e.g. (+)-catechin [5]. The white hair is dyed deep brown by the two-step treatment. The first one is the adsorption of bio-catechols onto hair and the second one is oxidation of the adsorbed bio-catechols by supplying O2 gas.

The applicability of the dyeing technique to dye silk fabrics was investigated in the research in order to establish the eco-dyeing and deep dyeing at low temperature in a short time. However, the technique requires a large amount of O2 gas to advance the oxidation. Then, the chemical oxidation techniques of (+)-catechin and the silk dyeing were studied by using H2O2 and NaIO4. The dyeability obtained by using them was compared with that obtained by using O2 or the metal mordanting dyeing [6, 7].

The five pieces of silk fabrics (4 cm × 4 cm) were immersed in 100 ml of 10 mM (+)-catechin aqueous solution (pH = 5.2) at 30 °C for 40 min, and then dipped into the metal salt solution at 30 °C for 40 min. The concentrations of metal ions were 10 mM for Al3+, Cu2+ or Fe2+ solution and 2.5 mM for Fe3+ solution (pH = 3.5, 4.7, 5.4 and 4.1, respectively). The textile samples were taken out from the solution immediately after the treatment, washed with 100 ml of the 0.3 wt% soap aqueous solution for 20 min and rinsed twice with 200 ml of distilled water at 30 °C for 15 min. The samples were air-dried under the circumstances of room temperature and humidity.

2.3 Oxidation dyeing method

The five pieces of silk fabrics (4 cm × 4 cm) were immersed in 100 ml of 10 mM (+)-catechin aqueous solution at 30 °C for 40 min, and then treated with each the oxidant solution. First one was 100 ml of 0.1 M Na2CO3 solution (pH = 11.3), into which O2 gas was previously introduced enough at 100 ml min⁻¹ of the rate for over 20 min. The O2 gas was introduced continuously during the treatment. Second one was the H2O2 solution, as mixed with 20 ml of 30 % H2O2 solution and 80 ml of 0.1 M Na2CO3 solution (final pH was 9.0). Third one was 10 mM NaIO4 solution prepared from 0.1 M phosphate buffer solution (NaH2PO4 / Na2HPO4, pH = 7.0). The washing and drying procedures after dyeing were the same as the mordanting method.

2.4 Colour fastness test to washing

The colour fastness test to washing was performed as the dyed textile samples were washed with 100 ml of 0.3 wt% Marseille soap solution at 30 °C for 20 min, were rinsed twice with 200 ml of distilled water at 30 °C for 15 min and were air-dried. The processes were repeated 5 times. The colour of washed silk was measured after every washing. The colour measurements were made as described at §2.5 (the following).

2.5 Colour measurements

The colour and spectrophotometric measurements of the samples have been made by a Konica Minolta CM-2600d spectrophotometer employing 10°-view angle, CIE standard illuminant D65 and SCI (spectral component included) mode. All the reflected lights from a sample including the regular reflection are integrated under the SCI mode. The resulting colour was expressed in L*a*b* standard colourimetric system (CIE 1976). The L* is the lightness index, and a* and b* are the chromaticity coordinates. The positive values of a* indicate red colours and its negative values indicate green ones, and the positive values of b* indicate yellow and the negative values indicate blue. The C* is the chroma calculated by \( C^* = \sqrt{(a^*)^2 + (b^*)^2} \). The colour difference \( \Delta E^* \) is obtained by \( \Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \), where \( \Delta L^* \), \( \Delta a^* \) and \( \Delta b^* \) are \( L^* \), \( a^* \) and \( b^* \) of each sample, respectively. The value of \( K/S \) is defined from Kubelka-Munk theory [8, 9] and calculated as \[ K/S = \frac{(1 - R_l)^2}{2R_s} \], where
$K$ is the absorption coefficient, $S$ the scattering coefficient and $R$, the reflectance of the light at a wavelength $\lambda$. The measurements of silk were conducted at three parts of each the sample (measured area: 3 mm$^2$). The arithmetic mean values were calculated from the measured values.

3. Results and Discussions

The (+)-catechin solution is pale yellow, and it does not dye silk fabrics singly. The colour of the (+)-catechin solution turns instantly into deep yellow, deep green, deep blue black or deep reddish brown by adding Al$^{3+}$, Cu$^{2+}$, Fe$^{2+}$, or Fe$^{3+}$ ion, respectively. This is caused by the complex formation from (+)-catechin and the metal cations. In the mordanting dyeing, the colours of the (+)-catechin-adsorbed silk textile and metal salt solutions are immediately changed by dipping the textile into the solution. The colur values obtained by the combination of (+)-catechin and Al$^{3+}$, Cu$^{2+}$, Fe$^{2+}$, or Fe$^{3+}$ ion are pale orange, pale brown, grey, or pale brown, respectively, as shown by the photographs in Table 1. The silk dyed with Fe$^{3+}$ gives relatively deeper colour, however, its $K/S$ values at the whole of wavelength are low (< 5 at every $\lambda$).

On the other hand, it was found that (+)-catechin solution turns red gradually. The colour development is due to the progress of oxidation by O$_2$, as shown in Fig.1(b). The reaction proceeds via two deprotonations and two times of one-electron oxidations at the catechol part [10, 11]. Furthermore, the products react with (+)-catechin and other intermediates to form coloured multimers such as dimers and trimers [12, 13]. It was also observed that (+)-catechin reacts with H$_2$O$_2$ to be a pigment. The resulting pigment loses its colour within 10 min of reaction time. This means that H$_2$O$_2$ reacts with the pigments from (+)-catechin to break its chemical structure and decolourise it. H$_2$O$_2$ has higher oxidation potential (standard electrode potential, $E^\circ = 1.776$ V [14]) comparing with that of O$_2$ ($E^\circ = 1.229$ V [14]).

NaIO$_4$ ($E^\circ = 1.653$ V [14]) is known to be oxidant exhibiting selectivity for catechols and works under weak-acidic and neutral conditions [15]. (+)-Catechin is oxidised with NaIO$_4$ at pH = 7 to form the corresponding o-quinones [16]. The results obtained show that (+)-catechin solution turns to deep red colour within a few seconds by mixing with NaIO$_4$ at pH = 7. The obtained solution contains insoluble materials. The decolourisation was not observed in the system.

The resulting colour values of treated silk fabrics are summarised in Table 1. The results exhibit that silk is hardly dyed by O$_2$ or H$_2$O$_2$ system, and is dyed by Al$^{3+}$, Cu$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, or NaIO$_4$ light brown, brown, deep brown, brown, or deep reddish brown as shown by the photographs in the table. The (+)-catechin-NaIO$_4$ system gives the deepest colour and the colour difference of the fabric between before and after dyeing is highest ($\Delta E^* = +67.4$, $\Delta L^* = + 42.7$, $\Delta a^* = +24.7$, $\Delta b^* = +46.0$). The $K/S$ spectrum for the silk dyed by NaIO$_4$ system exhibits intense signal at 370 nm and the $K/S$ value is over 20. The sums of $K/S$ values from 360 nm to 740 nm ($K/S_{tot}$), which correlate with the dyeability, were calculated and shown in Table 1. The order of $K/S_{tot}$ for the obtained samples is H$_2$O$_2$ < O$_2$ < Al$^{3+}$ < Cu$^{2+}$ < Fe$^{2+}$ < Fe$^{3+}$ << NaIO$_4$ dyeing system. The results show that the silk fibre is dyed with (+)-catechin by the mordanting dyeing methods and the oxidation dyeing method with NaIO$_4$.

All the dyeing techniques reported here are two-step ones and the first adsorption process of (+)-catechin is same for all the methods. The dye formation behaviours for the Fe$^{3+}$, O$_2$, and NaIO$_4$ systems at the second step were observed and compared with each other. While the silk adsorbed with (+)-catechin little changes in colour after the introduction of O$_2$, it turns to strongly-coloured instantly after exposed to Fe$^{3+}$ or NaIO$_4$ solution. The subsequent observation revealed that the Fe$^{3+}$ solution becomes darker with time and the colourants on the fabric desorb. In contrast, the NaIO$_4$ solution

| Photograph | Undyed silk fabric | Mordanting dyeing method | Dyed silk fabrics | Oxidation dyeing method |
|-------------|---------------------|--------------------------|------------------|-------------------------|
|             | Al$^{3+}$ | Cu$^{2+}$ | Fe$^{2+}$ | Fe$^{3+}$ | O$_2$ | H$_2$O$_2$ | NaIO$_4$ |
| $L^*$        | 94.7      | 89.4       | 81.0       | 56.3       | 79.0   | 91.7      | 94.0      | 52.0       |
| $a^*$        | 0.280     | 2.09       | 1.48       | -1.24      | 0.286  | 1.94     | 0.224     | 25.0       |
| $b^*$        | 0.140     | 11.8       | 12.0       | 3.51       | 8.74   | 5.59     | 2.19      | 46.1       |
| $C^*$        | 0.310     | 12.0       | 12.1       | 3.72       | 8.75   | 5.92     | 2.20      | 52.4       |
| $\Delta E^*$ | 1.07     | 3.91       | 9.10       | 53.7       | 11.2   | 2.12     | 1.51      | 230        |
| $K/S_{tot}^{a)}$ | 1.07     | 3.91       | 9.10       | 53.7       | 11.2   | 2.12     | 1.51      | 230        |

$^{a)}$ The value was calculated by $K/S_{total} = \sum_{\lambda=360nm}^{740nm} [K/S]_{\lambda}$, where $\Delta \lambda = 10$ nm.
keeps almost clear after immersing the fabric and the colouration occurs only at the fibres.

It is considered that the differences in the dyeability of the mordanting dyeing methods may be caused by the differences in the diffusion and adsorption behaviours of the metal ions, the resulting amount of formed colourants and their colours. On the other hand, the differences in the dyeability of the oxidation dyeing methods should be due to the differences in the oxidation ability of the oxidants.

In the oxidation process of NaIO₄ system, the oligomerisation of (+)-catechin may proceed at the fibre, then the desorption is thought to be suppressed. When silk was treated in (+)-catechin and NaIO₄ mixed solution, the fabric is little dyed as K/Sₜₒₜ = 18.0. The result indicates that the two-step processing is indispensable for the oxidation dyeing technique.

The colour fastness test to washing was performed for the silk samples dyed by the NaIO₄ colouration system. The obtained results show that the colour of the dyed silk is almost maintained visually and the colour difference value (ΔE*) between before and after five-time washings is ca. 8.84. The results imply the enough extent of fixation of the formed dyes.

The o-quinones react with primary amines in amino acids and proteins to form covalent bond between their o-quinone and amino groups [17]. The covalent bonding may result in the strong fixation of the oxidised (+)-catechin to silk. The moderate oxidation by the NaIO₄ may contribute to the colour fastness in addition to the higher dyeability.

4. Conclusions

The study revealed that the silk fabric is dyed with (+)-catechin by the mordanting dyeing and novel oxidation dyeing techniques. Silk is hardly dyed by O₂ or H₂O₂ system, whereas it is dyed by Al³⁺ (light brown), Cu²⁺ (brown), Fe²⁺ (deep brown), Fe³⁺ (brown) or NaIO₄ (deep reddish brown). The dyeability of the oxidation dyeing with NaIO₄ is much higher than that of mordanting dyeing. Silk fabrics can be dyed with neutral dye solution (pH=7.0) at low temperature (30 °C) by the combination of (+)-catechin and NaIO₄. Colour fastness obtained by the system to washing is enough extent in practical use.

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