Hair Colouring by Using Catechins from Green Tea and Chemical Oxidants

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Abstract

The hair dyeing using green tea extracts containing high amount of catechins in combination with chemical oxidants such as O2, H2O2 and NaIO4 was attempted in order to establish a novel hair dyeing technique without using aromatic amines contained in commercial oxidation dye products. The new hair dyeing technique consists of a two-step colouration system. The first step is treatment of hair with tea extract solution and the second one is oxidation treatment. Three kinds of oxidation methods such as (1) treating hair with basic dyeing solution (pH = 11.5) supplied with large amount of O2 gas (O2 method), (2) treating hair with H2O2 solution (pH = 9.5) (H2O2 method), (3) treating hair with NaIO4 solution (pH = 7) (NaIO4 method) were attempted as the second oxidation treatment. The results show that once dyed hair is discoloured by H2O2 in the oxidation process and white hair is hardly coloured by the method. In contrast, white hair is dyed brown by the O2 or NaIO4 method, and the dyeability increases with increasing temperature of the first tea extract treatment. This may be due to the increase in the amount of dye precursors adsorbed onto hair by heating. Colour fastness of the hair samples dyed by the O2 and NaIO4 method to washing is almost same level as that by the commercial oxidation dyes. The NaIO4 method is more useful than the O2 method because the supply of O2 gas is unnecessary for the NaIO4 one and it uses the neutral solution.

Key Words: Hair colouring, Green tea extract, Catechins, Oxidation, Colour fastness

1. Introduction

Today, many people apply colourants to change the colour of their hair for expressing their personality and fashion trends or covering white hair to maintain a youthful appearance. For example, over 60 % of Japanese women [1], 75 % of American women [2], and more than 60 % of European women [2] are estimated to dye their hair. Hair colouration has usually been done by the use of oxidation dyes. However, the components such as aromatic amines, i.e. p-phenylenediamine, cause very occasionally contact dermatitis to hairdressers and people who dyes hair themselves [3, 4].

Under such the situation, a novel alternative to the hair dyeing with oxidation dyes is desired and authors have been studying hair colouring by using biobased materials. Then, it was found that the oxidation products of (+)-catechin (Fig. 1(a)), which is contained in tea or several plants, can dye white hair yellow, orange and reddish brown [5, 6]. The obtaining colour can be controlled by the dyeing conditions such as temp., pH, additives, and the durability to washing and light is high enough. The oxidation proceeds at catechol part (o-dihydroxybenzene structure) of (+)-catechin by enzymatical and chemical reactions. The dyeability of hair is improved by designing the oxidising and dyeing process [7]. The chemical oxidising method is composed of the first treatment of hair with (+)-catechin solution and then the second treatment with basic solution into which high amount of O2 gas is introduced. The chemical technique dyes hair deep brown, which is the colour preferred by many Japanese women.

The problems toward the practical use of the chemical technique for hair dyeing are the supplying method of O2 gas from an external reservoir to the hair dyeing system and the basic condition (pH > 11), which is harmful to human skin and hair. In the study, hydrogen peroxide (H2O2) and sodium periodate (NaIO4) as the alternative...
2. Experimental

2.1 Materials

The human hair samples used for experiments were 2 types as follows: (1) chemically decolourised white hair (Damaged hair, length: ca. 10 cm, Mathai Japan), (2) original white hair with no chemical treatment (Healthy hair, length: ca. 10 cm, Beaulax). The chemical-bleached hair is damaged to become easier to be dyed. The hair is covered with cuticle cells which prevent penetration of materials [8]. The decolourisation causes the destruction of three dimensional network structure between the cuticle cells in hair. The 0.8 g of human hair samples were bundled by a nylon band and kept under a low humidity before use. The powder of tea extract Sunphenon 905 (SP905) kindly provided from Taiyo Kagaku was used as the dyestuff precursor without further purification. The SP905 is the extract of green tea leaf (Camellia sinensis) and contains catechins of high concentration as shown in Table 1 [9].

The chemical structures of the catechins were shown in Fig. 1. The chemical-bleached hair is damaged to become easier to be dyed. The hair is covered with cuticle cells which prevent penetration of materials [8]. The decolourisation causes the destruction of three dimensional network structure between the cuticle cells in hair. The 0.8 g of human hair samples were bundled by a nylon band and kept under a low humidity before use. The powder of tea extract Sunphenon 905 (SP905) kindly provided from Taiyo Kagaku was used as the dyestuff precursor without further purification. The SP905 is the extract of green tea leaf (Camellia sinensis) and contains catechins of high concentration as shown in Table 1 [9]. The chemical structures of the catechins were shown in Fig. 1. Sodium carbonate (Na₂CO₃, Fₚ = 105.99, Wako), monoethanol amine (MEA, Mₚ = 61.08, Wako), disodium hydrogen phosphate (Na₂HPO₄, Fₚ = 119.98, Wako) and sodium dihydrogen phosphate (NaH₂PO₄, Fₚ = 141.96, Wako) as pH regulators were used without further purification. Oxygen gas (over 99.5 vol%) was supplied to O₂ gas in the chemical method were examined in order to solve the problems and dye hair. A green tea extract containing high amount of catechins was used as the dyestuff precursor. The relationships between the dyeing condition and the dyeability were investigated. The colour fastness of the obtained hair to washing was also estimated.

| Catechins                  | Catechin mass content [wt%] |
|----------------------------|------------------------------|
| (+)-Catechin               | 1.4                          |
| (-)-Epicatechin            | 4.5                          |
| (-)-Gallocatechin          | 2.3                          |
| (-)-Epigallocatechin       | 3.8                          |
| (-)-Catechin gallate      | 0.8                          |
| (-)-Epicatechin gallate   | 11.9                         |
| (-)-Gallocatechin gallate | 7.5                          |
| (-)-Epigallocatechin gallate | 46.8                       |
| Total catechins           | 79.0                         |

Table 1 Composition of catechins in green tea extract Sunphenon 905 powder (Lot No. 20731I) [9].

| Catechin                        | R¹ | R² | C₂, C₃ |
|---------------------------------|----|----|--------|
| (+)-Catechin                    | H  | OH | 2R, 3S |
| (-)-Epicatechin                 | H  | OH | 2R, 3R |
| (-)-Gallocatechin               | OH | OH | 2R, 3R |
| (-)-Epigallocatechin            | OH | G  | 2S, 3R |
| (-)-Catechin gallate            | H  | G  | 2S, 3R |
| (-)-Epicatechin gallate         | H  | G  | 2R, 3R |
| (-)-Gallocatechin gallate       | OH | G  | 2S, 3R |
| (-)-Epigallocatechin gallate    | OH | G  | 2R, 3R |

Fig. 1 Chemical structures of catechins. Each of the chemical structure is indicated in the list below the figures.

of tubes. One contains p-aminophenol, toluene-2,5-diamine, resorcinol, 5-amino-o-cresol as dye precursors or a coupler and monoethanol amine as a base and the other contains hydrogen peroxide as oxidant. Kao Blauné Hair Manicure D13 (colour name: tea brown) was used as a commercial acid dye, which contains C.I. Acid Orange 7, C.I. Acid Black 1, C.I. Acid Red 52 and C.I. Acid Red 33. Hoyu colouring treatment (colour name: natural brown) was used as commercial basic dye, which contains HC Yellow No. 4, HC Blue No. 2, C.I. Basic Blue 75 and C.I. Basic Brown 16. All of the aqueous solutions were prepared with distilled water.

2.2 Hair dyeing

Each of the bundled white hair (0.8 g) was immersed into 100 mL of 0.3 wt% SP905 aqueous solution (pH = 4) at 30, 50 or 70 °C for 40 min, and then treated with the each oxidant solution at 30 °C for 40 min. First one was 100 mL of 0.1 M Na₂CO₃ aqueous solution at pH = 11.5, into which O₂ gas was previously introduced enough at the rate of 100 mL min⁻¹ for over 20 min. The O₂ gas was introduced continuously during the treatment. Second one was the H₂O₂ solution, as mixed 20 mL of 30 % (8.8 M) H₂O₂ solution with 80 mL of 1 M MEA solution (pH after mixing was 9.5). Third one was 10 mM of NaIO₄ solution prepared from 100 mL of 0.1 M phosphate buffer solution (NaH₂PO₄ / Na₂HPO₄, pH = 7). In the dyeing by the commercial oxidation dye, the creams from two tubes were mixed and then the mixture was applied to the hair by using a comb. The hair was kept at room temperature for 20 min. In the dyeing by the commercial acid dye (hair manicure) and the basic dye (colour treatment), the creams containing dyestuffs were applied to the hair by using a comb and the hair was allowed to stand at room temperature for 40 min. The dyed samples were washed with 100 mL of the 0.3 wt% SPE-1200K aqueous solution for 20 min after the each treatment 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 Colour fastness test to washing

The colour fastness test to washing was performed as follows: the healthy hair samples dyed by each method were washed with 100 mL of 0.3 wt% SPE-1200K solution at 30 °C for 20 min, rinsed twice with 200 mL of distilled water at 30 °C for 15 min and air-dried. The processes were repeated 31 times. The colour of washed hair was measured after every drying. The colour measurements were made as described at the next section.

2.4 Measurements

The colour and spectrophotometry of hair samples were measured by a Konica Minolta CM-2600d spectrophotometer employing 10°-view angle, CIE standard illuminant D65 and SCI (specular 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 its negative values indicate blue. The colour difference \( \Delta L^*, \Delta a^*, \Delta b^* \) are obtained by \( \Delta L^* = (L^*_2 - L^*_1), \Delta a^* = a^*_2 - a^*_1, \Delta b^* = b^*_2 - b^*_1 \), and \( L^*_1, a^*_1, b^*_1 \) are each \( L^*, a^*, b^* \) value, respectively. The \( K/S \) value is defined from Kubelka-Munk theory [10, 11] and calculated as \( K/S = (1 - R_i)^2/2R_i \), where \( K \) is the absorption coefficient, \( S \) the scattering coefficient and \( R_i \) the reflectance of the light at a wavelength \( \lambda \). The measurements of hair colour were conducted at three parts of the each sample (measured area: 3 mm²). The arithmetic mean values were calculated from the obtained values. The \( K/S_{tot} \), which is obtained by \( K/S_{tot} = \sum_{\lambda=350nm}^{700nm} (K/S)_{\lambda} \), was used for comparing extent of the colour depth of each hair.

3. Results and Discussions

The tea extract SP90S solution contains high amount of catechin as shown in Table 1 and its colour is wine red at the beginning. The colour gradually turns deeper under basic condition with the supply of \( O_2 \) gas and results in deep reddish brown after one hour. These are due to the oxidation of catechins at the catechol part (o-dihydroxybenzene part) or pyrogallol part (1,2,3-trihydroxybenzene part) to form corresponding o-benzoquinones [12] and the subsequent reactions such as dimerisation [13] and the formation of red theaflavins [14].

The colour of the damaged white hair turns slightly grey by treating in the SP90S solution at 30 °C. The hair changes in the colour into deep brown gradually during the 40 min of oxidation treatment with \( O_2 \) at pH = 11.5 and at 30 °C. The \( K/S \) spectra for the hair undyed, hair treated only with SP90S and hair treated with SP90S and oxidised with \( O_2 \) are shown in Fig. 2. While the \( K/S \) spectra of the hair undyed and hair treated only with SP90S show lower values, the spectrum of the hair treated with SP90S and oxidised has high values in the region from short to middle wavelength. The \( K/S_{tot} \) value, which is summation of \( K/S \) and means the colour depth, is 41.9 for undyed, 88.2 for hair treated only with SP90S, or 375 for hair treated with SP90S and oxidised with \( O_2 \), respectively. The results are comparable to those of the hair dyeing by (+)-catechin [7]. It can be said that this technique combining the green tea extract and \( O_2 \) oxidation is applicable to dye hair. However, the method requires continuous \( O_2 \) gas supply for a long time throughout the dyeing. This is not practically useful for low-cost hair dyeing.

Next, the method using \( H_2O_2 \) was examined because \( H_2O_2 \) is used in the commercial oxidation hair dye products and this is economic. The \( H_2O_2 \) has potential risk when it is applied to human body. However, it was used in the experiments of the study in order to clarify its oxidation effect on dyeing hair with the green tea extract. By the oxidation of \( H_2O_2 \) at pH = 9.5, the damaged hair previously treated with SP90S changes in colour into pale brown and the colour turns deeper with reaction time up to 7 min. The \( K/S_{tot} \) value is 117 at 7 min. The discolouration of hair, on the contrary, proceeds with reaction time up to 7 min. The \( \Delta L^*, \Delta a^*, \Delta b^* \) show lower values, the spectrum of the hair treated with SP90S and oxidised shows high values in the region from short to middle wavelength. The \( K/S_{tot} \) value, which is summation of \( K/S \) and means the colour depth, is 41.9 for undyed, 88.2 for hair treated only with SP90S, or 375 for hair treated with SP90S and oxidised with \( O_2 \), respectively. The results are comparable to those of the hair dyeing by (+)-catechin [7]. It can be said that this technique combining the green tea extract and \( O_2 \) oxidation is applicable to dye hair. However, the method requires continuous \( O_2 \) gas supply for a long time throughout the dyeing. This is not practically useful for low-cost hair dyeing.

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Then, the dyeing using \( NaO_2 \) was tried at pH = 7. The damaged hair previously treated with SP90S turns deep brown by the
The oxidation products contain larger molecules such as oligomers from catechins, which are harder to be adsorbed onto hair than catechins. Catechins in the hair are little desorbed in the NaIO₄ solution at pH = 7 and the oxidation proceeds in the hair to generate the oligomers. Because of these, the durability to washing for the hair dyed by the NaIO₄ method is probably higher than that with the O₂ method as shown later.

For practical use, the higher dyeability of the healthy hair (non-damaged hair) is necessary and the dyeing by the O₂ method or the NaIO₄ method was applied to the healthy hair (pretreatment temperature was 30 °C). The healthy hair is dyed poorly by both the methods. The K/Sₜot values obtained are 63.5 for the O₂ method and 72.6 for the NaIO₄ method. Thereupon, the temperature of the SP90S treatment was increased to improve the dyeability. Fig. 3 shows the relationships between the temperature during the SP90S treatment and the K/Sₜot value of the healthy hair dyed by the O₂ or NaIO₄ method (the temperature of oxidation was 30 °C). As increasing the temperature over 30 °C, the dyeability increases and the colours of the dyed hair are yellowish brown at 50 °C and deep brown at 70 °C. It can be thought that the amount of catechins adsorbed on hair matrixes increases by the increase in temperature and the resulting dyestuff amount in hair also increases. The higher temperature increases the diffusion rate of catechins from hair surface to inside.

The colour fastness test to washing with an anion surfactant was performed for the hair samples dyed by the O₂ method (SP90S treatment: 50 °C, oxidation: 30 °C), the NaIO₄ method (SP90S treatment: 50 °C, oxidation: 30 °C), the commercial oxidation dye (dyeing: room temperature), acid dye (dyeing: room temperature) and basic dye (dyeing: room temperature) and Table 2 exhibit the results. The healthy white hair samples were used for the test. The colours of hair before washing are yellowish brown for the O₂ method and the NaIO₄ method, brown for the oxidation dye system, slightly reddish brown for the acid dye system and pale reddish brown for the basic dye system. The number of washing in the test was 31 that corresponds to hair washing in a month (31 days). The obtained results show that the colour of the hairs dyed by the O₂

Table 2 The results of colour fastness test to washing for the dyed hairs. A single washing process contains a cleaning with an anion surfactant and twice rinsing with water. The hair for the test is the healthy white hair.

| Dyeing method            | ∆E*   | K/Sₜot ₜot | Before washing | After washing of 31 times | Reducing rate |
|--------------------------|-------|------------|----------------|---------------------------|---------------|
| O₂ method                | 8.98  | 163        | 138            | 15.5 %                    |
| NaIO₄ method             | 4.51  | 133        | 128            | 3.83 %                    |
| Commercial oxidation dye | 2.68  | 210        | 182            | 13.5 %                    |
| Commercial acid dye      | 14.3  | 437        | 271            | 38.0 %                    |
| Commercial basic dye     | 24.5  | 125        | 38.2           | 69.4 %                    |

a) The colour difference ∆E* is obtained by ∆E* = [(ΔL*)² + (Δa*)² + (Δb*)²]¹/², where ΔL*, Δa*, Δb* are

\[\Delta L^* = L^*_2 - L^*_1, \Delta a^* = a^*_2 - a^*_1, \Delta b^* = b^*_2 - b^*_1.\]

The subscript 1 and 2 mean for hair before washing and after washing of 31 times.

b) Summation of (K/S) of the dyed hair, which means colour strength of the hair surface, is calculated by

\[K/S_{tot} = \sum_{\lambda=500 \text{ nm}}^{700 \text{ nm}} (K/S)_{\lambda}.\]
method and the NaIO₄ method are mostly same and almost kept visually, and their colour difference ($\Delta E^*$) between before and after 31 times washing is 8.98 and 4.51, respectively. The $K/\%_{\text{tot}}$ values of hair dyed by the O₂ method and the NaIO₄ method decreases by 15.5% and 3.83% from before washing. The fastness for the hair colour obtained by the O₂ method is lower. The pigments formed in the oxidation process of O₂ at pH = 11.5 may be easier to be removed from hair. In contrast, in the NaIO₄ method, the oxidation proceeds in the hair to generate larger molecules, and the pigment may be harder to be desorbed from hair. The difference of fastness between the methods using tea extract would be resulting from the difference in the species of adsorbed materials, their adsorption amount, and their place of adsorption sites in hair matrix.

The $\Delta E^*$ values after 31 times of washing are 2.68 for oxidation dye, 14.3 for acid dye and 24.5 for basic dye. The decrease of $K/\%_{\text{tot}}$ values of hair dyed by the oxidation dye, the acid dye and the basic dye are 13.5 %, 38.0 % and 69.4 % by washing of 31 times. The order of the colour durability to washing for the dyeing systems is as follows: oxidation dye > NaIO₄ method > O₂ method > acid dye > basic dye, which is estimated from the $\Delta E^*$ values. The fastness for the NaIO₄ method is enough high for practical use because the $\Delta E^*$ is almost close to that of commercial oxidation dye.

4. Conclusions

In this study, novel white hair dyeing was tried by using green tea extract containing catechins and oxidants as O₂, H₂O₂ or NaIO₄. White hair is dyed by the O₂ or NaIO₄ system and the dyeability increases with an increase in temperature of the pre-treatment with the tea extract. The O₂ gas supply is unnecessary for the NaIO₄ method and the method uses mild neutral solution. Colour fastness of the hair obtained by the NaIO₄ system to washing is enough high in practical use. The safety study of NaIO₄ to human bodies is indispensable for commercial viability.

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