Transactions of the Materials Research Society of Japan 33[4] 865-868 (2008)

Effects of Permanent Waving and Bleaching Treatments on Damage of Human Hair

Yuuki Tomita, Minori Ishikawa and Shoji Takigami
Center for Material Research by Instrumental Analysis, Gunma University, 5-1, Tenjincho 1-chome, Kiryu, Gunma 376-8515, Japan
Fax: 81-0277-30-1141, e-mail: takigami@chem-bio.gunma-u.ac.jp

Permanent waving (P), bleaching (B), and bleaching and permanent waving (B&P) treatments have been done up to 3 times on virgin Japanese human hair. The properties of treated hairs were investigated by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and amino acid analysis. The cuticle layers were hardly changed by 3 times of P and B treatments. However, the damage of cuticle was observed for 3 times treated B&P hair. FT-IR spectrum of the original hair showed characteristic features of keratin fiber, i.e., amide I (~1640cm^{-1}), amide II (~1530cm^{-1}), and amide III (~1230cm^{-1}). New weak absorptions corresponding to cysteic acid appeared at ~1040 cm^{-1} and ~1180cm^{-1} on IR spectra of P and B treated hair. For B&P treated hair, the peaks of cysteic acid increased remarkably with increase of treatment times. Amino acid composition for each treated hair hardly changed except for cystine. The amount of the cysteic acid in the various treated hairs increased in order of P ≤ B << B&P treatments. It was found that the damage of hair is encouraged synergistically by repetition of B & P treatment.
Key words: permanent waving, bleaching, damaged hair, FT-IR, amino acid analysis

1. INTRODUCTION

Human hair has a hierarchical structure consisting of cuticle, cortex and medulla. Cuticle is formed by 6~10 layers of sheet-like cell with about 0.5 μm in thickness and it covers cortex [1]. Cortex is aggregate of cortex cells surrounded by cell membrane complex (CMC) and the amount is 85-90% of the whole hair components. Cortex contains two types of protein with different cystine content, low sulfur (LS) and high sulfur (HS) proteins. The LS protein is called intermediate filament (IF) protein which shows helical structure. The HS protein is amorphous globular protein [2]. The IF protein is embedded in intermediate filament associated protein (IFAP) by disulfide (S-S) linkages. The S-S groups form the cross-linkage in keratin fibers and contribute structural and chemical properties of keratin.

Recently, hair dyeing and permanent waving are very popular as the fashion, especially younger person. Decomposition of melanin by a bleaching agent is necessary before hair dyeing. The bleaching and permanent waving treatments cause damage of hair. We reported that human hair was damaged remarkably by repetition of bleaching and permanent waving (B&P) treatments and a part of S-S bonds of cystine residues changed to cysteic acid by the treatment [3].

In this study, permanent waving (P), bleaching (B), and B&P treatments were performed on virgin human hair and effect of the treatments on damage of hair was elucidated using SEM, FT-IR, and amino acid analysis. The mechanism of formation of damaged hair was also investigated.

2. EXPERIMENTAL

2.1 Materials

Virgin hair of 4 years old Japanese girl was used as a starting material. The hair was immersed in 0.5% aqueous Laureth-9 solution (50ml) containing saturated EDTA for 1h at 35 °C. They were rinsed thoroughly with distilled water before air-drying. Thioglycolic acid (TGA) and other chemicals used were special reagent grade.

2.2 Hair treatments

Bleaching (B), permanent waving (P), and bleaching and permanent waving (B&P) treatments were carried out on the purified virgin hair. The B treatment was performed in 3% hydrogen peroxide solution at pH10.3 for 30min at 35°C, and the bleached hair was rinsed by distilled water. The P treatment was carried out using 6% TGA aqueous solution at 35°C for 15min at pH8.5 adjusted by aqueous ammonia. Then the sample was oxidized by 8% sodium bromate aqueous solution at pH7.2 for 15min at 35°C and was rinsed with distilled water. In the B&P treatment, bleaching and permanent waving were performed alternately. Each treatment was repeated for 3times and the treated sample was immersed in Britton-Robinson buffer solution at pH4.6 for 15min and finally rinsed thoroughly with distilled water before air-drying.

2.3 SEM measurement

The hair samples were evaporated with gold. Surface of the treated hairs were observed using a Hitachi S-3000N scanning electron microscope (SEM) at an accelerating voltage of 10kV.

2.4 FT-IR measurement

The Fourier transform infrared (FT-IR) measurements of the treated hairs were carried out using a Magna 560 FT-IR spectrometer equipped with a CONTINU M infrared microscope (Nicolet). The FT-IR spectra of the samples were analyzed by the attenuated total reflection (ATR) method. A ZnSe polarizer was used as a high refractive index material.

2.5 Amino acid analysis

Weighed hair sample (~50mg) was placed in a test tube and 6 M HCl (1ml) was added. After the freeze-thaw was repeated for 3~4 times, the tube was sealed. The sample was hydrolyzed at 110 °C for 24h and then excess HCl was evaporated under reduced pressure. The hydrolyzate was vacuum-dried over sodium hydroxide for overnight. It was dissolved in known amount of sodium citrate buffer solution (pH2.2), and was filtered through a 0.45 m syringe filter. The amino acid composition of the filtrate was analyzed by the Post-column fluorimetric detection using a Prominence amino acid analysis system equipped with a Shim-pack Amino-Na column (Shimadzu).

3. RESULTS

Permanent waving (P), bleaching (B), and bleaching and permanent waving (B&P) treatments have been done up to 3 times on virgin hair. Figure 1 shows the scanning electron micrographs of the P, B, and B&P treated hairs. The surfaces of P treated and B treated hairs were covered with sturdy cuticles and the cuticle layers were hardly damaged by the treatments regardless of treatment times.

On the other hand, the surface of B&P treated hair was gradually damaged by the treatment and peeling of the cuticle was observed for 3 times treated hair (see Fig.1-i). To investigate chemical structure change by the treatments, FT-IR spectra of the P, B, and B&P treated hairs were measured using the FT-IR microscope and are shown in Figures 2, 3, and 4, respectively. All of the treated hairs showed characteristic features of keratin fiber [4~6], i.e., amide I (~1640 cm^{-1}), amide II (~1530 cm^{-1}), amide III (~1230 cm^{-1}), CH scissoring vibration (~1450 cm^{-1}) and CH wagging vibration (~1390 cm^{-1}). Very weak overlapped peaks were observed at ~1040 cm^{-1} and ~1180 cm^{-1} on the spectrum of the original hair. The absorptions correspond to symmetric stretching vibration of S=O group due to cysteic acid [4~6]. The peaks due to cysteic acid became clearly when the P, B, and B&P treatments were performed repeatedly, especially B&P treated hairs (see Fig. 4).

Since absorbencies due to the other functional groups hardly changed, the ratio of amide I peak to that for cysteic acid at ~1040 cm^{-1} was calculated. Figure 5 shows the relationships between the ratio and the treatment times. For the P treated hairs, the ratio increased with increase of the treatment times. The increment of the ratio for the B treated hairs was higher than that for the P treated hairs. On the other hand, for the B&P treated hairs, the peaks increased remarkably when the treatment exceeded 2 times. It was found that formation of cysteic acid is encouraged by the B&P treatment.

To investigate details of the chemical structure, amino acid compositions of various treated hairs were measured by the amino acid analyzer. The amino acid composition is determined as a molar content that is calculated from total mole of amino acid based on detectable 17 types of amino acid. Table 1 shows the amino acid compositions of the various treated hairs together with the original hair. Regardless of treatment methods and times, the amino acid compositions hardly change except for cystine. The cystine content decreases with increase of the treatment times for the P, B, and P&B treated hairs, especially for the B&P treatment.

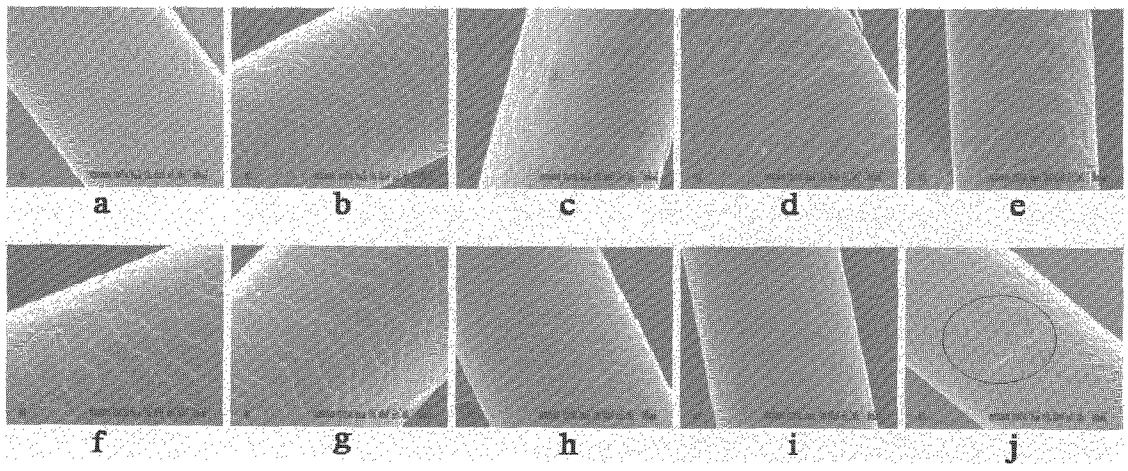

Fig.1. The scanning electron micrographs of the P, B, and B P treated hairs of dry condition.
a: original, b: P 1 time, c: P 2 times, d: P 3 times, e: B 1 time, f: B 2 times,
g: B 3 times, h: B P 1 time, i: B P 2 times, j: B P 3 times

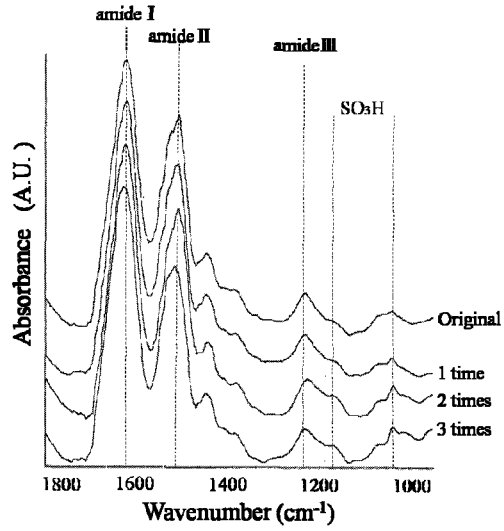

Fig.2. FT-IR spectra of P treated hairs.

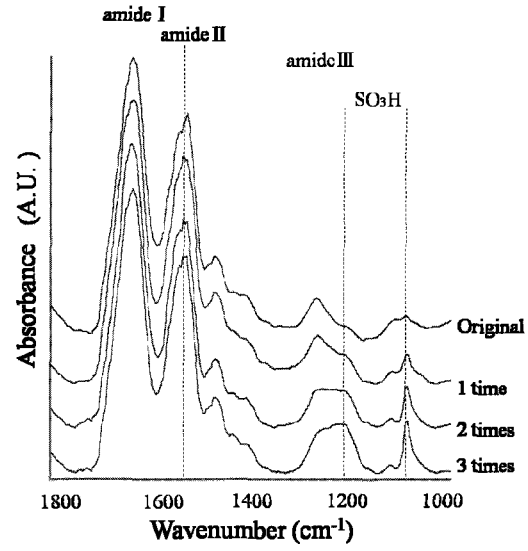

Fig.3. FT-IR spectra of B treated hairs

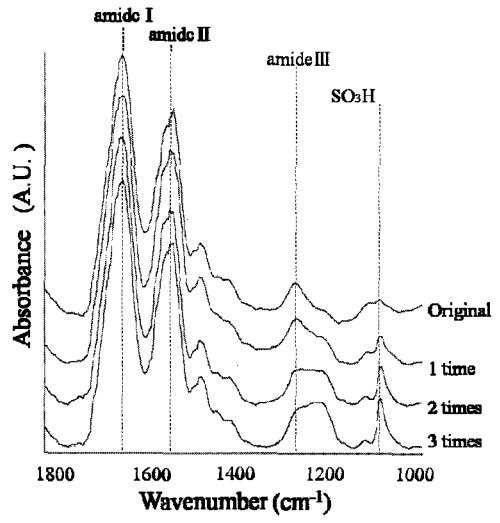

Fig.4. FT-IR spectra of B&P treated hairs.

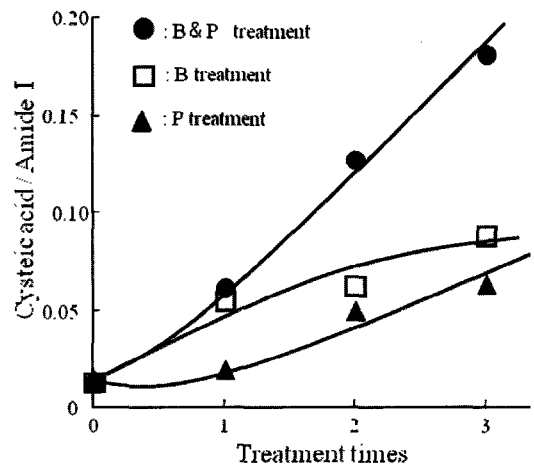

Fig.5. The ratio of amide I to cysteic acid at ~1040 cm^{-1} vs. treatment times.

Table.1. Amino acid compositions for Permanent wave(P), Bleach(B), and Bleach&Permanent (B&P) treated hairs. Each treatment was performed 1 and 3 times.

	Content in mol%						
Amino acid	Original	P・1	P・3	B・1	B・3	B&P・1	B&P・3
Asp	7.9	8.0	7.7	7.8	8.0	8.1	8.2
Thr	8.0	7.9	8.0	7.8	8.4	7.7	8.1
Ser	14.0	14.4	13.1	12.9	14.3	13.5	13.7
Glu	18.0	17.9	18.1	18.2	18.2	18.2	18.6
Pro	2.6	2.5	2.1	2.6	2.4	2.2	2.1
Gly	6.2	6.3	5.8	6.1	6.1	6.0	5.9
Ara	6.3	6.9	6.2	6.2	6.1	6.5	6.4
Cys	4.1	3.8	3.6	4.0	3.7	3.4	2.4
Val	5.1	4.8	6.4	6.8	5.5	5.3	5.8
Mel	0.3	0.4	0.4	0.3	0.3	0.4	0.4
Lle	2.6	2.4	3.4	3.5	2.8	2.8	3.1
Leu	9.3	9.3	9.7	9.7	9.4	9.8	9.8
Tyr	2.3	2.8	2.6	1.8	2.6	2.9	2.6
Phe	2.2	2.2	2.2	2.1	2.1	2.3	2.2
His	1.1	1.1	1.0	1.0	1.0	1.0	1.1
Lys	2.5	2.6	2.2	2.2	2.0	2.6	2.3
Arg	7.1	7.3	7.5	7.0	7.0	7.3	7.5

4. DISCUSSION

In appearance, the cuticle layers were scarcely damaged by the permanent waving (P) and the bleaching (B) treatments up to 3 times. However, a part of peeling of the cuticle was observed for the B&P treated hair. The amino acid composition except for cystine hardly changed regardless of the treatment methods and times. The cystine content decreased with increase of the treatment times. Although the Shim-pack Amino-Na column is not so suitable to analyze cysteic acid, a peak due to cysteic acid can be detected on the chromatogram. Therefore, the fraction of cysteic acid is determined as the area ratio against the total amino acid peak area. Figure 6 shows the relationships between the fraction of cysteic acid and treatment times for the P, B, and B&P treated hairs. The fraction increases with increasing treatment times for the P and the B treatments. For the B&P treatment, the fraction increases remarkably when the treatment exceeds 2 times. These behaviors are almost similar to the results obtained by FT-IR measurements (see Fig. 5). It was found that the amount of cysteic acid in the various treated hairs increased in order of P ≤ B << B&P treatments.

The cysteic acid is produced by oxidation of the S-S linkages and the oxidation reaction occurs in the P and B treatment processes. The permanent waving treatment is performed by two steps [7], the first step is reduction reaction and the second one is oxidation reaction as follows;

First step (reduction reaction):

$$\text{Ker-S-S-Ker} + \text{R-SH} \rightarrow \text{Ker-S-S-R} + \text{Ker-SH} \quad (1)$$

$$\text{Ker-S-S-R} + \text{R-SH} \rightarrow \text{Ker-SH} + \text{R-S-S-R} \quad (2)$$

Second step (oxidation reaction):

$$2\text{Ker-SH} + 1/2\ O_2 \rightarrow \text{Ker-S-S-Ker} + H_2O \quad (3)$$

where Ker-, R-SH and R-S-S-R mean keratin, thioglycolic acid and dithiodiglycolic acid, respectively.

During the oxidation process, cysteic acid is formed as side reactions [8];

$$\text{Ker-SH} + 3/2\ O_2 \rightarrow \text{Ker-SO}_3\text{H} \quad (4)$$

$$\text{Ker-S-S-Ker} + 3\ O_2 \rightarrow \text{Ker-SO}_3\text{H} \quad (5)$$

On the other hand, Robbins [9] reported that the oxidation of S-S linkages in the bleaching treatment occurs as S-S cleavage system as follows;

$$\text{Ker-S-S-Ker} \rightarrow \text{Ker-SO-SKer} \rightarrow \text{Ker-SO}_2\text{-SKer} \rightarrow [\text{Ker-SO}_2\text{-SO-Ker}] \rightarrow \text{Ker-SO}_2\text{-SO}_2\text{-Ker} \rightarrow 2\text{Ker-SO}_3\text{H} \quad (6)$$

In the permanent waving treatment, the S-S linkages are cleaved by the reduction reaction and the linkages are regenerated by the oxidation reaction. Therefore, it is presumed that the hair keratin changes to loose structure and the S-S linkages come to be oxidized easily by a weak oxidizer such as sodium bromate.

In the bleaching treatment, the hair keratin is oxidized with a strong oxidizer like hydrogen peroxide. However, since the keratin keeps own structure, formation of cysteic acid will be repressed, even if the treatment times increase.

On the other hand, after the first B&P treatment, the strong oxidizer can penetrate into the hair keratin with loose structure. As the result, the hair keratin will be easily oxidized and a large amount of cysteic acid should be formed and the damage of hair is encouraged synergistically by repetition of B&P treatment.

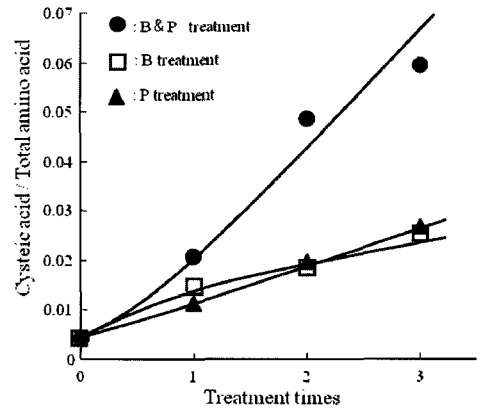

Fig.6. Relationships between fraction of cysteic acid and treatment times for P, B, and B&P treated hairs.

CONCLUSION

The cuticle layers were scarcely damaged by the permanent waving (P) and the bleaching (B) treatments up to 3 times. However, the surface of B&P treated hair was gradually damaged by repetition of the treatment. Cysteic acid was formed by the P, B, and B&P treatments. The amount of cysteic acid in the treated hairs increased in order of P ≤ B << B&P treatments. The damage of hair is encouraged synergistically by repetition of B&P treatment.

5. REFERENCES.

[1] K. Arai, *Nippon Keshohin Gijutsusha Kaigi*, **37**, 68-83(2003)

[2] Fraser R. D. B. et.al., Nature , **193**, 1052~1055 (1962)

[3] M. Amaya, Y. Iijima, and S. Takigami, *Transactions of Materials Research Society of Japan*, in press

[4] A. Kuzuhara, *Biopolymers*, 77, 335-344 (2005)

[5] J.S Churuch, G.L. Corino, and A.L. Woodhead, *Biopolymers*, 42, 7-17 (1997)

[6] H.Zahn, S.Hilterhaus, and A.Strubmann, *J. Soc. Cosmet. Chem.*, 37, 159-175(1986)

[7] M. Hosokawa, *Saisin nomouhatsukagaku*, Ed. by Mouhatsukagaku gijutsushakyoukai, Fragrance Journal Ltd, Tokyo (2003) pp220~221

[8] M. Hosokawa, *Saisin nomouhatsukagaku*, Ed. by Mouhatsukagaku gijutsushakyoukai, Fragrance Journal Ltd, Tokyo (2003) pp221~224

[9] Robbins C., *J. Soc. Cosmet. Chem.*, **22**, 339~348 (1971)

(Recieved May 5, 2008;Accepted May 8, 2008)