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Reduction mechanism of tioglycolic acid on keratin fibers using microspectrophotometry and FT-Raman spectroscopy

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Abstract

In order to investigate the reduction mechanism of thioglycolic acid (TG) on the keratin fibers, cross-sectional samples of white human hair treated with TG were prepared. The heterogeneous reaction between TG and keratin fibers involving the diffusion of TG into human hair was analyzed at the molecular level using microspectrophotometry and FT-Raman spectroscopy. The diffusion of TG into human hair clearly increased by increasing the treatment time and by raising pH. The TG relative concentration and the disconnected relative concentration of disulfide (−SS−) groups at various depths of the hair samples with pH 9.0 were in good agreement, indicating that the reaction rate (the disconnection of −SS− groups) was faster than the diffusion rate of TG into human hair. From these experiments, we demonstrated that TG diffuses gradually beyond the cuticle region, and toward the inside of the cortex region along with the disconnection of −SS− groups.

Keywords: Keratin fibers; Reducing mechanism of thioglycolic acid; FT-Raman spectroscopy

1. Introduction

The setting treatment for wool fibers, and the permanent waving treatment for human hair fibers consists of two different processes, disconnection (the reduction process) and reconnection of disulfide (−SS−) groups (the oxidation process), and is widely used in the textile and hair styling industry. Also, the chemistry of the setting process and the changes in the chemical and physical properties of keratin fibers with reduction treatment have been widely studied [1–4]. However, studies on the mechanism connecting the chemical reaction between a reducing agent and the keratin fiber material, occurring on a molecular level, are still lacking comprehensiveness. Specifically, thioglycolic acid (TG) was used as a reducing agent in the first process (disconnection of −SS− groups). Therefore, it is important to investigate how TG diffuses into keratin fibers and how the chemical reaction between the reducing agent and keratin fibers occurs.

Herrmann [5] and Inoue et al. [6] evaluated the penetration of reducing agents into human hair treated beforehand with an iodine solution by observing the disappearance of the iodine color with optical microscopy. Wickett [7] evaluated the penetration of the reducing agent into the human hair, treated with reducing agents, and then dyed with methylene blue, by observing it with an optical microscope. However, these methods can not obtain the information about the diffusion behavior of a reducing agent into the human hair.

On the other hand, the work of Lin and Koenig has provided assignments for the side and main chain vibrations in wool keratin [8]. Raman spectroscopy has been used in previous work for fiber identification and characterization [9,10] and in structural studies of wool fabrics [11]. Hogg et al. reported structural change in wool fabrics subjected to hydrogen peroxide bleaching by employing FT-Raman spectroscopy [12]. Also, Jones et al. investigated the photo-oxidation of wool with FT-Raman spectroscopy [13]. The advantage of Raman spectroscopy for studying keratin fibers is that it is nondestructive and provides information about −SS− groups through reduction and oxidation, since bands can be assigned to S−S and C−S vibrations of cystine. Tanaka et al. investigated the influence of

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permanent waving treatment on –SS– groups in human hair [14]. Panda investigated the influence of permanent waving treatment, bleaching treatment, and photo-oxidation on human hair [15]. However, these methods can not obtain the information about the disconnection behavior of –SS– groups in human hair involving the diffusion of TG.

In this study, in order to investigate the reduction mechanism of TG on the keratin fibers, cross-sectional samples of white human hair treated with TG were prepared. The TG parts in the cross-sectional samples were dyed with methylene blue, and the influence of pH and treatment time on the penetration of TG was investigated with optical microscopy. Also, the diffusion behavior of TG into human hair was analyzed by measuring the diffusion profile of TG using microspectrophotometry. Moreover, the structure of hair fibers at various depths of the cross-sectional samples was analyzed using the FT-Raman technique. We have reported that the heterogeneous reaction (the disconnection of –SS– groups) between TG and keratin fibers involving the diffusion of TG into human hair was analyzed at the molecular level.

2. Experimental

2.1. Materials

Virgin Chinese white hair (average fiber diameter: 65 μm) as a keratin fiber was purchased from Beaulax Co. (Tokyo, Japan). Ammonium thioglycolate (content: 50 wt% TG solution) as a reducing agent was supplied by Osaka Sasaki Chemicals (Osaka, Japan). Tissue-Tek O.C.T.4583 Compound (Sakura Finetechnical Co., Tokyo, Japan) was used as an embedding resin to make up the fiber cross-section. Also, methylene blue as a basic dye, iodoacetamide and 25 wt% ammonia solution were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan).

2.2. Preparation of human hair treated with TG

The above human hair was immersed in a solution of 6.0 wt% TG adjusted varying pH (7.0, 8.0, 9.0; with ammonia water) at a ratio of hair to solution of 1:15. The hair samples were soaked at 25 °C for varying durations (3, 5, 15 min). After washing in distilled water for 1 min, the hair samples were dried at room temperature.

2.3. Preparation of human hair to measure using FT-Raman spectroscopy

Half of one of the above human hair fibers was used as an untreated sample (control sample). The other half of the human hair fiber was prepared by the following procedures. The piece of human hair was immersed in a solution of 6.0 wt% TG adjusted pH 9.0 (with ammonia water) at a ratio of hair to solution of 1:15. The hair sample was soaked at 25 °C for 5 min. After washing in distilled water for 1 min, the free thiol (–SH) groups that occurred by treating with TG, were blockaded by the following iodoacetamide treatment. The hair sample was immersed in a solution of 0.1 M iodoacetamide at a ratio of hair to solution of 1:250. The hair was soaked at 50 °C and for 30 min. Finally, the hair sample treated with TG was prepared by washing in distilled water for 1 min, and then drying at room temperature.

2.4. Evaluation of the penetration of TG into human hair

White human hair fibers treated with TG as described in the previous Section 2.2 were embedded in a resin (Tissue-Tek O.C.T.4583 Compound) and frozen. The frozen blocks were microtomed on a Leica CM1800 (Leica Instruments GmbH, Heidelberger, Germany) to 10 μm thickness, and mounted on a slide glass. Next, the TG penetrated part of the cross sectional samples were dyed with a solution of 0.005 wt% methylene blue at a room temperature with a syringe. Finally, the penetration of TG into the cross-sectional samples was examined by optical microscopy.

2.5. Evaluation of setting ability

Setting ability of human hair was evaluated according to the Kirby method [16]. A bundle sample (20 pieces, 20 cm) of virgin straight hair with uniform cuticle direction was soaked for 10 min at 50 °C in a solution of 0.5 wt% sodium laurylsulfate at a ratio of hair to solution 1:60. Next, the hair bundle sample was washed in distilled water, and then dried in air.

The Virgin straight hair bundle was interlaced between two rows of pegs (diameter: 3 mm) without tension, and held at each end with rubber bands. Next, the hair bundle sample was soaked for varying durations (3, 5, 15 min) at 25 °C in a solution of 6.0 wt% TG adjusted varying pH (7.0, 9.0; with ammonia water) at a ratio of hair to solution of 1:250. After washing in distilled water, the hair bundle was soaked for 15 min at 25 °C in a solution of 6.0 wt% sodium bromate at a ratio of hair:solution = 1:250. After washing in distilled water, the hair sample was slipped carefully out of the pegboard, and then set softly on a glass plate (finishing procedure). Finally, the length of the waved hair was measured from the first to the fourth crest of the wave, and the waving efficiency was estimated by formula 1 (measuring procedure). In this case, it is A : the distance between 5 pegs on center = constant = 24 mm, B : the length of a section of the waved hair (between the 5 pegs), after being removed from the pegboard, C : the length of the section of the waved hair after it was removed from the

pegboard and stretched = constant = 70 mm:

Waving Efficiency(%)

$$= 100 - \{100 \times (B - A)/(C - A)\} \quad (1)$$

2.6. Microspectrophotometry

The cross-sectional intensity scans of the hair samples were obtained using a microspectrophotometer (MSP) (DMSP-II, Olympus Optical Co. Ltd., Tokyo, Japan).

The cross-sectional samples mounted on a slide glass were dropped with a solution of 0.005 wt% methylene blue at a room temperature with a syringe. The penetrated TG parts of cross-sectional samples were dyed at a room temperature for 1 min. Next, the cover glasses were placed on the cross-sectional samples, and the slide glass mounted cross-sectional samples were set on the speciman stage. Finally, the diffusion behavior of TG that penetrated into human hair was examined at a wavelength of 664 nm (λ_{max} of methylene blue) with a microspectrophotometer. Here, the cross-sectional intensity scan was measured with light source conditions: tungsten filament lamp, spot diameter: 5.3 μm, scanning speed: 10 μm/min, recording speed: 20 mm/min. Also, as a blank, the cross-sectional intensity scan of the same cross-sectional sample was measured at a wavelength of 430 nm.

2.7. FT-Raman spectra

FT-Raman spectra of the hair samples were obtained using a Ramaonor T-64000 (Jobin Yvon, Longjumeau, France) equiped with a microprobe. The samples were excited with an argon laser operating at 514.5 nm and emitting 50 mW of optical power focused on the sample. Spectra were collected at 2.3 cm^{-1} resolution with 1 scan (1000 s). The cross-section samples were produced using white human hair, and sections of the hair at varying depths (1, 5, 7, 10, 15, 20 and 30 μm) from the surface (spot diameter: 1 μm) were measured.

3. Results and discussion

3.1. Penetration of TG into human hair

TG has anionic charges above pH 7.0 due to a carboxyl group in the molecule. So, the penetration of TG into the human hair can be observed by dyeing TG penetrated parts with basic dye (methylene blue etc.). Here, we prepared the cross-sectional samples of human hair treated with TG. Next, the penetration of TG for the cross-sectional samples dyed with methylene blue was estimated by optical microscopy. The photomicrograph of the white human hair cross-sectioned and finally dyed with methylene blue is shown in Fig. 1. The photomicrograph of the white human hair treated with TG at 25 °C and pH 9.0 for 5 min, then cross-sectioned and finally dyed with methylene blue, is shown in Fig. 2. The photomicrograph of the white human hair treated with TG at 25 °C and pH 9.0 for 15 min, then cross-sectioned and finally dyed with methylene blue, is shown in Fig. 3. The white human hair sample untreated with TG adsorbed the methylene blue marginally into the surface of the cuticle, but did not adsorb the methylene blue into the cortex. On the other hand, the white human hair treated with TG at 25 °C and pH 9.0 for 5 min, adsorbed the methylene blue through the cuticle and partially into the cortex (Fig. 2). Also, this sample absorbed the methylene blue into the medulla. We believe that the TG that existed in the surface of the cuticle, inserted into the medulla when preparing the cross-sectional sample. This suggests that the penetration of TG can be observed by using the above method. Moreover, the white human hair treated with TG at 25 °C and pH 9.0 for 15 min, was dyed with methylene blue from the cuticle through the complete cortex and the medulla (Fig. 3). Furthermore, we observed cuticle damage due to the long treatment time.

The influence of pH and treatment time on the penetration of TG into human hair was investigated by using the above method. The penetration of TG (at 25 °C) estimated by optical microscopy for cross-sectional samples dyed with methylene blue, is shown in Table 1. The penetration of TG into human hair clearly increased by increasing the treatment time and by raising the pH. This suggests that the penetration of TG into human hair is influenced by pH and treatment time.

3.2. Diffusion behavior of TG into human hair

Microspectrophotometry has been used to analyze the diffusion behavior of disperse dyes into various fibers [17,18]. Han et al. analyzed the diffusion behavior of semipermanent hair dyes into human hair fibers using microspectrophotometry, and then reported that the diffusion coefficient of HC Red 3 into human hair was to the order of 10^{-10} cm^2/s [19]. We reported that the diffusion

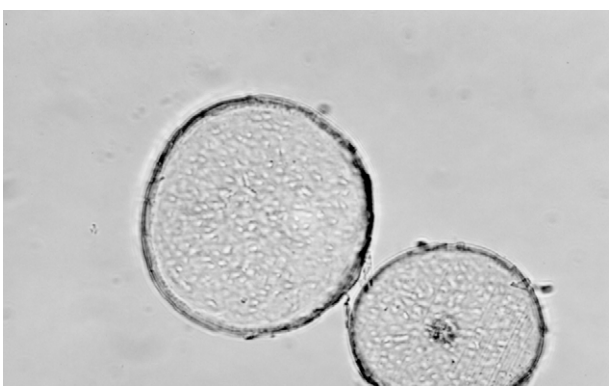

Fig. 1. Photomicrograph of white human hair cross-sectioned and finally dyed with methylene blue.

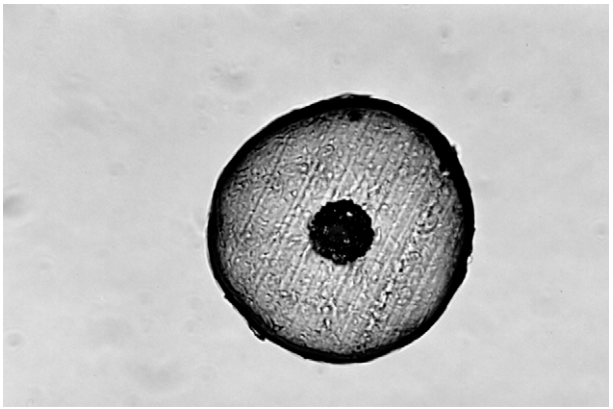

Fig. 2. Photomicrograph of white human hair treated with TG at 25 °C and pH 9.0 for 5 min, then cross-sectioned and finally dyed with methylene blue.

coefficient of polyethyleneimine (the number-average molecular weight: 300, 600) into bleached human hair was to the order of 10^{-10} cm^2/s using microspectrophotometry [20,21].

In this study, the diffusion behavior of TG into human hair was analyzed using microspectrophotometry. The cross-sectional intensity scans at 664 and 430 nm of the white human hair treated with TG at 25 °C and pH 9.0 for 5 min, then cross-sectioned and finally dyed with methylene blue, is shown in Fig. 4. Methylene blue concentration, namely TG concentration decreased from the fiber surface to cortex as shown by scanning. Also, the pseudo peak in the vicinity of the fiber surface arises due to the difference in the refractive index of water and the refractive index of hair fiber (Veckerain phenomenon). So, the diffusion profile of TG was drawn by subtracting the cross-sectional intensity scan at 430 nm (blank) from the cross-sectional intensity scan at 664 nm.

The TG relative concentration (c/c_0) profile at 25 °C and pH 9.0 for 5 min is shown in Fig. 5. Here, it is c_0 : TG concentration at fiber surface, c : TG concentration when distance from the fiber surface is x. The diffusion pattern of TG comparatively revealed Fickian type characteristics.

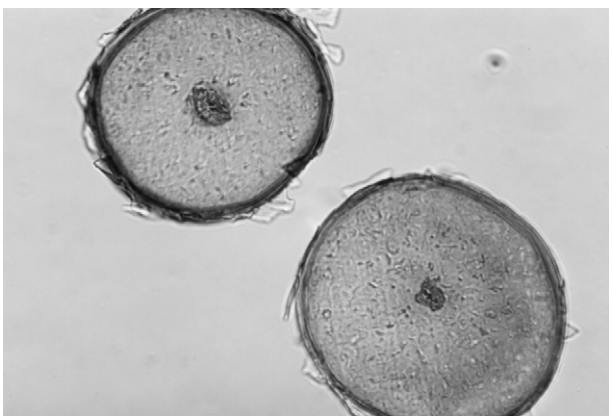

Fig. 3. Photomicrograph of white human hair treated with TG at 25 °C and pH 9.0 for 15 min, then cross-sectioned and finally dyed with methylene blue.

Table 1
Penetration of TG (at 25 °C) estimated by optical microscopy for cross-sectional samples dyed with methylene blue

PH	Penetration (μm)		
	3 min	5 min	15 min
7.0	–	4.63	13.9
8.0	–	9.26	33.3
9.0	9.26	23.2	Complete

The interpretation for the diffusion coefficient of TG is complicated due to involving the reducing reaction of –SS– groups in human hair. The activator for the disconnection of –SS– groups is the merucaptide ion (RS–), not the merucaptan. So, the reaction rate is significantly influenced by pH. In the case of raising pH, the reaction rate (the disconnection of –SS– groups) is faster than the diffusion rate since merucaptide ion concentration is high [2]. However, in the case of lowering pH below 7.0, the reducing reaction becomes a rate-determining step since the decrease in the reaction rate is more than the decrease in the diffusion rate. Actually, the penetration of TG into human hair was quite different at pH 7.0 and pH 9.0 (Table 1).

Moreover, the apparent diffusion coefficient at each concentration determined from the TG relative concentration profile using an Eq. (2) developed by Matano [22,23] and an Eq. (3) developed by Karasawa et al. [23,24]. In this case, it is $D_{c=c1}$: diffusion coefficient at concentration $c1$, x : distance from the fiber surface, c_0 : TG concentration at the fiber surface ($x = 0$), c : TG concentration when distance from the fiber surface is x, C : relative concentration, β and γ : variable parameter.

$$D_{c=c1} = -\frac{1}{2t}\frac{dx}{dc}\int_0^{c1} x\,dc \tag{2}$$

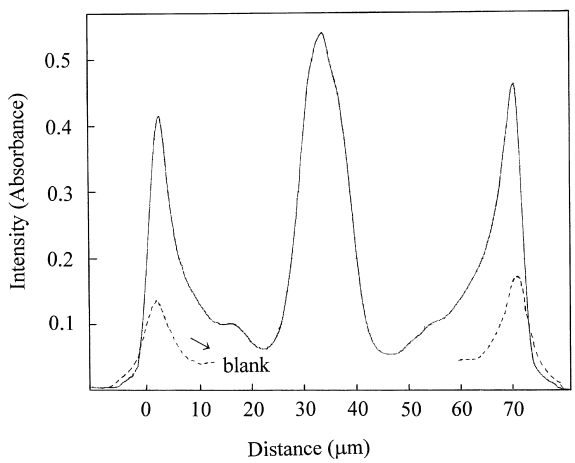

Fig. 4. Cross-sectional intensity scans at 664 and 430 nm (blank) of white human hair treated with TG at 25 °C and pH 9.0 for 5 min, then cross-sectioned and finally dyed with methylene blue.

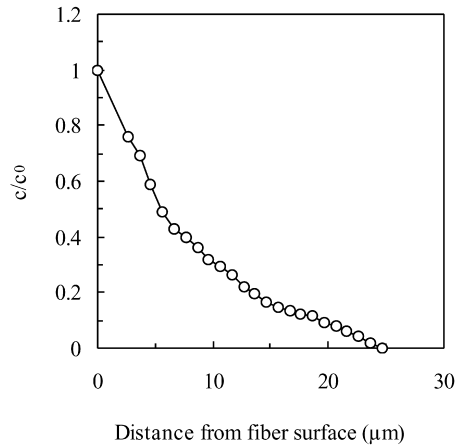

Fig. 5. TG relative concentration (c/c_0) profile at 25 °C and pH 9.0 for 5 min.

$$C = \frac{c}{c_0} = \exp(\beta x^{\gamma}) \quad (3)$$

The apparent diffusion coefficient (D) of TG into human hair as a function of the relative concentration (c/c_0) calculated from the TG relative concentration profile (Fig. 5), is shown in Fig. 6. The apparent diffusion coefficient (D) of TG slightly decreased by increasing the relative concentration (c/c_0), suggesting a weak static interaction between TG and human hair. However, since the apparent diffusion coefficient of TG for the most part did not depend on the concentration, the apparent diffusion coefficients were calculated from the average value at TG relative concentrations of 10, 20, 30, 40, 50, 60, 70, 80 and 90%.

The apparent diffusion coefficients calculated from the TG relative concentration profiles are shown in Table 2. The apparent diffusion coefficient of TG (23.6×10^{-10} cm^2/s) at pH 9.0 (treatment time: 5 min) increased about 8 times in comparison with that of TG (3.00×10^{-10} cm^2/s) at pH 7.0 (treatment time: 15 min). Also, the apparent diffusion coefficient of TG depended on the pH of the TG solution.

From this experiment, the apparent diffusion coefficient of TG into human hair at pH 9.0 is found to be very high compared with that of HC Red 3 and polyethyleneimine (M_w = 300, 600).

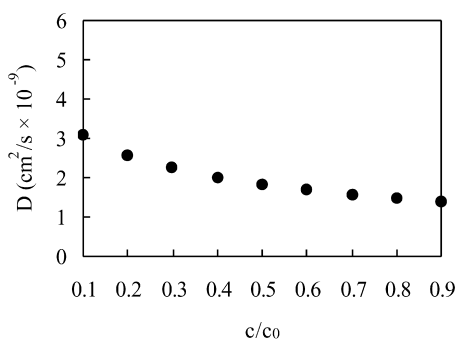

Fig. 6. Apparent diffusion coefficient (D) of TG into human hair as a function of the relative concentration (c/c_0) calculated from the TG relative concentration profile (Fig. 5).

Table 2
Apparent diffusion coefficients calculated from the TG concentration profiles (n = 4)

PH	$D \times 10^{10}$ (cm^2/s)[a]
9.0	23.6 ± 3.4
7.0	3.00 ± 0.62

[a] Mean ± standard deviation.

3.3. Structure of hair fiber

Measurement by FT-Raman spectroscopy becomes a beneficial means of investigating the reducing and oxidizing mechanism due to it being able to obtain information on disulfide (–SS–) groups in human hair.

So, we measured the FT-Raman spectra of the human hair fiber untreated and treated with TG at various depths. The FT-Raman spectra of the untreated human hair fiber at depths of 1, 5, 10 and 30 μm are shown in Fig. 7. The depth of 1 μm from fiber surface corresponds to the cuticle region, and the depth of 5–30 μm from fiber surface corresponds to the cortex region. It is shown that the spectral pattern of the human hair fiber at the depth of 1 μm was different with that of the human hair fiber at the depth of 5, 10 and 30 μm.

First, the spectral assignments of human hair fiber were performed based on that of wool fiber, which have been given by Lin and Koenig [8], Carter et al. [25]. The bands of particular interest lie in the wave number range of 500–1800 cm^{-1}. The frequencies and tentative assignments of

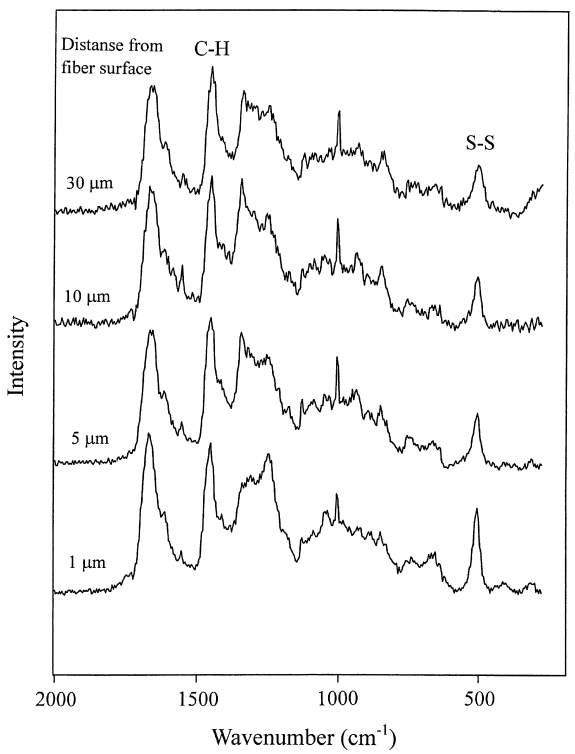

Fig. 7. FT-Raman spectra of the untreated human hair fiber at depths of 1, 5, 10 and 30 μm.

untreated human hair fiber (the cuticle region and the cortex region) are shown in Table 3. The band at 932 cm^{-1}, assigned to C–C skeletal stretching of the α-helical backbone, appears in the case of the cortex region only. This is in agreement with the findings by Fraser et al., in which microfibril that exists in the cortex is mainly composed of α-helical protein [26,27]. Also, for the amide I region, the peak at 1658 cm^{-1}, assigned to α-helical conformation was observed. On the other hand, in the case of the cuticle region (depth of 1 μm from fiber surface), the band at 932 cm^{-1}, assigned to C–C skeletal stretching of the α-helical backbone does not appear. This suggests that α-helical conformation does not exist in the cuticle region.

The FT-Raman spectra of the human hair fiber treated with TG (at 25 °C and pH 9.0 for 5 min) at depths of 1, 5, 7, 10, 15 and 30 μm are shown in Fig. 8. Similarly in the case of the untreated human hair fiber, the spectral pattern of the cuticle region was different from that of the cortex region. The peak intensity at 510 cm^{-1} assigned to the –SS– groups (the stretching vibration of S–S bond), decreased when progressing from center to fiber surface. On the other hand, the band at 932 cm^{-1}, assigned to C–C skeletal stretching of the α-helical backbone, does not disappear when progressing from the center to fiber surface with the cortex region at a depth of 5–30 μm from fiber surface. This suggests that the α-helical conformation is not influence by the disconnection of –SS– groups. This result is in agreement with the opinion of Freser et al., in which the intramoleculer –SS– groups does not form in the α-helical backbone [28].

Table 3
Frequencies and tentative assignments of untreated human hair (the cuticle region and the cortex region) as compared with that of wool

Human hair		Wool		Assignment
Cuticle[a] (cm^{-1})	Cortex[b] (cm^{-1})	Ref. [25] (cm^{-1})	Ref. [8] (cm^{-1})	
1669	1658	1658	1653	Amide I
1613	1612	1615	1614	Tyr and Trp
1553	1552	1558	1553	Trp
1449	1449	1450	1448	CH_2 bending mode
ND[c]	1338	1340	1338	CH_2 bend, Trp
ND	1315	1316	1318	Cα-H bend
1245	1246	1245	1244	Amide III (unordered)
ND	1210	1209	1207	Tyr and Phe
ND	1174	1180	1176	Tyr
1123	1123	1126	1126	C–N stretch
ND	1030	1034	1031	Phe
1002	1001	1006	1002	Phe
959	ND	959	952	CH_2 rock
ND	932	935	934	Skeletal C–C stretch (α)
884	880	883	881	Trp
851	852	852	851	Tyr
ND	750	752	752	Trp
670	669	665	661	Cys C–S stretch
642	642	644	642	Tyr
509	510	512	512	Cys S–S stretch g–g

[a] Depth of 1 μm from hair surface.
[b] Depth of 5 μm from hair surface.
[c] Non-detect.

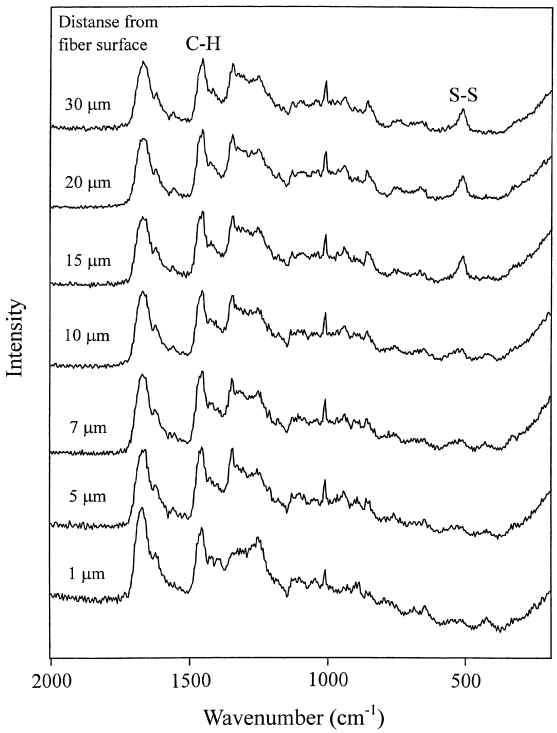

Fig. 8. FT-Raman spectra of the human hair fiber treated with TG (at 25 °C and pH 9.0 for 5 min) at depths of 1, 5, 7, 10, 15 and 30 μm.

Next, the disulfide (–SS–) content at various depths of the hair fibers untreated and treated with TG was compared by FT-Raman spectroscopy. Normalization of Raman spectra of keratin fibers is often carried out based on the C–H band at 1450 cm^{-1} [13], amide I band at 1657 cm^{-1} [25], and the Phenylalanine (Phe) peak at 1003 cm^{-1} [29–31]. In particular, the normalization of the Phe peak, which is not influenced by the chemical modification, is effective when estimating the –SS– content of the keratin samples affected by the chemical modification. Here, we chose the C–H band, which is assigned at 1450 cm^{-1}, for normalization because the peak area is large.

The ratio of the peak area of the S–S band (drawn baseline between 450 and 610 cm^{-1}) naturally existing in the human hair on the basis of the peak area of the C–H band (drawn baseline between 1375 and 1500 cm^{-1}), is believed to be the standard of –SS– content. The comparison of the ratio values for treated and untreated samples at depths of between 1 and 30 μm from the fiber surface are shown in Tables 4 and 5. The depth profile, which is a function of the –SS– content (the ratio of the peak area: B/A = S–S band/C–H band) and the distance from fiber surface, of human hair untreated and treated with TG at 25 °C and pH 9.0 for 5 min is shown in Fig. 9. The –SS– content (the ratio of the peak area: B/A = S–S band/C–H band) of the cuticle region was clearly higher than that of the cortex region. Also, the ratio of the peak area (the ratio of the peak area:

Table 4
Relationship between distance from fiber surface and disulfide content in untreated human hair

Distance from fiber surface (μm)	Peak area		Disulfide content:ratio of peak area (*B*/*A*)
	A : C–H[a]	*B* : S–S[b]	
1	98.49	50.05	0.51
5	81.20	29.50	0.36
10	62.94	24.39	0.39
30	38.41	13.34	0.35

[a] Drawn baseline between 1375 and 1500 cm^{-1}.
[b] Drawn baseline between 450 and 610 cm^{-1}.

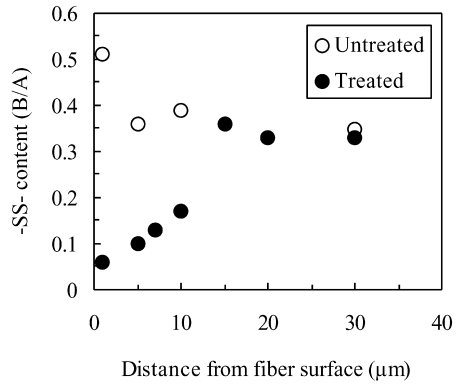

Fig. 9. Depth profile, which is a function of the –SS– content (the ratio of the peak area: *B*/*A* = S–S band/C–H band) and the distance from fiber surface, of human hair untreated and treated with TG at 25 °C and pH 9.0 for 5 min.

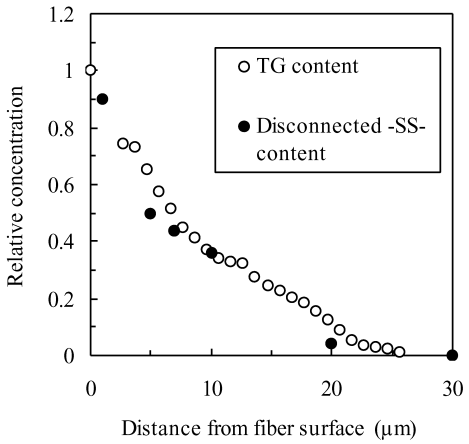

Fig. 10. Relationship between the TG relative concentration and the disconnected relative concentration of –SS– groups of human hair treated with TG at 25 °C and pH 9.0 for 5 min.

B/*A* = S–S band/C–H band) of the cortex region at depths of between 5 and 30 μm from the fiber surface were constant. This suggests that the –SS– content is equally distributed in the cortex region.

The relationship between the TG relative concentration and the disconnected relative concentration of –SS– groups of human hair treated with TG at 25 °C and pH 9.0 for 5 min is shown in Fig. 10. Here, it was assumed that the –SS– content is equally distributed in the cortex region (the ratio of the peak area: *B*/*A* = 0.35), and the relative disconnected –SS– content of the treated human hair at the depth of 1 μm from fiber surface is 0.9. The TG relative concentration and the disconnected relative concentration of –SS– groups at various depths of the hair samples with pH 9.0 were in good agreement, indicating that the reaction rate (the disconnection of –SS– groups) was faster than the diffusion rate of TG into human hair.

From this experiment, we demonstrated that diffusion of TG and the disconnection of –SS– groups proceeded together, gradually, beyond the cuticle region, and toward the inside of the cortex region for samples at pH 9.0.

Table 5
Relationship between distance from fiber surface and disulfide content in human hair treated with 6.0% TG at 25 °C, pH 9.0 for 5 min

Distance from fiber surface (μm)	Peak area		Disulfide content:ratio of peak area (*B*/*A*)
	A : C–H[a]	*B* : S–S[b]	
1	214.95	12.54	0.06
5	207.70	20.51	0.10
7	221.83	28.16	0.13
10	240.67	40.78	0.17
15	194.23	68.96	0.36
20	310.59	101.50	0.33
30	269.61	88.46	0.33

[a] Drawn baseline between 1375 and 1500 cm^{-1}.
[b] Drawn baseline between 450 and 610 cm^{-1}.

3.4. Setting ability of the waved hair

In the section above (Section 3.1), we showed that the penetration of TG into human hair clearly increased by increasing the treatment time and by raising the pH. In this study, moreover, the relationship between the penetration of TG into human hair and the setting ability of the waved hair samples treated with TG were investigated. The waving efficiency of the waved hair samples at 25 °C is shown in Table 6. Similarly, in the case of the penetration of TG into human hair, the waving efficiency of the waved hair samples treated with TG clearly increased by increasing the treatment time and by raising pH. This result reveals that the penetration of TG into human hair is correlated with the setting ability of the waved hair samples treated with TG. This suggests that the setting ability of the waved hair treated with TG directly reflects the content of disconnected –SS– groups.

4. Conclusions

The TG parts of cross-sectional samples of human hair treated with TG were dyed with methylene blue, and then the penetration of TG into human hair was evaluated by optical microscopy. The penetration of TG into human hair clearly increased by increasing the treatment time and by raising the pH.

Next, the diffusion behavior of TG into human hair was analyzed by measuring the TG concentration profile of TG using microspectrophotometry. The diffusion pattern of TG comparatively revealed Fickian type characteristics. Also, the apparent diffusion coefficient of TG into human hair at pH 9.0 determined from the TG concentration profile, is found to be to the order of 10^{-9} cm^2/s. On the other hand, the apparent diffusion coefficient of TG into human hair at pH 7.0 is found to be to the order of 10^{-10} cm^2/s, and the apparent diffusion coefficient of TG clearly depended on the pH of the TG solution.

Moreover, the structure of hair fibers at various depths of the cross-sectional samples was analyzed using the FT-Raman technique. The TG relative concentration and the disconnected relative concentration of disulfide (–SS–) groups at various depths of the hair samples with pH 9.0 were in good agreement, indicating that the reaction rate (the disconnection of –SS– groups) was faster than the diffusion rate of TG into human hair.

Table 6
Waving efficiency of the waved hair samples at 25 °C

pH	Waving efficiency (%)		
	3 min	5 min	15 min
7.0	–	–	12.1
9.0	22.8	48.4	79.1

Kirby method.

From these experiments, we demonstrated that TG diffuses gradually beyond the cuticle region, and toward the inside of the cortex region along with the disconnection of –SS– groups. Also, the penetration of TG into human hair was correlated with the setting ability of the waved hair samples treated with TG, suggesting that the setting ability of the waved hair treated with TG directly reflects the content of disconnected –SS– groups.

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