

## Properties of damaged hair and prevention of hair damage by chemically modified keratin

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### Abstract

Bleaching and permanent waving treatments have been done up to 5 times on virgin Japanese human hair. The colour of the hair became brown and the touch changed harder with increasing treatment times. When the treatment exceeded 3 times, the damage of the cuticle layers became remarkably and a part of cuticle was peeled off. FT-IR spectrum of the original hair showed amide I ( $\sim 1640\text{ cm}^{-1}$ ), amide II ( $\sim 1530\text{ cm}^{-1}$ ), amide III ( $\sim 1230\text{ cm}^{-1}$ ) and weak absorptions corresponding to cysteic acid overlapped at  $\sim 1040\text{ cm}^{-1}$  and  $\sim 1180\text{ cm}^{-1}$ . Intensity of the absorption at  $\sim 1040\text{ cm}^{-1}$  increased with increase of treatment times. The original hair showed peaks at  $\sim 163\text{ eV}$  and  $\sim 169\text{ eV}$  on the XPS spectrum. The former peak is considered to be S-S bond of cystine residue and the latter is due to S-O bond of cysteic acid. To investigate the prevention of hair damage, chemically modified wool keratin was added in permanent waving agent and the bleaching and permanent waving treatments have been done. The cuticle layers of treated hair using the wool keratin were hardly damaged even if the treatment was repeated for 3 times.

Key words: SEM, FT-IR, XPS, damaged hair

### 1. INTRODUCTION

Human hair has a hierarchical structure consisting of cuticle, cortex and medulla. Human hair is composed of two types of protein, low sulfur (LS) and high sulfur (HS) proteins. The LS protein makes up microfibril (IF protein) and the HS protein composes amorphous matrix (IFAP) [1]. The IF protein ( $\alpha$ -helical proteins) is embedded in IFAP with high cystine content consisting of disulfide (SS) groups. The SS groups form the cross-linkage in keratin fibers and contribute structural and chemical properties of keratin. The aims of this study are elucidation the influence of bleaching and permanent waving treatments on the treated hair keratin using SEM, FT-IR, and XPS. It was studied investigation the prevention of hair damage using chemically modified wool keratin.

### 2. EXPERIMENTAL

#### 2.1 Materials

Virgin hair of 12 years old Japanese girl was used as a starting material. The tresses (ca. 1.5g and 25cm long) were immersed in 0.5% aqueous Laureth-9 solution (50ml) containing 20mM EDTA for 1h at  $33^\circ\text{C}$ . 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 of the hair was performed in 3% hydrogen peroxide solution at pH10.3 for 30min at  $35^\circ\text{C}$ , and then they were rinsed by distilled

water. The permanent waving treatment of the bleached hair was carried out using 6% TGA aqueous solution at  $35^\circ\text{C}$  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  $35^\circ\text{C}$  and was rinsed with distilled water. This process was repeated for 5times 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

Surface of the bleaching and permanent waving treated hairs were obtained using a Hitachi S-3000N scanning electron microscope (SEM) at an accelerating voltage at 10~15kV. The hair samples were evaporated with gold before observation. Water swollen treated hairs were also observed at the accelerating voltage of 15 kV under 50 Pa at  $-20^\circ\text{C}$ .

#### 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 CONTINUUM 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 XPS measurement

The x-ray photoelectron spectroscopy (XPS)

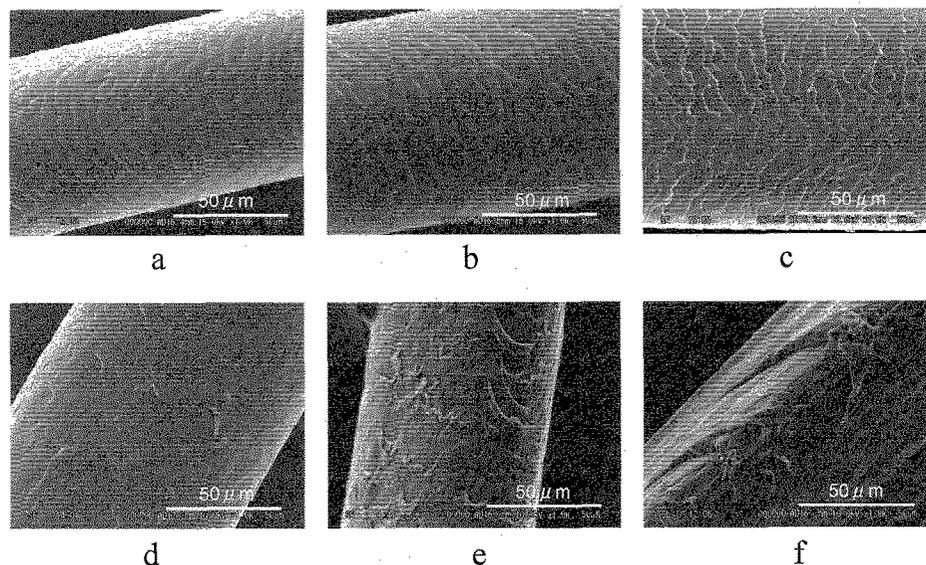


Fig.1. The scanning electron micrographs of the B&P treated hairs of the dry condition. a: original b: 1 time c: 2 times d: 3 times e: 4 times f: 5 times

measurements were carried out using a JPS-9200 spectrometer (JEOL). Excitation of the treated sample was accomplished with non-monochromatized Mg K $\alpha$  X-ray beam generated at 10 kV and 10 mA. The etching of the sample surface was performed using argon plasma at acceleration voltage 3kV.

### 2.6 Chemically modified wool keratin treatment

Pure wool was treated with TGA under alkali condition and carboxymethyl alanyl disulfide wool keratin (i.e., chemically modified keratin) was synthesized. The details of the synthesis was described elsewhere [2,3]. The carboxymethyl alanyl disulfide wool keratin (CMADWK) was added in the permanent waving agent at pH9.3 and the concentration of CMADWK was adjusted to 3 %. The bleaching and permanent waving treatments were performed as the same manner described in the paragraph of 2.2 using the agent containing CMADWK.

## 3. RESULTS AND DISCUSSION

### 3.1 Properties of damaged hair

Bleaching and permanent waving (B&P) treatments were performed up to 5 times. Colour of the hair became brown and the touch changed harder with increasing the treatment times. Figure 1 shows the scanning electron micrographs of the B&P treated hairs of the dry condition. The surface of original hair was covered with sturdy cuticle layers and the cuticle layers were hardly damaged by the B&P treatment till 2 times. When the treatment exceeded 3 times, the damage of the cuticle became remarkably and a part of cuticle was peeled off.

To investigate chemical structural change of

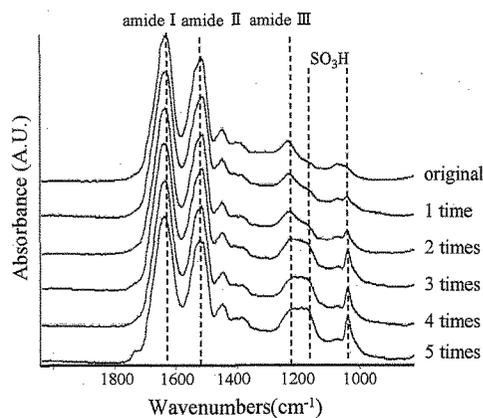


Fig.2. FT-IR spectra of the B&P treated hairs.

the B&P treated hairs, the hairs were measured using the FT-IR microscope. Figure 2 shows FT-IR spectra of the B&P treated hairs. The original hair showed characteristic features of keratin fiber [4-6], i.e., amide I ( $\sim 1640\text{ cm}^{-1}$ ), amide II ( $\sim 1530\text{ cm}^{-1}$ ), amide III ( $\sim 1230\text{ cm}^{-1}$ ), CH scissoring vibration ( $\sim 1450\text{ cm}^{-1}$ ) and CH wagging vibration ( $\sim 1390\text{ cm}^{-1}$ ). Weak absorptions overlapped at  $\sim 1040\text{ cm}^{-1}$  and  $\sim 1180\text{ cm}^{-1}$  on the IR spectrum. The absorptions correspond to symmetric stretching vibration of S=O group due to cysteic acid [6] and their intensity increased with increase of the treatment times. Figure 3 shows the ratio of amide I peak to that for cysteic acid at  $\sim 1040\text{ cm}^{-1}$ . The ratio increased remarkably up to 3 times treatment and then increased gradually. It was found that formation of cysteic acid is enhanced by the B&P treatment.

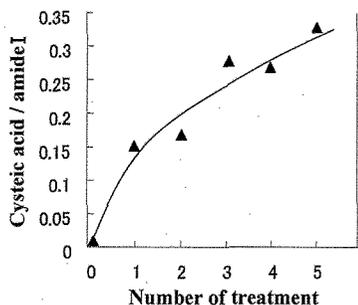


Fig.3. The ratio of amide I peak to that for cysteic acid at  $\sim 1040\text{ cm}^{-1}$ .

Figure 4 shows XPS depth direction multispectra of S2p for surfaces of the treated hairs. The original hair showed two peaks, the binding energies of the dominant peak and a weak peak are  $\sim 163\text{ eV}$  and  $\sim 169\text{ eV}$ , respectively. The former peak is characteristic of disulfide bond (RS-SR) and the latter corresponds to S-O bond of sulfonate, namely cysteic acid. Similar XPS patterns were reported for virgin European brown hair [7]. In the case of B&P treated hairs, the S-O peak appeared more clearly and the intensity increased with increase of the treatment times.

The S2p was divided into 1/2 and 3/2 and abundance ratios of S-S bond and S-O bond were determined by the curve fitting method. Figure 5 shows relationships between the abundance ratios of S-S bond and S-O bond and etching time for the B&P treated hairs. For the original hair, the ratio of S-O bond was 20 % at the surface of original hair and S-O bond disappeared by the argon plasma etching for 40 sec, the depth calibrated by SiO<sub>2</sub> is 3.3 nm (see Fig. 5a).

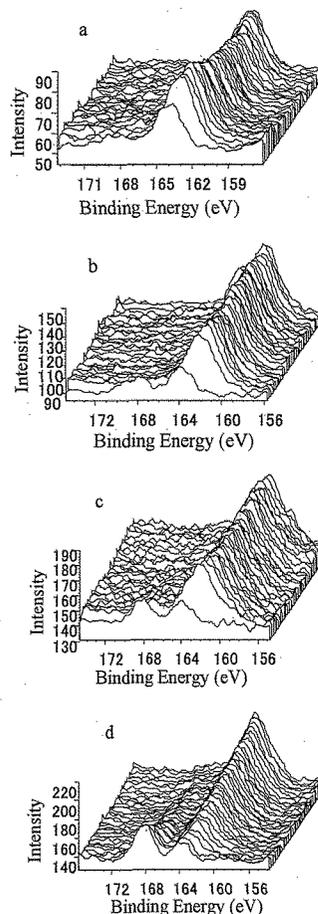


Fig.4. XPS depth direction multispectra of S2p for surfaces of the treated hairs.  
a: original b: 1 time c: 3 times d: 5 times

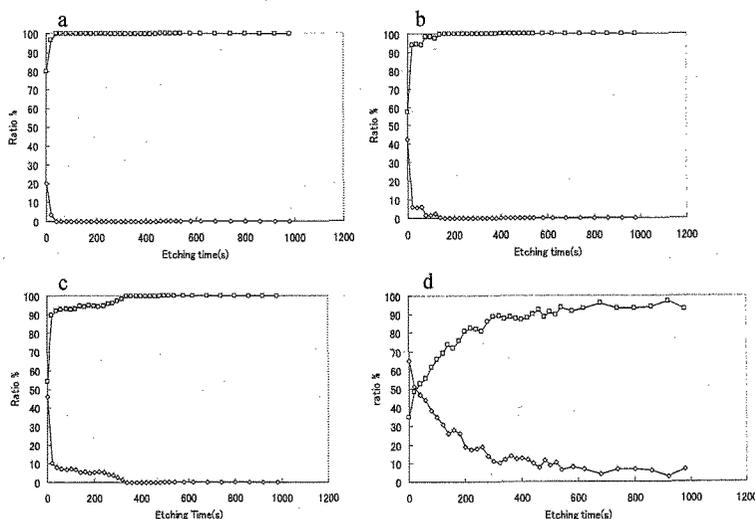


Fig.5. Relationships between the abundance ratios of S-S bond and S-O bond and etching time for the B&P treated hairs. a: original b: 1 time c: 3 times d: 5 times

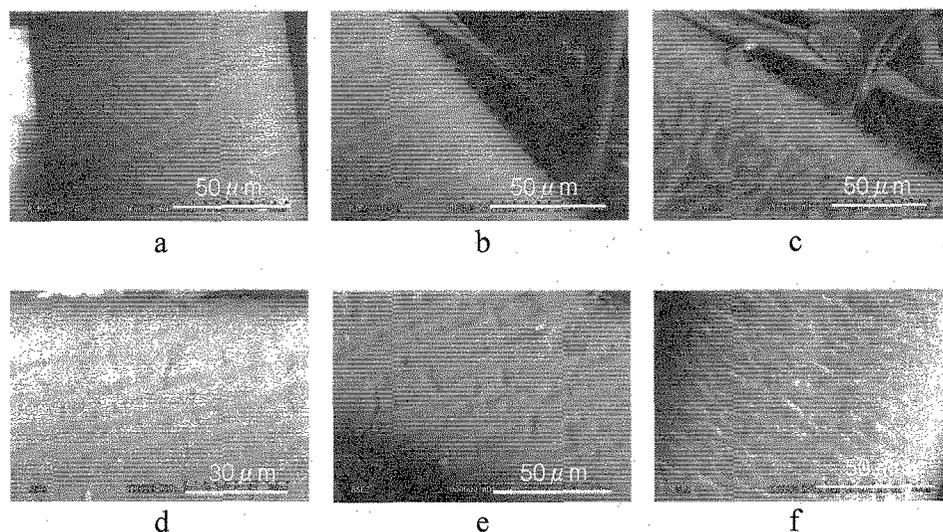


Fig.6. SEM images of the water swollen hairs treated in the permanent waving agent with and without CMADWK. without CMADWK (a: 1 time b: 2 times c: 3 times) with CMADWK (d: 1 time e: 2 times f: 3 times)

A parts of cystine linkage was oxidized by sunlight and small amount of cysteic acid is formed on the surface of cuticle. The ratios of S-S bond and S-O bond vs. etching time for the B&P treated hairs are shown in Figures 5b~5d. The ratio of S-O bond at the surface increased with increase of the treatment times and the value of the 5 times treated hair showed 65%. On the other hand, S-O bonds were observed at longer etching time with increase of the B&P treatment. This means that the formation of cysteic acid occurred at deeper place of the cuticle. These results correspond with those of FT-IR.

### 3.2 Prevention of hair damage

To investigate the prevention of hair damage, CMADWK was added in the permanent waving agent and B&P treatments have been done. Figure 6 shows SEM images of the water swollen hairs treated in the permanent waving agent with and without CMADWK. Under the wet condition, the damage of the treated hair can be detected better than the dry state. As the cuticle layer did not close by the B&P treatment, it was found that the hair was damaged a little by the treatment twice (see Fig. 1c and Fig. 6b). On the contrary, the cuticle layers of the hairs treated using CMADWK were hardly damaged even if the B&P treatment was repeated for 3 times.

## 4. CONCLUSION

Bleaching and permanent waving treatments have been done up to 5 times. When the treatment exceeded 3 times, the damage of the cuticle layers became remarkably and a part of cuticle was peeled off. The SS bonds of cystine residue were oxidized and changed to cysteic acid by the bleaching and permanent waving treatments. The

cuticle layers of treated hair using the CMADWK were hardly damaged even if the treatment was repeated for 3 times.

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(Received February 16, 2007; Accepted July 12, 2007)