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

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oxidants 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.

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 90S (SP90S) kindly provided from Taiyo Kagaku was used as the dyestuff precursor without further purification. The SP90S 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, *F_w* = 105.99, Wako), monoethanol amine (MEA, *M_w* = 61.08, Wako), disodium hydrogen phosphate (NaH₂PO₄, *F_w* = 119.98, Wako) and sodium dihydrogen phosphate (NaHPO₄, *F_w* = 141.96, Wako) as pH regulators were used without further purification. Oxygen gas (over 99.5 vol%) was supplied into a reactor from a gas cylinder. Hydrogen peroxide aqueous solution (30 % H₂O₂, *M_w* = 34.01, Wako) and sodium periodate (NaIO₄, *F_w* = 213.89, Wako) were used as oxidants without further purification. SINOLIN SPE-1200K (New Japan Chemical) that contains 25.4 wt% of sodium dodecylpolyoxyethylene sulphate (C₁₂H₂₅O(CH₂CH₂O)_{*n*}SO₃Na, the average of *n* is 2) was used as an anionic detergent for washing hair. Kao Blauné shining hair colour cream 3MD (colour name: medium brown) was used as a commercial oxidation dye, which is composed of two kinds

Catechins	R ¹	R ²	C2, C3
(a) (+)-Catechin	H	OH	2 <i>R</i> , 3 <i>S</i>
(b) (–)-Epicatechin	H	OH	2 <i>R</i> , 3 <i>R</i>
(c) (–)-Gallocatechin	OH	OH	2 <i>S</i> , 3 <i>R</i>
(d) (–)-Epigallocatechin	OH	OH	2 <i>R</i> , 3 <i>R</i>
(e) (–)-Catechin gallate	H	G	2 <i>S</i> , 3 <i>R</i>
(f) (–)-Epicatechin gallate	H	G	2 <i>R</i> , 3 <i>R</i>
(g) (–)-Gallocatechin gallate	OH	G	2 <i>S</i> , 3 <i>R</i>
(h) (–)-Epigallocatechin gallate	OH	G	2 <i>R</i> , 3 <i>R</i>

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% SP90S 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

Table 1 Composition of catechins in green tea extract Sunphenon 90S powder (Lot No. 207311)[9].

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

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 spectrophotance 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 ΔE^* is obtained by $\Delta E^* = \{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\}^{1/2}$, where ΔL^* , Δa^* , Δb^* are $\Delta L^* = L^*_2 - L^*_1$, $\Delta a^* = a^*_2 - a^*_1$, $\Delta b^* = b^*_2 - b^*_1$ and L^*_n , a^*_n , b^*_n are each L^* , a^* , b^* value, respectively. The K/S value is defined from Kubelka-Munk theory [10, 11] and calculated as $(K/S)_\lambda = (1 - R_\lambda)^2 / 2R_\lambda$, where K is the absorption coefficient, S the scattering coefficient and R_λ the reflectance of the light at a wavelength λ . The measurements of hair colour were conducted at three parts of the each sample (measured area: 3 mm ϕ). The arithmetic mean values were calculated from the obtained values. The K/S_{tot} , which is obtained by $K/S_{tot} = \sum_{\lambda=360\text{ nm}}^{740\text{ nm}} (K/S)_\lambda$, 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 O₂ 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

Fig. 2 K/S spectra for undyed hair (broken line), hair treated with SP90S (dotted line), hair dyed with SP90S and O₂ (thin solid line) and hair dyed with SP90S and NaIO₄ (thick solid line). The used hair was the damaged hair, which is easier to dye. Both of the temperatures at the SP90S treatment and the oxidation treatment with O₂ or NaIO₄ were 30 °C.

colour into deep brown gradually during the 40 min of oxidation treatment with O₂ 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 O₂ 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 O₂, 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 O₂ oxidation is applicable to dye hair. However, the method requires continuous O₂ gas supply for a long time throughout the dyeing. This is not practically useful for low-cost hair dyeing.

Next, the method using H₂O₂ was examined because H₂O₂ is used in the commercial oxidation hair dye products and this is economic. The H₂O₂ 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 H₂O₂ 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 after 7 min of oxidation time. The maximum colour depth reached in the oxidation system is insufficient for hair dyeing. The results show that H₂O₂ is not applicable as an oxidant to the dyeing system using the green tea extract.

Then, the dyeing using NaIO₄ was tried at pH = 7. The damaged hair previously treated with SP90S turns deep brown by the

Fig. 3 Relationships between the temperature during the SP90S treatment and K/S_{tot} for the hair dyed by O_2 method (open circle) and NaIO_4 method (filled circle). The used hair was healthy hair, which is harder to dye. The temperature of the oxidation treatment with O_2 or NaIO_4 was 30 °C.

oxidation with NaIO_4 . Its K/S spectrum exhibits high values as similar to that of the O_2 system as shown in Fig. 2. The K/S_{tot} for the hair dyed by the NaIO_4 method is 350. The obtained colour, which is expressed in $L^*a^*b^*$ standard colourimetric system, is L^* : 32.2, a^* : 10.8, b^* : 20.4 and is high enough for practical use. Therefore, the results show that the damaged hair is dyed by the pretreatment with the green tea extract and the following oxidation with NaIO_4 . The oxidation activity of H_2O_2 is high and it attacks the formed dyestuffs and unreacted catechins on the hair in the dyeing process. On the other hand, NaIO_4 oxidises catechols selectively to give *o*-benzoquinones [15]. The obtained colour of the hair is not decolourised in the oxidation process using NaIO_4 . Also, catechins dissolve easily in basic aqueous solution. In the oxidation process of O_2 method (pH = 11.5), some of catechins in the hair pretreated with SP90S are desorbed to be oxidised in the oxidation solution.

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 NaIO_4 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 NaIO_4 method is probably higher than that with the O_2 method as shown later.

For practical use, the higher dyeability of the healthy hair (non-damaged hair) is necessary and the dyeing by the O_2 method or the NaIO_4 method was applied to the healthy hair (pretreatment temperature was 30 °C). The healthy hair is dyed poorly by both the methods. The K/S_{tot} values obtained are 63.5 for the O_2 method and 72.6 for the NaIO_4 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/S_{tot} value of the healthy hair dyed by the O_2 or NaIO_4 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 O_2 method (SP90S treatment: 50 °C, oxidation: 30 °C), the NaIO_4 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 O_2 method and the NaIO_4 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 O_2

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	ΔE^* a)	K/S_{tot} b)		
		Before washing	After washing of 31 times	Reducing rate
O_2 method	8.98	163	138	15.5 %
NaIO_4 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 ΔE^* is obtained by $\Delta E^* = \{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\}^{1/2}$, 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 $(K/S)_\lambda$ of the dyed hair, which means colour strength of the hair surface, is calculated by

$$K/S_{\text{tot}} = \sum_{\lambda=360 \text{ nm}}^{740 \text{ nm}} (K/S)_\lambda$$

method and the NaIO_4 method are mostly same and almost kept visually, and their colour difference (ΔE^*) between before and after 31 times washing is 8.98 and 4.51, respectively. The K/S_{tot} values of hair dyed by the O_2 method and the NaIO_4 method decreases by 15.5 % and 3.83 % from before washing. The fastness for the hair colour obtained by the O_2 method is lower. The pigments formed in the oxidation process of O_2 at pH = 11.5 may be easier to be removed from hair. In contrast, in the NaIO_4 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 ΔE^* 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/S_{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 > NaIO_4 method > O_2 method > acid dye > basic dye, which is estimated from the ΔE^* values. The fastness for the NaIO_4 method is enough high for practical use because the ΔE^* 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 O_2 , H_2O_2 or NaIO_4 . White hair is dyed by the O_2 or NaIO_4 system and the dyeability increases with an increase in temperature of the pre-treatment with the tea extract. The O_2 gas supply is unnecessary for the NaIO_4 method and the method uses mild neutral solution. Colour fastness of the hair obtained by the NaIO_4 system to washing is enough high in practical use. The safety study of NaIO_4 to human bodies is indispensable for commercial viability.

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References

[1] National Beauty & Barber Manufacturers' Association Japan,

chôsa iinkai (2017) "Salon user chôsa 2016 nen (zyôsei chôsa)", Chapter 7, Hair colouring (in Japanese)

- [2] Bechtold T (2009) "Handbook of Natural Colorants" (Bechtold T, Mussak R ed), Chapter 19, pp339-350, John Willey Sons, New York
- [3] Søsted H, Agner T, Andersen KE, Menné T (2002) Contact Dermatitis, **47**, 299-303. doi: 10.1034/j.1600-0536.2002.470508.x
- [4] Uter W, Lessmann H, Geier J, Schnuch A (2003) Contact Dermatitis, **49**, 236-240. doi: 10.1111/j.0105-1873.2003.0233.x
- [5] Yasunaga H, Takahashi A, Ito K, Ueda M, Urakawa H (2012) Journal of Cosmetics, Dermatological Sciences and Applications, **2**, 158-163. doi: 10.4236/jcdsa.2012.23031
- [6] Matsubara T, Taniguchi S, Morimoto S, Yano A, Hara A, Wataoka I, Urakawa H, Yasunaga H (2015) Journal of Cosmetics, Dermatological Sciences and Applications, **5**, 94-106. doi: 10.4236/jcdsa.2015.52012
- [7] Matsubara T, Seki C, Wataoka I, Urakawa H, Yasunaga H (2015) Asian Textile Conference (ATC-13) Conference Proceedings, 3C, 1061-1064, Geelong, Australia, 3-6 Nov
- [8] Robbins CR (2012) "Chemical and Physical Behavior of Human Hair", 5th edition, Springer-Verlag Berlin Heidelberg
- [9] The Data Provided from Taiyo Kagaku Co Ltd
- [10] Kubelka P, Munk F (1931) Zeitschrift für Technische Physik, **12**, 593-601
- [11] Kubelka P (1948) Journal of the Optical Society of America, **38**, 448-457. doi: 10.1364/JOSA.38.000448
- [12] Matsubara T, Wataoka I, Urakawa H, Yasunaga H (2013) International Journal of Cosmetic Science, **35**, 362-367. doi: 10.1111/ics.12051
- [13] Guyot S, Vercauteren J, Cheynier V (1996) Phytochemistry, **42**, 1279-1288. doi: 10.1016/0031-9422(96)00127-6
- [14] Tanaka T, Mine C, Inoue K, Matsuda M, Kouno I (2002) Journal of Agricultural and Food Chemistry, **50**, 2142-2148. doi: 10.1021/jf011301a
- [15] Weidman SW, Kaiser ET (1966) Journal of the American Chemical Society, **88**, 5820-5827. doi: 10.1021/ja00976a024

文献（日本語表記）

- [1] 全国理美容製造者協会 調査委員会(2017) "サロンユーザー調査 2016年〔女性調査〕", 7, ヘアカラーについて