EFFECT OF OXIDATION STRESS ON THE MECHANICAL PROPERTY OF HUMAN HAIR

Yoko Akiyama,* Yusuke Doi,* Yukako Matsue,** Fumihito Mishima,* and Shigehiro Nishijima*

Abstract

The tactile sensation of human hair during combing by finger or brush is deteriorated by damages induced by external stimuli, such as UV irradiation or bleaching. It is because the characteristics of human hair are affected by external environments. It is reported that the damage on human hair by UV irradiation is accelerated in bleached hair. In this study, changes in physical property of bleached and UV-irradiated hair were examined. Bending stiffness of bleached hair was larger than that of normal hair, and was increased further by UV irradiation. The results of FT-IR measurement showed that the bleach treatment and subsequent UV irradiation induces the S–S bond scission which causes elution or denaturation of amorphous matrix in the cortex layer. Elution of matrix protein causes decrease in water retention capacity, which decreases the flexibility of hair fibre. It was considered that the change in chemical structure induced by UV irradiation was more accelerated in the bleached hair, because reactive oxygen species is generated by residual hydrogen peroxide which causes the oxidative damage.

Key Words

Human hair, bleaching, ultraviolet, bending stiffness, FT-IR, reactive oxygen species

1. Introduction

It is empirically known that the tactile sensation of human hair during combing by finger or brush is deteriorated by damages induced by external stimuli. One of the main factors which cause hair damage is UV radiation. The damage caused by UV exposure is smaller for black hair which is generally typified by Asian hair, because it includes much melanin pigment [1], [2]. Even if the hair originally includes much melanin, the damages by UV exposure might be promoted by colouring and bleaching treatment, because of remaining agents and denaturation of hair itself [3]. It is also reported that more than 90% of the 18-MEA was removed by UV radiation with corresponding exposure for three summer months [4]. By elucidating the mechanism of oxidative damage by chemicals and UV, a guideline to prevent the hair damage would be clarified.

In this study, the mechanism of hair damage induced by the chemicals and UV irradiation was examined, by establishing a relationship between mechanical properties and microscopic structure. At first, the oxidative damage of human hair is considered from a macroscopic view by the bending test of a hair. To examine the microscopic damage mechanism, FT-IR was measured to track the structural change inside the hair fibre. Based on the results, the process of oxidation damage and the changing mechanism of the bending property were examined using the mechanical model of human hair fibre.

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2. Experimental Methods [5]

2.1 Treatment of Hair Samples

The virgin hair (Chinese hair), which neither underwent colouring nor other chemical treatment was used as the "untreated hair". The effect of bleach treatment, UV irradiation and their combined effect were investigated based on this unprocessed hair. "Bleached hair" with bleach treatment, "UV hair" with UV irradiation and "bleached UV hair" with UV irradiation after bleach treatment were, respectively, prepared. "Bleached hair" was prepared by soaking in 1:1 mixed solution of 8.6 wt% ammonia solution and 17.2% H_2O_2 for 30 min at 20°C, and then washed by ion exchange water and dried. UV irradiation was conducted with Xenon Wethermeter 7.5 kW (Suga Test Instrument Co., Ltd). The temperature in the chamber was 25 ± 1°C, wavelength was 300–700 nm and integrated radiation quantity was 1.2×10^7 J/m^2 (in the range from 300 to 400 nm).

2.2 Bending Test of the Human Hair

The test sheet which consists of 200 densely arrayed fibres of the hair was prepared for the bending test as shown in Fig. 1(a). The sample sheet was mounted into a test jig

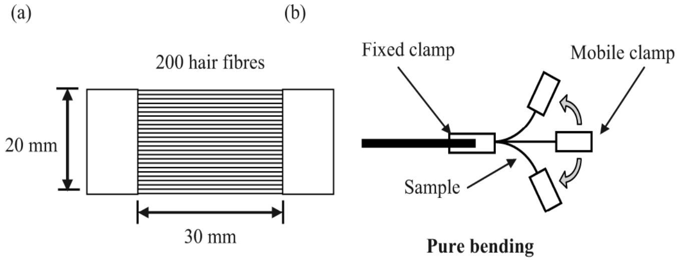

Figure 1. The schematic view of bending test: (a) hair sample for bending and (b) schematic diagram of the test.

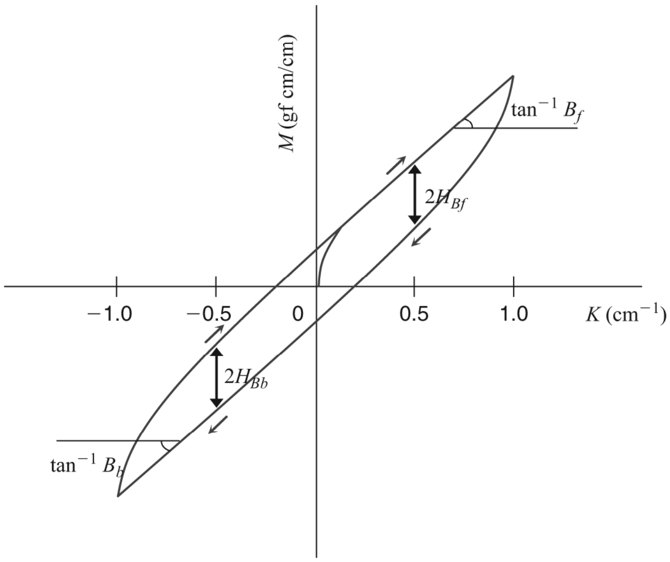

Figure 2. Typical bending moment-curvature curve. B_f is the gradient for the forward bending and B_b is for backward. H_{Bb} and H_{Bf} stand for the bending hysteresis, respectively, at the curvatures of -0.5 and $0.5\,\mathrm{cm}^{-1}$.

of pure bending tester (KES-FB2, Kato Tech Co., Ltd) with the gap of 1 cm and was angled by curvature range of $K = -1.0$ to $1.0\,\mathrm{cm}^{-1}$ at 25 ± 1.0°C and $60 \pm 10\%$ relative humidity at the bending speed of $0.50\,\mathrm{cm}^{-1}\,\mathrm{s}$ (Fig. 1(b)). Two sample sheets were prepared for each condition, and each sample was measured five times.

A typical bending moment as a function of curvature (maximum curvature was $1.0\,\mathrm{cm}^{-1}$) was shown in Fig. 2.

The bending moment corresponds to the moment per unit width for the sheet sample. The bending moment M is shown by following equation.

$$M = BK \pm H_b \tag{1}$$

Here, B is the bending stiffness per unit width ($\mathrm{gf\,cm^2/cm}$), and $2H_b$ is hysteresis width which indicates the bending property of the sample. B is the gradient of the M–K curve.

To determine B, the gradient B_f of M–K curve in the range from -0.5 to $0.5\,\mathrm{cm}^{-1}$ was calculated by collinear approximation, and then the gradient B_b in the same range when the sample is bent to the opposite side was also calculated in the same way. The average gradient of B_f and B_b was substituted into (1).

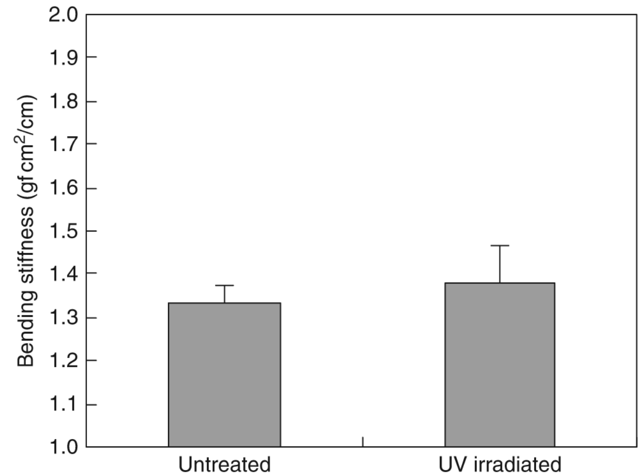

Figure 3. Average bending stiffness of untreated hair before and after UV irradiation, $p > 0.05$.

$$B = (B_f \pm B_b)/2 \tag{2}$$

The width of bending hysteresis $2H_b$ was calculated with the following equation from the hysteresis at the curvature of $\pm 0.5\,\mathrm{cm}^{-1}$.

$$2H_b = 2(H_{bf} \pm H_{bb})/2 \tag{3}$$

Bending stiffness B indicates the difficulty in bending, and larger value indicates that the sample is hard to bend. On the other hand, bending hysteresis $2H_b$ corresponds to the elasticity against the bending stress, and larger value corresponds to low reversibility against bending deformation.

2.3 FT-IR Measurement of the Hair Sample

The chemical structure of "untreated hair", "bleached hair" and "bleached UV hair" were measured by attenuated total reflection (ATR) method of FT-IR. The spectra were measured by using FT/IR-470 Plus (JASCO Co. Ltd, Japan) attached with ATR unit (ZnSe crystal) [3]. Spectra resolution was $2\,\mathrm{cm}^{-1}$ and the integration frequency was 128 for both background and sample measurement. The obtained absorption spectra was corrected and then normalized by the characteristic absorption band of amide III (1231–1235 cm^{-1}) as the internal reference.

3. Results

3.1 Bending Test of Human Hair Sample

The average bending stiffness and bending hysteresis were calculated from the M–K curve obtained by the bending test of hair samples. First, change in the bending stiffness by UV irradiation with and without bleach treatment was examined. The difference between two conditions

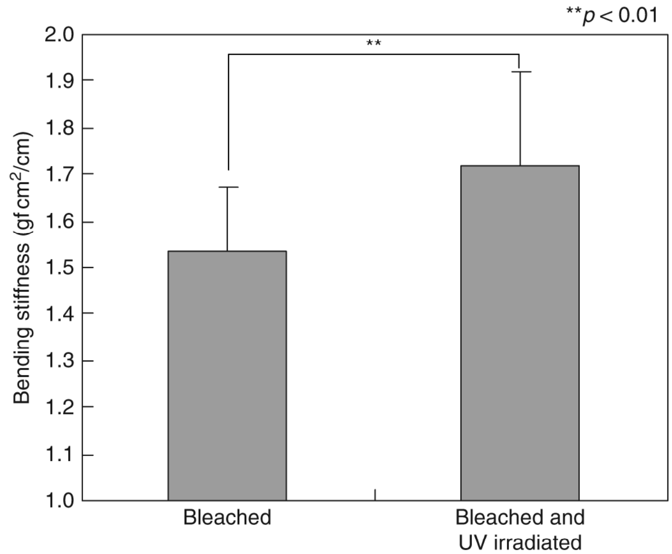

Figure 4. Average bending stiffness of bleached hair before and after UV irradiation.

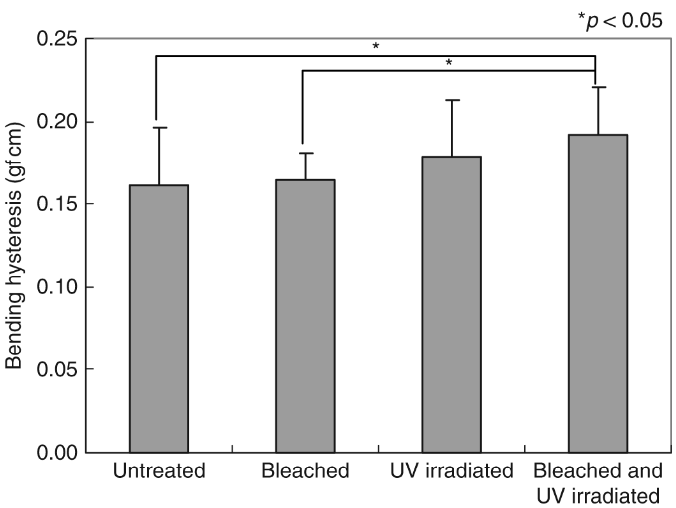

Figure 5. Average bending hysteresis of each hair sample.

was examined by t-test, and level of significance p was calculated. In the case of UV irradiation to the untreated hair, change in bending stiffness was small (Fig. 3). On the other hand, a significant difference was observed between irradiated and non-irradiated sample for bleached hair (Fig. 4). This indicates the possibility that the independent effect of UV irradiation on the mechanical property of human hair is small, but the change in the mechanical property is accelerated by the bleach treatment.

Figure 5 shows the bending hysteresis width of the treated hair samples. There was no significant difference between untreated and bleached hair.

On the other hand, in the same way as bending stiffness, the significant change was observed by UV irradiation for bleached sample. The increase in the hysteresis width by UV irradiation corresponds to the deterioration of the reversibility against bending deformation. From these results, it is concluded that the effect of UV was not detected for untreated hair, whereas the bending stiffness was increased and reversibility was decreased by UV irradiation for bleached hair.

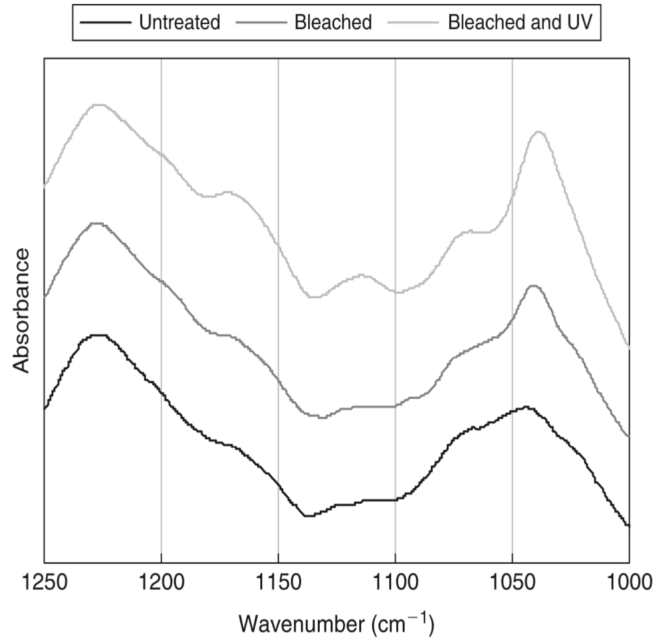

Figure 6. IR spectra of hair samples in absorption band of sulfur oxides.

3.2 FT-IR Spectra of Hair Samples

Figure 6 shows FT-IR spectra of human hair around the characteristic absorption band of sulfur oxide originated from cystine.

The peaks around 1040 and 1175 cm^{-1} corresponds to the characteristic band of cysteine acid, $–SO_3H$. The peaks of cysteine acid were observed in the bleached hair sample, and the intensity of these peaks became relatively high by UV irradiation. This residue is considered to be formed by oxidative cleavage of S–S bond. The peaks around 1075 and 1120 cm^{-1}, respectively, correspond to cystine monoxide R–SO–S–R of cystine and cystine monoxide $R–SO_2–S–R$ which are the oxidized intermediates.

These peaks are particularly significant for bleached UV hair. Based on the results, it is considered that S–S bond scission by following process (Fig. 7) through oxidized intermediate is induced by UV irradiation after bleach treatment [6].

Figure 8 shows the FT-IR spectra in the range of 1600–1700 cm^{-1}. This absorption band corresponds to C=O stretching vibration (amide I) in the peptide bond in the main chain of polypeptide in the human hair. The peaks originating from C=O stretching vibration shifts depending on the secondary structure of proteins (α-helix and β-sheet). In the bleached hair and bleached UV hair, the peaks around 1625 cm^{-1} decreased, which attributes to β-sheet or random coil observed in untreated hair, whereas the peak of α-helix around 1650 cm^{-1} became clear. This

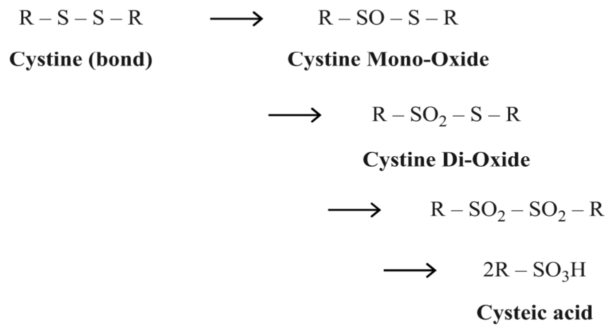

Figure 7. Oxidative scission of disulfide bonds in bleached hair by UV irradiation.

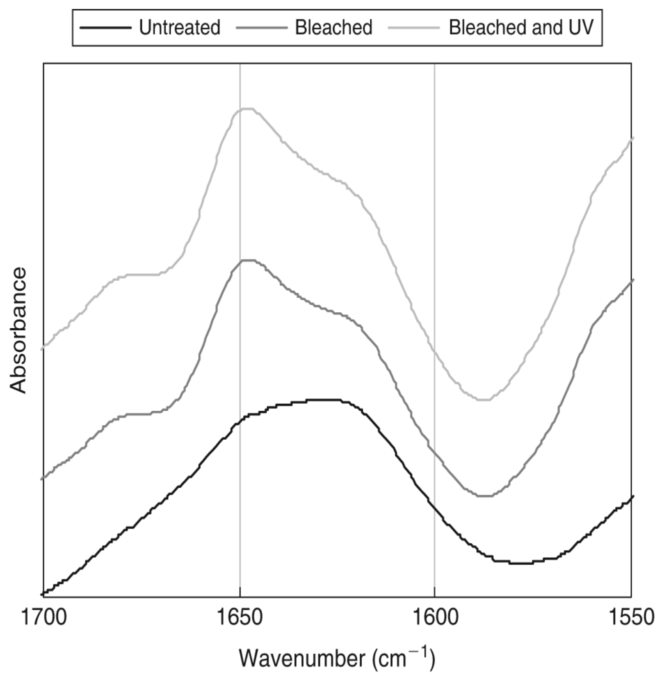

Figure 8. IR spectra of hair samples in absorption band of secondary structure of protein.

shows that α-helix structure became dominant in the secondary structure of protein by bleaching and UV irradiation. But it is quite unlikely for the protein structure to undergo a direct transition by bleach or UV irradiation. Therefore, it is considered that the β-sheet or random coil region in the protein was eluted or denatured by fragmentation, and consequently the ratio of α-helix increased. Particularly by bleach treatment, scission of peptide bond of main chain and disappearance of ionic bond between chains by alkaline component in the bleaching agent will be caused in addition to above-mentioned S–S bond scission (decrease in the intermolecular crosslinking) is expected to occur. These reactions promote the elution of proteins from the hair fibre. In addition, most of keratin in the amorphous region (matrix) in the cortex is in the spherical random coil because of shorter molecular length and smaller molecular weight, and thus it is most easy to elute.

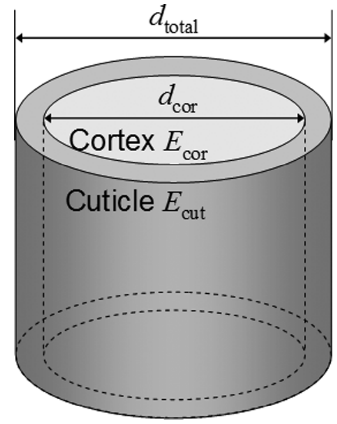

Figure 9. Double layer model of a hair fibre.

In this way, the bleach treatment and subsequent UV irradiation is considered to induce decrease in matrix protein by elution.

4. Discussions

4.1 UV Damage after Bleach Treatment

As mentioned above, deterioration in the mechanical property and chemical structure induced by UV irradiation was promoted for the bleached hair. One of the reasons is considered to be residual bleach reagent. The main content of bleaching reagent is hydrogen peroxide and ammonia solution. Oxidation ability of hydrogen oxide itself is not so high, but it can be easily decomposed to form the reactive oxygen species (ROS) such as hydroxyl radical with high-oxidation ability. By the oxidation ability of ROS, oxidative cleavage of S–S bond by above process is caused. In addition, in the bleaching process, the melanin is degraded into the low-molecular substance and is then eluted out of the hair fibre. Melanin behaves not only as an absorbent around the UV region but also as a radical scavenger which is degraded by ROS in priority to protein components of the hair fibre [6]. In addition to ROS formation by residual hydrogen peroxide, decrease in the defensive function against oxidative stress is caused by bleach treatment, and these factors promote the UV damage.

The human hair composed mainly of keratin and has three morphological regions; the cuticle, medulla and cortex. The cuticle is an outermost layer, the medulla is a central layer and the cortex is the intermediate layer. In general, the damage induced by UV irradiation is larger for amino acids and proteins in the cuticle than in the cortex. This is because external layer of fibre is exposed by high-intensity UV [7], and melanin content which absorbs UV in the cuticle is extremely low. Based on these facts, there is a possibility that the mechanical property of hair is also degraded in the case of UV irradiation to black hair.

We therefore discussed from the viewpoint of material mechanics about the respective contributions of mechanical properties of cortex and cuticle layers to the bending property of whole hair fibre. Figure 9 shows the double layer model of hair fibre consisting of cortex and cuticle. Here, the medulla layer was neglected because the volume fraction of medulla is only several percent and also because some of hair fibres have no medulla layer. The cross-sectional shape of hair fibre was presumed as a perfect circle in which the diameter of hair fibre was d_{total} and that of cortex layer was d_{cor}. The cortex and cuticle were, respectively, presumed as homogeneous substances with Young's modulus of E_{cor} and E_{cut}. The contributions of Young's modulus of cortex and cuticle layers to whole hair fibre were calculated with these parameters.

On the basis of general expression of material mechanics, the bending stress by bending moment M and curvature radius ρ is related as follows [8].

$$M = \frac{E \cdot I}{\rho} \tag{4}$$

Here, E is Young's modulus and I is geometric moment of inertia. Geometric moment of inertia depends on the cross-sectional shape and area, and stands for the difficulty of deformation against bending. From this equation, larger value of EI gives smaller value of $1/\rho$ (=K), which indicates that the substance is difficult to bend. EI is called as bending rigidity, which corresponds to bending stiffness B in bending test. When this relation was applied to double layer model of hair fibre, following relation is derived.

$$M = \frac{E_{total} \cdot I_{total}}{\rho} = \frac{(E_{cor} \cdot I_{cor} + E_{cut} \cdot I_{cut})}{\rho} \tag{5}$$

E_{total} is Young's modulus of whole hair fibre, and I_{total} is geometric moment of inertia of whole human hair. I_{cor} is geometric moment of inertia of cortex layer shown as follows.

$$I_{cor} = \frac{\pi}{64} d_{cor}^4 \tag{6}$$

On the other hand, I_{cut} is that of cuticle layer shown as follows.

$$I_{cut} = \frac{\pi}{64}(d_{total}^4 - d_{cor}^4) \tag{7}$$

From above relations, bending rigidity $E_{total} \cdot I_{total}$ of whole hair fibre is shown as follows. Generally, the thickness of cuticle layer is 10% of diameter of hair fibre, i.e. $d_{cor} = 0.8 d_{total}$.

$$\begin{aligned} E_{total} \cdot I_{total} &= E_{cor} \cdot \frac{\pi}{64}(0.8 d_{total})^4 \\ &\quad + E_{cut} \cdot \frac{\pi}{64}\{d_{total}^4 - (0.8 d_{total})^4\} \\ &= \frac{\pi}{64} d_{total}^4 (0.41 E_{cor} + 0.59 E_{cut}) \end{aligned} \tag{8}$$

Equation (8) shows that the contribution to Young's modulus of whole hair of cortex layer and cuticle layer is 41% and 59%, respectively. It indicates that mechanical property of cuticle layer contributes largely in the bending property of whole hair fibre in spite of the cross section of cuticle being only about 36% against the whole cross section of human hair. It is supposable from the fact that the cuticle layer is located on the outermost layer of the hair, and the strain and generated stress by external bending force is larger for cuticle than cortex relatively located near the neutral axis (Fig. 10). In addition, from nano-indentation studies [9], [10], it is reported that Young's modulus of cuticle is larger than that of cortex, which is also the factor that the contribution of the cuticle is larger.

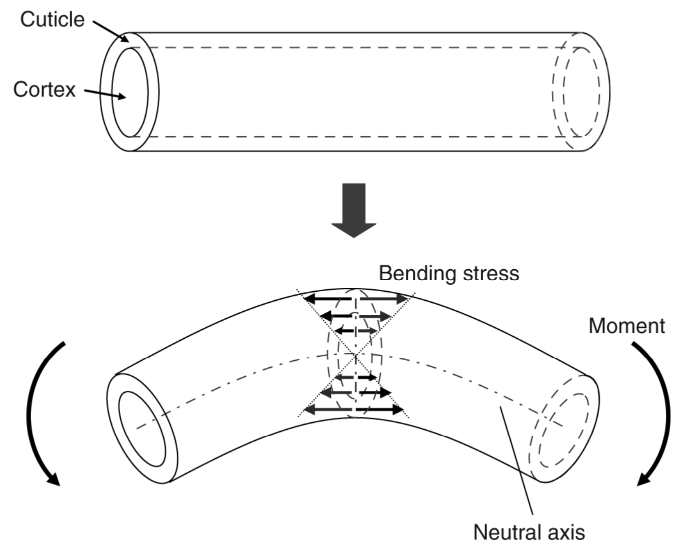

Figure 10. Bending stress in hair fibre consisting of cuticle and cortex.

In this way, it was shown that degradation of cuticle layer will contribute largely in the bending property of hair fibre. In this study, however, there was no significant difference between untreated hair (black hair) and UV hair. Nogueira *et al.* [2] reported that the UV-B irradiation (1.5×10^7 J/m^2 under 50% RH) to the black hair and native blond hair with low melanin content had no effect on the mechanical property. On the other hand, Matsuzaki *et al.* [11] confirmed that the UV irradiation to the human hair under dry condition had no effect on the mechanical property, but that small change was detected by irradiation under wet condition. From these results, it is considered that independent UV effect on the hair is small, but the deterioration is promoted by the indirect effect in the presence of the substance which has a potential to be radical precursor such as water and bleach reagent.

4.2 The Mechanism of Change in Mechanical Property of Human Hair

Scission of S–S bond and decrease in crosslink density is expected to have a softening effect on the fibre, but it is quite unlikely to have a direct effect on the increase in the bending stiffness [12]–[14]. Thus, the cause of increase in the bending stiffness is indirect effect of elution and denaturation of hair protein caused by scission of S–S bond.

From FT-IR spectra, it is supposed that most of the eluted or denaturated substance is matrix protein in the amorphous region in cortex. Here, Wortmann *et al.* [15] insisted that the contribution of amorphous matrix protein on the bending stiffness is relatively small. On the basis of this idea, the direct effect of S–S bond scission itself on the bending stiffness is sufficiently small. Fukuda *et al.* [16] reported about hygroscopic property of fibre that amorphous protein can be the main water sorption site. From this, elution or denaturation of matrix protein causes decrease in water retention capacity, which reduces the water content of hair. The decrease in the water content strengthens the inter/intramolecular hydrogen bond between protein molecules and decreases the flexibility of hair. In this way, it is supposed that the degradation of amorphous matrix causes loss of the moisturizing effect of the hair, which increases the bending stress. Increase in bending hysteresis corresponding to the deterioration of the recovery property also related to the water content of hair. It is reported by the ^{1}H-NMR study [17] that the water content of the hair fibre decreased by bleach treatment because of decrease in the water absorption site, and the water molecule bound strongly to the hair surface as primary water compared with normal hair. A highly moisturized hair fibre with much free water transforms elastically, whereas poorly moisturized one has plasticity. In other words, it is considered that the elastic limit is decreased by decrease in the water content, which causes plastic deformation easily.

5. Conclusions

The oxidation stress on human hair induced by bleach treatment and UV irradiation was investigated by bending test. In the case of UV irradiation to the untreated hair, change in bending stiffness and recovery was not observed, but a significant difference was observed between irradiated and non-irradiated sample for bleached hair. The mechanism of change in the physical properties was examined by FT-IR. The results showed that the bleach treatment and subsequent UV irradiation induces the S–S bond scission which causes elution or denaturation of amorphous matrix in the cortex layer. Elution or of matrix protein causes decrease in water retention capacity, which decreases the flexibility of hair fibre. As a result, deterioration in the mechanical property and chemical structure induced by UV irradiation was promoted with the bleached hair, because of ROS formation by residual hydrogen peroxide and decrease in the defensive function against oxidative stress.

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