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Influence of internal structures of hair fiber on hair appearance. III. Generation of light-scattering factors in hair cuticles and the influence on hair shine

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Synopsis

The effects of thermal treatments on hair fiber induced by blow-drying have been investigated. It was found that the hair shows whitish and powdery appearance after heat drying, especially when dark hair is rapidly dried from a wet condition. For all kinds of hair, the appearance of numerous glittering speckles was confirmed on the cuticle surface by optical microscopic observations. SEM images of hair transverse and longitudinal sections with glittering speckles revealed that the splitting of cuticle layers generated by blow-drying occurred not only at the outermost parts of cuticle cells but also at the inner parts of the cellular interfaces. The release and uptake of moisture through fiber surfaces induces deformation of cuticle cells, probably because of anisotropic swelling or drying of the cells. The cuticles with glittering speckles are found to be fragile and are easily damaged in combination with other mechanical stresses such as combing force. Furthermore, the authors have found an efficient system for both improving hair shine and preventing cuticle damage caused by the blow-drying/combing process.

INTRODUCTION

The structure of human hair is a highly organized stratum that is very resistant to external stimuli. However, morphological changes can occur through daily hair care routines, chemical treatments, exposure to UV-light, and other stresses. Hair damage leads to a change in not only the physical properties of hair, by becoming harsh, stiff, weak, and brittle, but also in optical properties such as shine. Hair shine is one of the largest concerns of consumers, and as a result, numerous studies regarding hair shine have been conducted. Although most of the studies discuss the optical properties at the hair surface, we have found that structural changes occur in the internal hair fiber through daily hair care routines. These actions in the daily hair care routine influence hair appearance, such as light scattering from the cuticle cell, cortex, and medulla tissues (1–4).

In this paper, the effects of blow-drying treatments on human hair have been investigated. As is well known, blow-drying with a hair-dryer is nowadays one of the common customs in daily life, and thus structural changes occurring in the hair cuticle by blow-drying have been reported (5–8). Studies regarding cuticle damage have been conducted from the viewpoint of both thermal transition (5–7) and changes in the moisture content (8) in hair keratin. We have made a further examination of hair cuticles, focusing on structural changes caused by blow-drying, and discovered the generation of splitting spaces between the cuticle layers. This phenomenon is considered to occur frequently in the daily hair care routine and influences both hair shine as well as the cuticle degradation process. The authors present an analysis of the generation mechanism of the interlayer spaces of cuticle layers through blow-drying and the effect of this phenomenon on hair cuticle damage.

EXPERIMENTAL

MATERIALS AND METHODS

The fibers used in this study were chemically untreated hair of Japanese women in the 20-to-40 age range. In order to condition hair moisture, the fibers were kept overnight at a constant temperature and humidity. A blow-dry treatment was administered using a hair dryer with a heated air blower for 30 seconds. The hair samples were heated at 70°C by the blow-dry treatment. The amount of scattered light from the interlayer space of the cuticle cell was evaluated using optical microscope views of the fibers at a low magnification (×50). We classified the hair fibers into five grades according to the amount of glittering speckles they contained, and used these grades as the standards. The evaluation was performed by comparing these standard sheets as references. Evaluation of light scattering by blow-drying was also conducted for the fibers treated with an aqueous solution of malic acid (MA: 4 wt%)/benzyloxyethanol (BOE: 10%)/15% ethanol at 25°C for an hour.

The measurements of hair moisture before and after the MA/BOE treatment were performed by conventional Karl Fischer method. The hair fiber was introduced into 50 ml of the solvent to be used as the azeotrope formula and distilled until most of the solvent had been collected. A small excess of Karl Fischer reagent was added to the distillate, and the back was titrated with water in methanol.

The hair cuticle damage caused by hair care routine with blow-drying was evaluated. Each hair care cycle consisted of shampooing/rinsing and combing during blow-drying, and the number of applied cycles was 150 times. The hair damage was evaluated by means of counting the total number of cuticle layers before and after cycles with the help of the FE-SEM observation of the hair transverse sections. A total of ten fibers per each sample was analyzed. In order to evaluate the protection effect of the malic acid (MA)/ BOE treatment against hair damage, hair fibers were treated with a MA/BOE solution after rinsing each time.

INSTRUMENTATION

Scanning electron microscope (SEM) observations were performed on the hair surface and sections. SEM observations were carried out using a Hitachi S-4000 scanning electron microscope. For the observations of transverse and longitudinal sections, the hair fibers were embedded in an epoxy resin (Epon802) and cut using an ultramicrotome (Nova Ultratome) equipped with a glass knife. All samples were coated with a layer of Pd/Pt in a sputter-coating unit (Jeol JFC-1100).

Transmission electron microscope (TEM) observations were performed in order to observe the fine structure of the cuticle cells. The hair samples were embedded in an Epon802 resin after blow-drying in a combing process. Ultrathin sections (100 nm) were prepared using the ultramicrotome for longitudinal sections of the hair fiber. TEM observations were conducted using a Jeol JEM-2000FX transmission electron microscope.

The secondary structure of the cuticle keratin was examined by Fourier transform infrared attenuated total reflectance (FT-IR/ATR) spectroscopy. The spectra were collected on a Bio-Rad FTS-60A spectrometer with the use of a zinc selenide crystal designed at a 45-degree angle of incidence. The fibers were immersed in de-ionized water followed by 30 seconds of blow-drying at 70°C, and the number of applied cycles was 5 or 30 times each.

Measurements of the moisture content at the fiber surface were performed using near-infrared photoacoustic spectroscopy (NIR-PAS). The NIR-PAS instrument is an originally constructed *in vivo* NIR-PAS spectrometer equipped with a hand-made measurement cell and a laser diode as a thermal source. A total of 30 fibers per sample were used for PAS analysis, and the variation in moisture in the cuticle cell was examined after blow-drying. In order to maintain uniformity in the humidifying conditions, all the PAS measurements were performed in an environmental control room (23°C/75% RH).

RESULTS AND DISCUSSION

STRUCTURAL CHANGES IN THE HAIR CUTICLE

Many consumers perceive some changes in their hair such as disentangling, feel, bounce, shine, etc., after using a hair dryer. The half-head test was carried out in order to elucidate the effect of blow-drying applied to hair in a wet condition (Figure 1). The left half-head was dried by applied hot air drying, and the right half-head was air-dried. It was confirmed that the left half-head showed a whitish and powdery appearance, and consequently hair gloss was suppressed. Optical microscope observations of the hair fiber revealed that several glittering speckles appeared after heat drying (Figure 2). Several colored glittering speckles, sometimes red, blue, green, etc., were shown in the high-magnification optical microscopic image (Figure 3), suggesting light reflection due to interference of light at the cuticle layer. SEM analysis results of fiber surfaces before and after blow-drying are shown in Figure 4. The existence of concave-shaped scale edges owing to cuticle layer splitting are shown (circled in Figure 4) in blow-dried fibers. Through SEM observations of transverse and longitudinal sections, it was confirmed that structural changes caused by blow-drying also occurred between inner cuticle layers (Figure 5).

Figure 1. Half-head trial. Left half-head after applied hot-air drying (70°C/30 sec). The other half was air-dried with a whitish appearance.

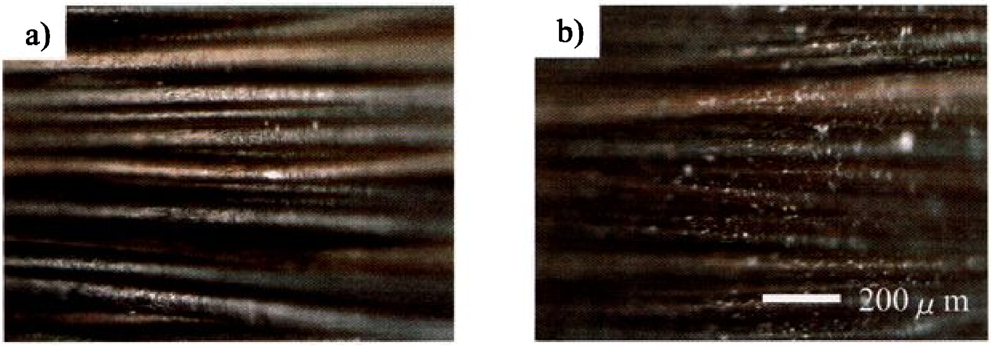

Figure 2. Optical microscope observations of hair tresses (a) before and (b) after hot-air blow-drying at 70°C for 30 sec.

The hair damage caused by blow-drying has been reported in the literature (5–8). Thermal treatment of hair operating in the temperature range above 100°C caused irreversible structural changes of hair fiber due to the transformation of the keratin secondary structure (5–7). Additionally, it was reported that blow-drying cycles at 75°C caused crack formation at the edges of the cuticle cell as a result of swelling and deswelling of the hair fiber (8). Compared to these phenomena, however, the generation

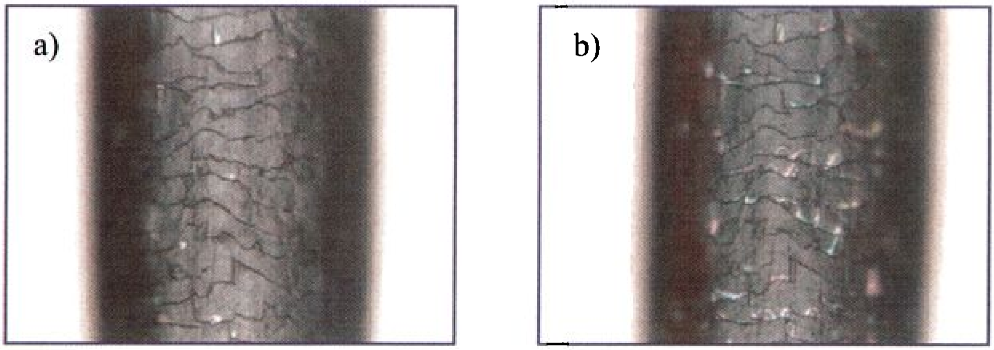

Figure 3. Optical microscope observations of hair fiber (a) before and (b) after hot-air blow-drying at 70°C for 30 sec. The analysis was performed on the same part of the hair fiber.

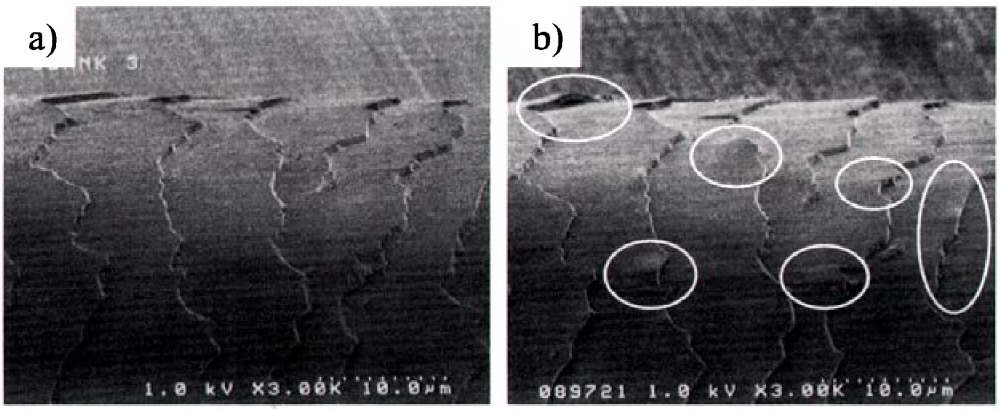

Figure 4. SEM observations of fiber surface (a) before and (b) after hot-air blow-drying (70°C/30 sec). The analysis was performed on the same part of the hair fiber.

of splitting spaces in the cuticle layers through blow-drying is considered to be a more frequent occurrence in daily hair care routines.

GENERATION MECHANISMS OF LIGHT SCATTERING IN THE HAIR CUTICLE

Figure 6 shows the FT-IR/ATR spectra of hair fibers after application of different blow-drying cycles. The ATR technique provides surface-specific spectra (within 1 micrometer from the surface) with minimal interference from scattering effects, and the measurement depth is therefore within the thickness of the cuticle tissue. The amide I (1650 cm^{-1}) and amide II (1540 cm^{-1}) were the most prominent features of the spectra. The peak observed in the absorbance at ~3250 cm^{-1} showed an increase as a function of the number of cycles. This peak is considered to be the peak of an OH group in water molecules that are contained not only in hair fibers, but also in the ambient air. All of the measurements were performed in the dried ambient air, but it was very difficult to control the moisture in the analysis chamber, and, therefore, the peak intensity varied contingently. It is well known that the amide I and II peaks reflect the secondary structure of keratin (9), but no significant changes in these peaks were observed.

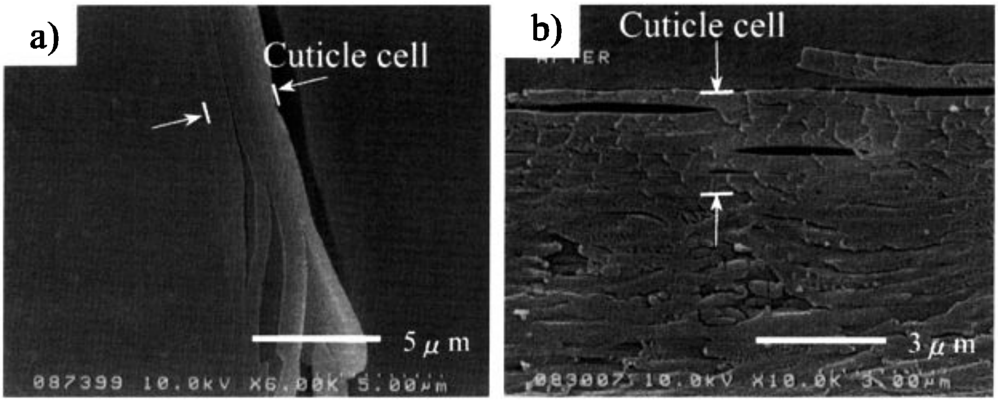

Figure 5. SEM observations of hair fibers for (a) cross and (b) longitudinal sections after hot air blow-drying (70°C/30 sec).

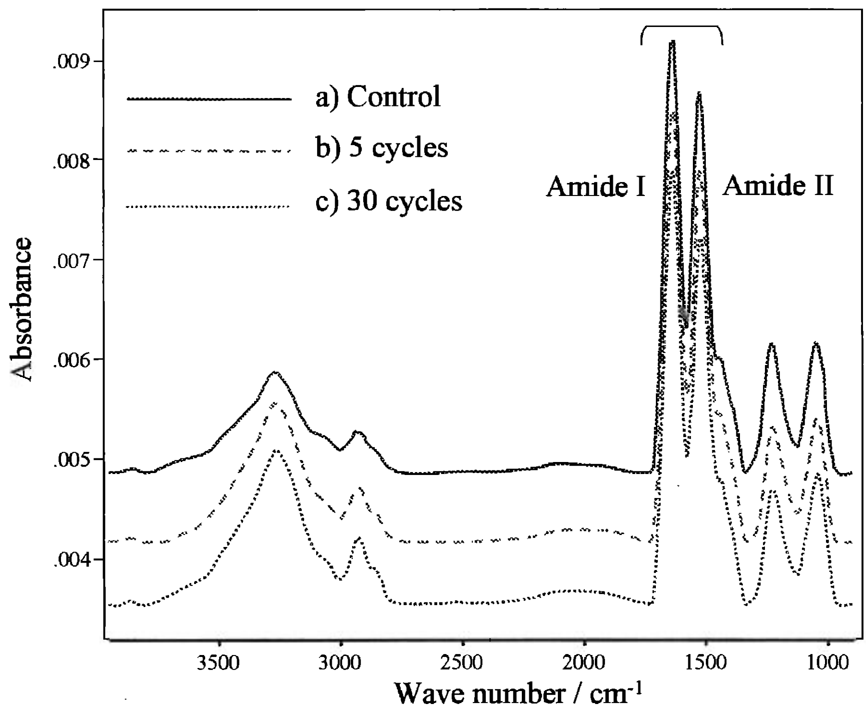

Figure 6. FT-IR spectra of hair cuticle (a) before, (b) after five thermal cycles, and (c) after 30 thermal cycles. Each cycle consisted of immersion into de-ionized water followed by 30 seconds of blow-drying at 70°C.

We have explored the effect of abrupt changes of moisture content in the hair fiber. Figure 7 shows the relationship between the initial moisture content of the hair fiber and the light-scattering level from glittering speckles on the hair surface just after blow-drying. The amount of glittering speckles was found to be dependent on the initial moisture content. The more the hair fiber is moisturized, the more glittering speckles are observed.

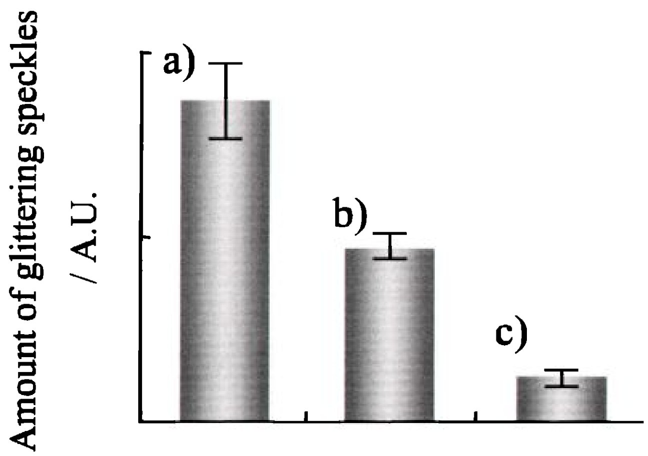

Figure 7. Light-scattering level from glittering speckles of the cuticle just after blow-drying (70°C/30 sec) from (a) wet (immersed in de-ionized water), (b) damp (moisture controlled at 75% RH/23°C), and (c) dry (dried in silica-gel desiccator) conditions.

Figure 8 shows optical microscope images of the hair surface before blow-drying, just after blow-drying, and five minutes after blow-drying. The light-scattering level from glittering speckles was more intense for the hair standing for five minutes at a high-humidity condition after blow-drying. The effects of humidity on the relaxation process are shown in Figure 9. In the humidifying process after blow-drying, more glittering speckles were observed in the case of relaxation in a condition of higher humidity. All these facts from Figures 6–9 suggest that the generation of the speckles is essentially not caused by heat, but by an abrupt and dramatic change in moisture content. After that, these speckles almost disappeared within ten minutes, because the hair fiber was in a high-humidity equilibrium.

Figure 10 illustrates the variation of moisture content in the hair fiber from just after blow-drying. Surface moisture was measured using the NIR-PAS method. The thermal diffusion depth is considered to be comparable with the total thickness of cuticle cells (about 2–3 micrometers). The rate of bulk moisture absorption was measured by monitoring weight changes. The scale of 0% shown in the graph corresponds to the moisture content for the hair fiber that was dried in a silica-gel desiccator, and the 100% scale corresponds to hair equilibrium, with an atmosphere at 23°C/75% RH each. The

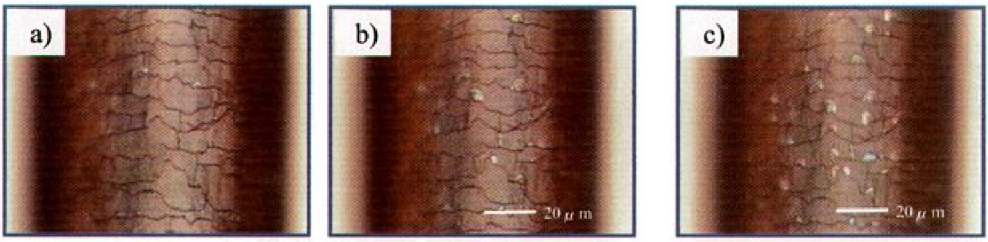

Figure 8. Variation in the amount of glittering speckles on the fiber surface (a) before, (b) just after blow-drying, and (c) five minutes after blow-drying. The gradual increase in glittering speckles was observed after stopping blow-drying at a high-humidity condition. The analysis was performed on the same part of the hair fiber.

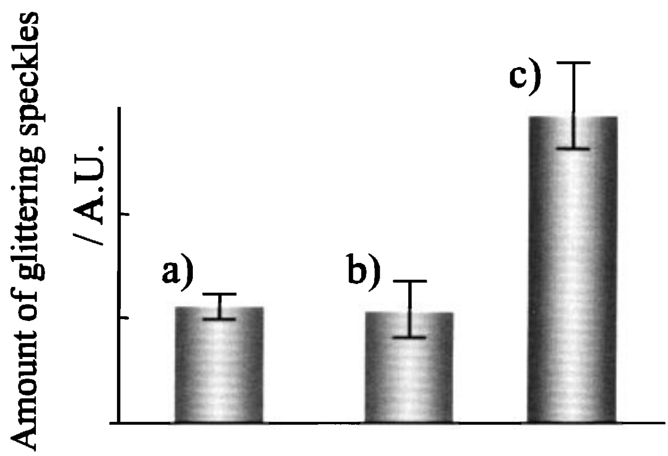

Figure 9. Light-scattering level from glittering speckles of cuticle (a) just after blow-drying, and five minutes after blow-drying in relaxing (b) low-humidity (30% RH) and (c) high-humidity (75% RH) conditions.

moisture contents were represented by the relative percentage from the original water content of the fiber. The bulk moisture content of the fiber increased gradually and reached equilibrium within an hour. On the other hand, the surface moisture content increased rapidly within two minutes after stopping the blow-drying process. The generation of glittering speckles on the fiber surface corresponded to moisture regain in the fiber surface region. In addition, these glittering speckles decreased as the bulk moisture content reached equilibrium (Figure 11). The influence of moisture change on the generation of the speckles was confirmed more precisely. The speckles were confirmed to appear during the relaxation process in high humidity (23°C/75% RH) for five minutes after the fibers had been transferred from a dried state in a silica-gel desiccator (Figure 12).

These results can be summarized as follows. The structural changes in the cuticle cell caused by blow-drying are closely related to the change in moisture content in the hair fiber. Although there are many hypotheses that can be proposed to explain this phenomenon, we believe that the generation of splitting spaces between the cuticle layers is caused by two different mechanisms. The first is that the abrupt desorption of moisture from the wet hair caused by blow-drying may cause mechanical stress on the cuticle cells, and, as a result, deformation of the cuticle layers occurs. The second mechanism is that the dramatic absorption of moisture from the hair in its dry state also causes mechanical stress on the cuticle cells by inhomogeneous swelling. Both procedures only result from rapid shrinkage or swelling of the cuticle cell, and therefore a gradual change in moisture does not cause these phenomena. The glittering speckles are observed to a high degree just after an abrupt change in moisture occurs. The moisture content will soon be in equilibrium, and thus these speckles almost disappear within ten minutes. These structural changes in hair cuticles are believed to occur in a daily hair care routine, but they have been unnoticed thus far because deformation of cuticle layers will disappear upon relaxing at high humidity conditions or wetting with water.

HAIR DEGRADATION MECHANISM

In most cases, structural changes in the hair cuticle by blow-drying are reversed in a

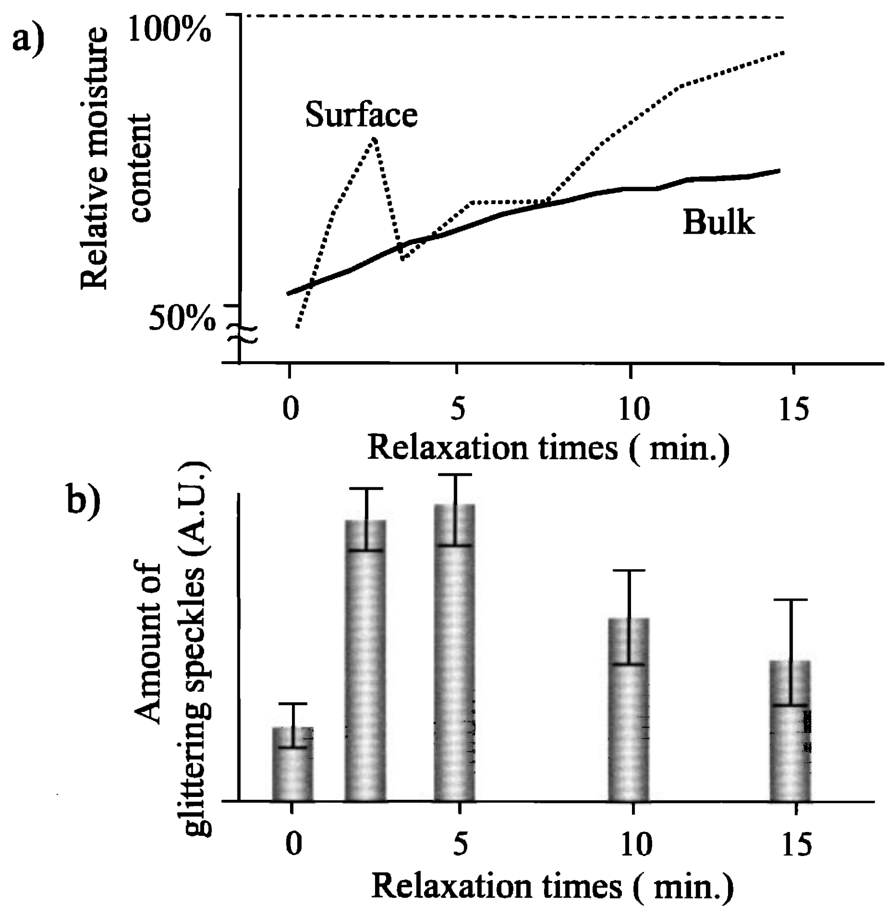

Figure 10. Variation in (a) moisture content in fiber surface compared to the bulk content, and (b) amount of glittering speckles as a function of the relaxation times.

short period by relaxation in high humidity. The repeated applications of hair care cycles, shampooing, rinsing, blow-drying, etc., however, seem to cause several glittering speckles to become fixed. These speckles won't disappear even after wetting and using a natural drying process, especially at the tip part of the hair. Furthermore, it is considered that this harsh structural change will cause serious cuticle damage by other mechanical stresses, such as abrasion or combing force.

Figure 13 shows microphotographs of the same part of a fiber surface before and after the blow-drying/combing process observed by optical and electron microscopes. The optical microscope images revealed that some of the cuticle cells had chipped away after combing, selectively at the cuticles with glittering speckles (circled in Figure 13). Moreover, rough-surfaced residues at the same part of the fiber surface were shown through SEM observation where pieces of cuticle cell had been chipped away by combing. Through TEM observation of a longitudinal section (Figure 14), these rough-surfaced residues shown in the SEM image were revealed to be endocuticles.

Figure 15 shows a possible mechanism for fracturing a cuticle edge with a glittering

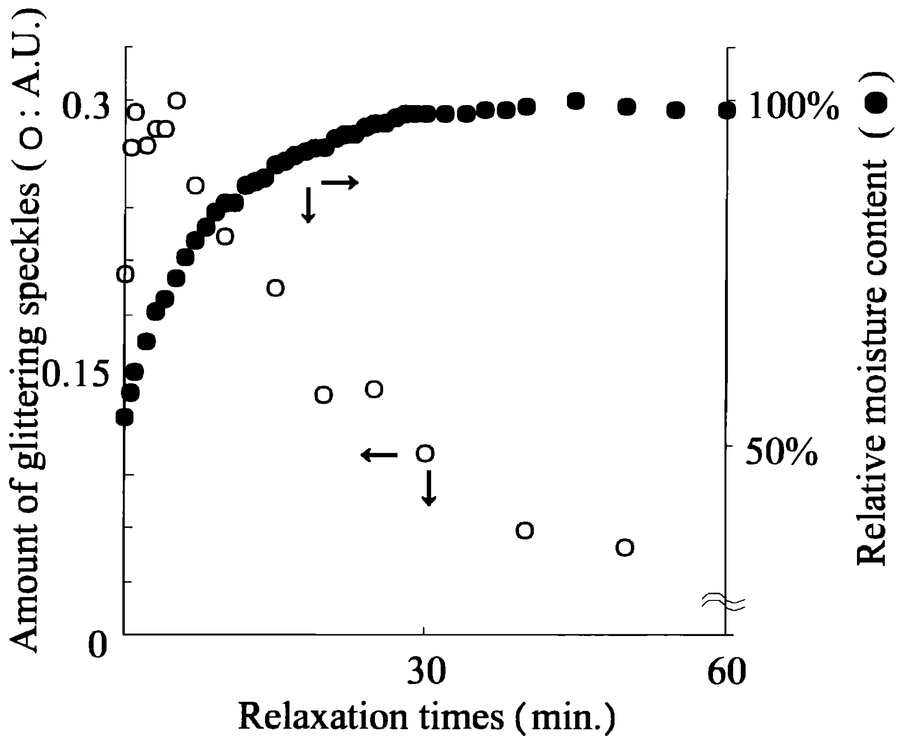

Figure 11. Variation in moisture content in hair fiber (●) and amount of glittering speckles (O) upon relaxation in a high-humidity condition (75%/23°C).

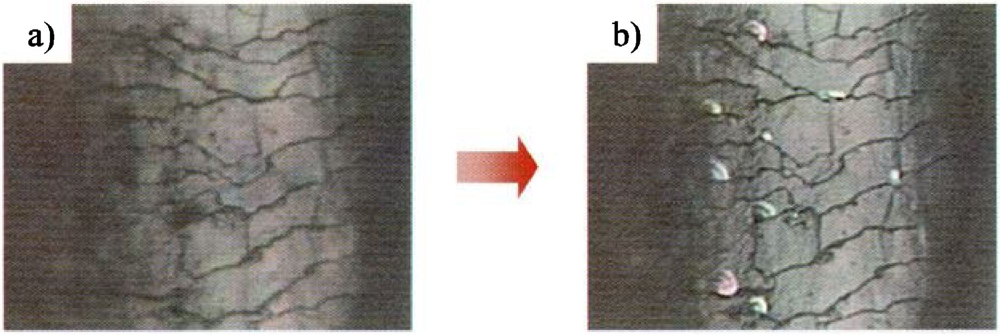

Figure 12. Optical microscope observations of hair fiber dried in silica-gel desiccator (a) just after being dried and (b) relaxing in a high-humidity (75% RH/23°C) condition. The analysis was performed on the same part of the hair fiber.

patch by combing. First, (a) a cuticle cell is transformed by the blow-drying process, and (b) the exocuticle cracking occurs because the exocuticle, which is harder but brittler than the endocuticle, doesn't comply with the combing force. Finally, (c) the endocuticle is torn by further combing force and the cuticle edge is chipped away.

PROTECTION TECHNOLOGY OF HAIR CUTICLE DAMAGE

The authors examined the suppression technology against generation of glittering speck-

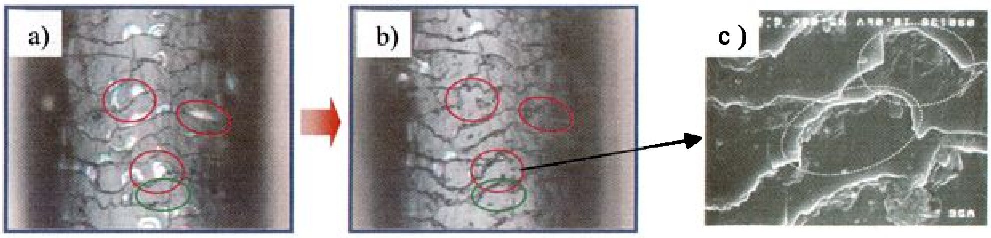

Figure 13. Optical and electron microphotographs of fiber surface before and after blow-drying/combing process. Optical microscope observations of fiber surfaces (a) before combing and (b) after combing. (c) SEM observation. The analysis was performed on the same part of the hair fiber.

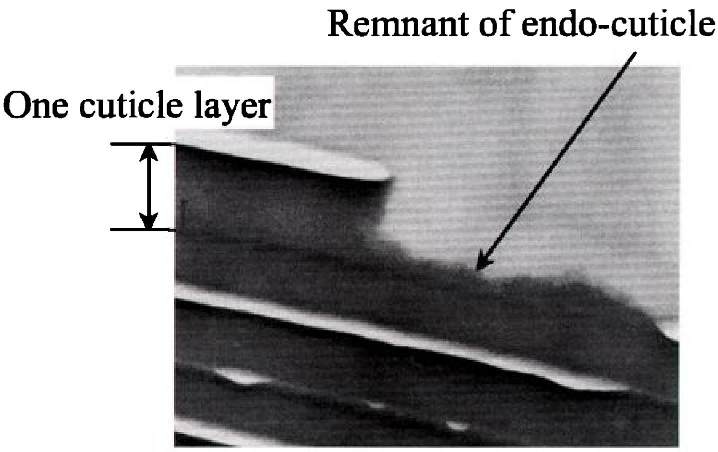

Figure 14. TEM image of longitudinal section of hair fiber after blow-drying/combing process.

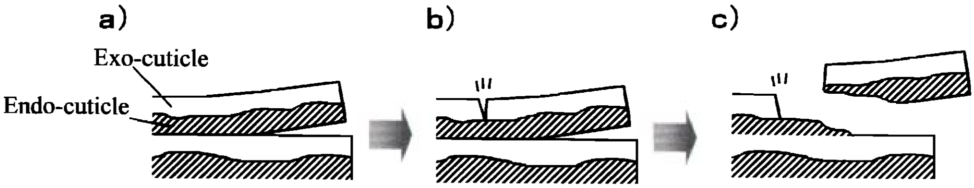

Figure 15. Schematic diagram illustrating a typical sequence of cuticle damage in which the hair cuticles with glittering speckles are tipped away by combing. (a) After blow-drying. (b) After combing process. (c) Fracturing of cuticle cell by additional combing force.

les and the protection effect from cuticle damage. They examined several kinds of materials, including organic solvents, moisturizers, and organic acids, and finally found that treatment with the malic acid (MA)/BOE solution described in the Experimental section, which is also effective for suppression of light scattering from the medulla (1–3), suppresses the generation of glittering speckles (2,3). Figure 16 shows the SEM images of the adjacent parts of the same fiber before and after the treatment with the MA/BOE solution. Through the SEM observations of a longitudinal section, it was confirmed that the cuticle cells swelled from the MA/BOE treatment, and thus the generation of glittering speckles was suppressed by the squeeze of cuticle layers. On the other hand, the analysis by Karl Fischer's method revealed that the moisture content of the hair fiber treated with the MA/BOE solution decreased from its the initial state (Figure 17).

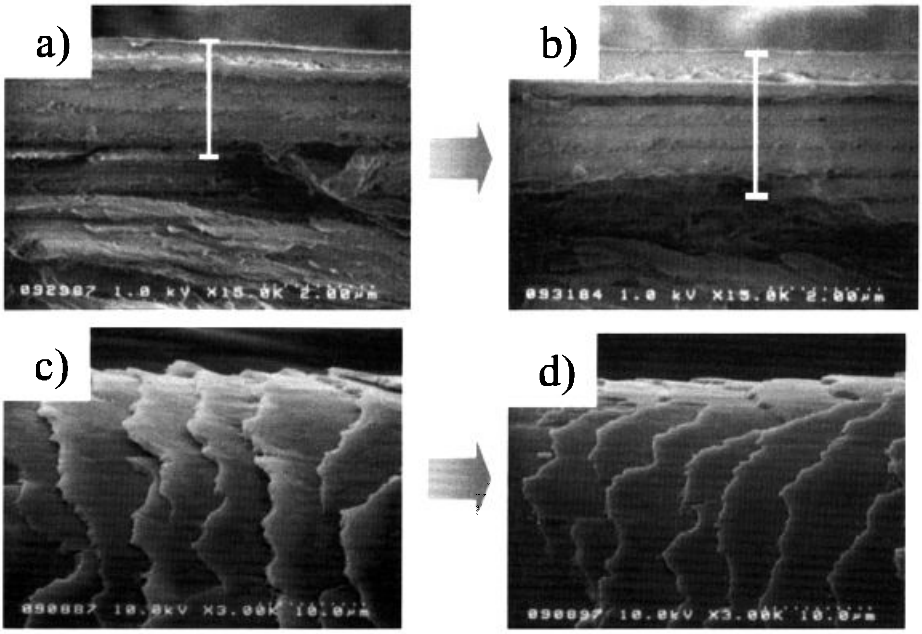

Figure 16. SEM observations of longitudinal and cross sections of hair fibers before (a,c) and after (b,d) MA/BOE treatment. The hair fiber was treated for one hour at 25°C.

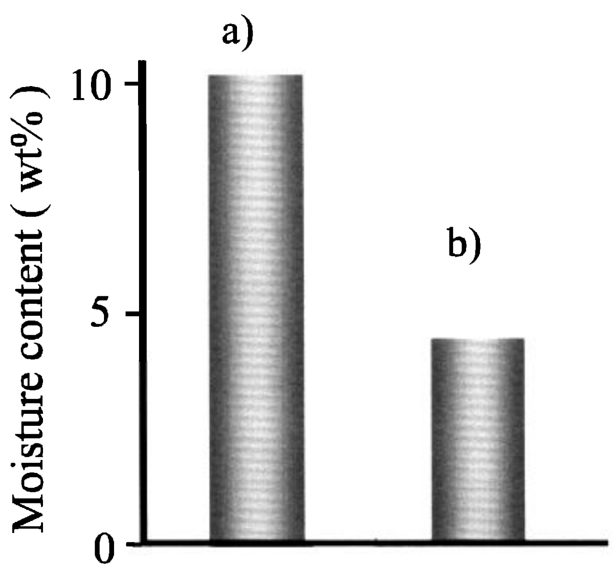

Figure 17. Variation of moisture content in hair fiber (a) before and (b) after MA/BOE treatment. The hair fiber was treated for one hour at 25°C.

Furthermore, the amount of agents (MA and BOE) that penetrated the hair was more than 10 wt%. The authors consider that the aqueous molecule is replaced by MA and BOE after the treatment, and that therefore the hair fiber treated with MA/BOE solution prevents the change in moisture content during the blow-drying process.

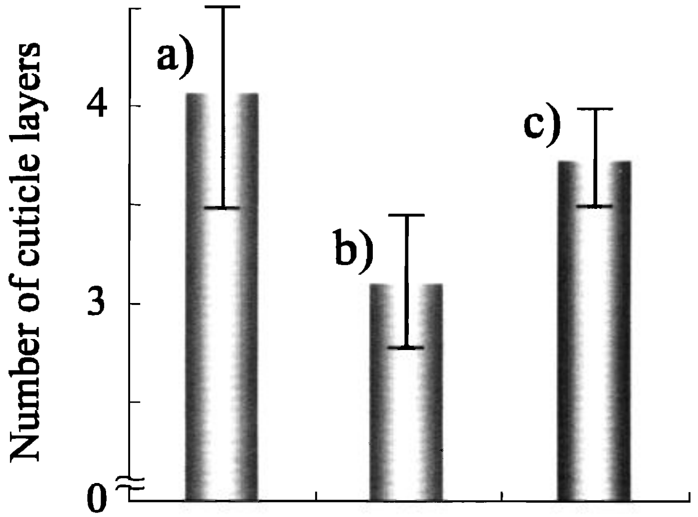

Figure 18. Mean total number of cuticle layers before and after cleansing/combing cycle.

In order to evaluate the protection effect of the MA/BOE against damage to the cuticle, a decrease in the number of the cells was counted after 150 times through the hair care cycle: shampooing/rinsing/blow-drying with combing. Figure 18 shows the comparison of the mean total number of cuticle layers before and after hair care cycles. The lack of cuticle layers was confirmed in fibers both with and without MA/BOE treatment during the cycles, but the fracture of cuticle layers was suppressed by MA/BOE treatment. It can be said, therefore, that MA/BOE treatment is effective both for developing hair shine and for protection from cuticle damage by the blow-drying/combing process.

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