Diffusion Behavior of Reducing Agents into Keratin Fibers Using Microspectrophotometry

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Received 18 March 2003; accepted 25 May 2004
DOI 10.1002/app.21019
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: To investigate the penetration of thioglycolic acid (TG), thiolactic acid (TL), and L-cysteine (CYS), into keratin fibers, cross-sectional samples of virgin white human hair treated with TG, TL, and CYS were prepared. A new method for analyzing the diffusion behavior of reducing agents into human hair was developed. The diffusion pattern of reducing agents into human hair, which cannot be determined by optical microscopy, can be determined by the method developed. The method involves treating virgin hair fibers with TG, TL, and CYS. After the treatment, the cross-sectioned hair samples were dyed with methylene blue and the cross-sectional intensity scans were measured at a wavelength of 664 nm (λ_{max} of methylene blue) with a microspectrophotometer. The three different diffusion patterns from the three reducing agents were obtained. The penetration of TG and TL into virgin human hair clearly increased by increasing the treatment time and pH. On the other hand, the penetration of CYS was less than TG and TL (CYS could not penetrate into the cortex region of the virgin human hair). Also, the diffusion pattern of TG showed Fickian type characteristics. The apparent diffusion coefficient of TG into human hair at pH 9.0 determined from the TG concentration profile was found to be 10^{-9} cm^2/s. On the other hand, the apparent diffusion coefficient of TG into human hair at pH 7.0 was 10^{-10} cm^2/s, and thus, the apparent diffusion coefficient of TG depended on the pH of the TG solution. From these experiments, we have concluded that the diffusion patterns of the three reducing agents in this study depended on the electrostatic interaction between the human hair and the reducing agents. J Appl Polym Sci 94: 1131–1138, 2004

Key words: keratin fibers; diffusion; reducing agents; biopolymers; microspectrophotometry

INTRODUCTION

The setting treatment for wool fibers and the permanent waving treatment for human hair fibers consists of two different processes, disconnection (the reducing process) and reconnection of disulfide (–SS–) groups (the oxidizing process), and is widely used in the textile and beauty treatment industry. Also, the chemistry of the setting process and the changes in the chemical and physical properties of keratin fibers that have undergone reduction treatment have been widely studied.[1–4] Specifically, thioglycolic acid (TG) and L-cysteine (CYS) was used as reducing agents in the first process (disconnection of –SS– groups). The penetration of reducing agents into human hair becomes the trigger of the waving formation. Although TG has good performance in the waving formation of human hair, it is well known that the hair treated with TG is damaged.[5–8] In a previous paper, we demonstrated that TG diffuses gradually beyond the cuticle region and toward the inside of the cortex region along with the disconnection of the –SS– groups.[9] On the other hand, it has been shown in experiments that hair treated with CYS is damaged less than hair treated with TG, although CYS does not perform well with regard to the waving formation of human hair. However, detailed studies on the reduction mechanism of CYS are still lacking. Therefore, it is important to study the diffusion behavior of reducing agents into keratin fibers when trying to understand the relationship between the setting ability and the degree of damage of waved hair.

Herrmann[10] and Inoue et al.[11] evaluated the penetration of reducing agents into human hair pretreated with an iodine solution by observing the disappearance of the iodine color with optical microscopy. Wickett[12] evaluated the penetration of the reducing agent into human hair treated with reducing agents and then dyed with methylene blue, by observing it with an optical microscope. However, these methods cannot obtain information about the diffusion behavior of a reducing agent into the human hair.

In this study, to study the diffusion behavior of reducing agents into keratin fibers, cross-sectional samples of virgin white human hair treated with TG, thiolactic acid (TL), and CYS were prepared. The TG, TL, and CYS parts in the cross-sectional samples were

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dyed with methylene blue, and the influence of pH and treatment time on the penetration of TG, TL, and CYS was investigated with optical microscopy. The diffusion behavior of TG, TL, and CYS into virgin human hair was analyzed by measuring the diffusion profile of TG, TL, and CYS using a microspectrophotometer. We have reported the three different diffusion patterns of reduction agents obtained.

EXPERIMENTAL

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 % thioglycolic acid solution), thiolactic acid, and L-cysteine as reducing agents were 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. Methylene blue as a basic dye and 25 wt % ammonia solution were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan).

Preparation of human hair treated with TG

Human hair was immersed in a solution of 6.0 wt % TG adjusted to varying pH values (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, and 15 min). After washing in distilled water for 1 min, the hair samples were dried at room temperature.

Preparation of human hair treated with TL

Human hair was immersed in a solution of 6.91 wt % TL adjusted to varying pH values (7.0, 7.6, 8.0, 9.0, 9.5; 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, and 20 min). After washing in distilled water for 1 min, the hair samples were dried at room temperature.

Preparation of human hair treated with CYS

Human hair was immersed in a solution of 7.87 wt % CYS adjusted to varying pH values (7.0, 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 (5, 15, and 30 min). After washing in distilled water for 1 min, the hair samples were dried at room temperature.

Evaluation of the penetration of reducing agents into human hair

White human hair fibers treated with TG, TL, and CYS as described in the previous sections 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, Heidelberg, Germany) to 10 μm thickness, and mounted on a slide glass. Next, the TG, TL, and CYS penetrated part of the cross-sectional samples were dyed with a solution of 0.005 wt % methylene blue at room temperature with a syringe. Finally, the penetration of TG, TL, and CYS into human hair was observed by optical microscopy.

Microspectrophotometry

The cross-sectional intensity scans of the cross-sectioned hair samples were measured using a microspectrophotometer (DMSP-II, Olympus Optical Co. Ltd., Tokyo, Japan). This instrument is a microscopic photometer equipped with an interference filter for spectroscopic measurements.[13,14]

A solution of 0.005 wt % methylene blue at room temperature was dropped on the cross-sectional samples mounted on a slide glass with a syringe. The TG, TL, and CYS penetrated into cross-sectional samples were dyed at 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 patterns of TG, TL, and CYS penetrated into human hair were 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; and 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.

Evaluation of setting ability

Setting ability of human hair was evaluated according to the Kirby method.[15] 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 of 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, and 15 min) at 25°C in a solution of 6.0 wt % thioglycolic acid adjusted to varying pH values (7.0,

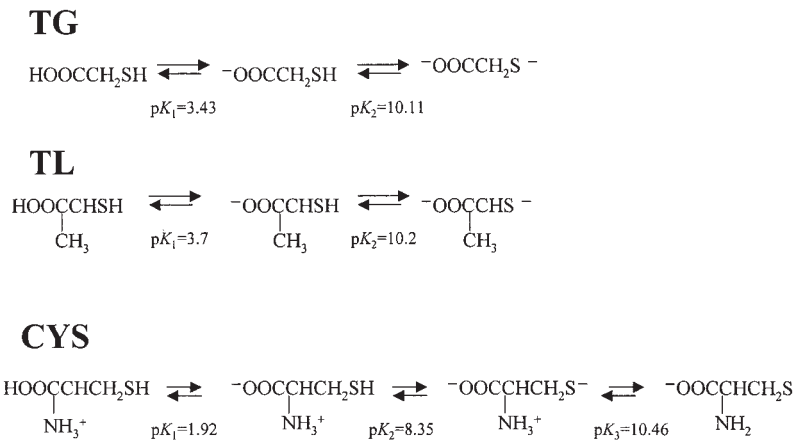

Figure 1 Relationship between chemical structure and acid dissociation for TG, TL, and CYS.

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 to solution of 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 (the 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 eq. (1) (the 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.

$$\text{Waving Efficiency (\%)} = 100 - [100 \times (B - A)/(C - A)] \quad (1)$$

Evaluation of the degree of damage

The waved hair samples were conditioned at 60% RH and at 23°C for 24 h. The tensile strength of a single fiber was measured at a rate of extension of 100% per minute using a Rheo Meter NRM-2002J (Fudoh, Japan).

RESULTS AND DISCUSSION

Penetration of TG, TL, and CYS into human hair

The relationship between the chemical structure and the acid dissociation constant for TG, TL, and CYS is shown in Figure 1. TG, TL, and CYS have anionic charges above pH 7.0 due to a carboxyl group in the molecule. So, the penetration of the reducing agents (TG, TL, and CYS) into the human hair can be observed by dyeing the reducing agent penetrated parts with basic dye (methylene blue etc.).

Here, we prepared cross-sectional samples of human hair treated with TG, TL, and CYS. Next, the penetration of TG, TL, and CYS for the cross-sectional samples dyed with methylene blue was observed by optical microscopy. The photomicrograph of the white human hair cross-sectioned and finally dyed with methylene blue is shown in Figure 2. 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 Figure 3. 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 Figure 4. 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. 3). This sample also absorbed the methylene blue

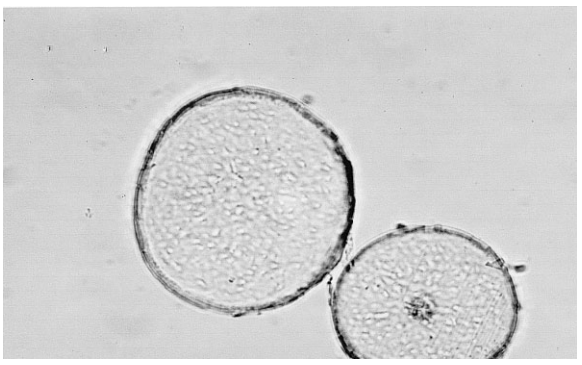

Figure 2 Photomicrograph of white human hair cross-sectioned and finally dyed with methylene blue.

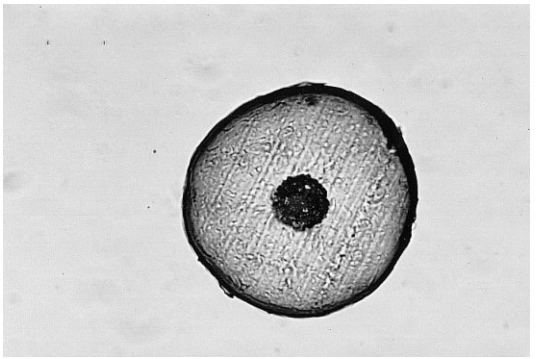

Figure 3 Photomicrograph of white human hair treated with TG at 25°C and pH 9.0 for 5 min, then cross-sectioned, and finally dyed with methylene blue.

TABLE I
Penetration of TG, TL, and CYS (at 25°C) into Virgin Human Hair Estimated by Optical Microscopy for Cross-sectional Samples Dyed with Methylene Blue

Reducing agent	pH	Penetration (μm)			
		3 min	5 min	15 min	30 min
TG	7.0	O[a]	4.63	13.9	ND[b]
	8.0	O	9.26	33.3	ND
	9.0	9.26	23.2	Complete	ND
TL	7.0	O	O	9.26	ND
	8.0	O	O	20.4	ND
	9.0	O	14.8	35.2	ND
CYS	7.0	O	O	O	4.63
	9.0	O	9.26	9.26	ND

[a] Reducing agent not significantly penetrated.
[b] Not done.

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 reducing agents 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. 4).

The influence of pH and treatment time on the penetration of reducing agents into human hair was investigated by using the above method. The penetration of TG, TL, and CYS (at 25°C) into virgin human hair estimated by optical microscopy for cross-sectional samples dyed with methylene blue is shown in Table I. The penetration of TG and TL into virgin human hair clearly increased by increasing the treatment time and pH. Also, the penetration of TG into virgin human hair is higher than that of TL into virgin human hair. On the other hand, the penetration of CYS into virgin human hair was almost unchanged by increasing the treatment time at 25°C and pH 9.0 and was weaker than TG and TL. The photomicrograph of the white human hair treated with CYS at 25°C and pH 9.0 for 5 min, then cross-sectioned, and finally dyed with methylene blue, is shown in Figure 5. The photomicrograph of the white human hair treated with CYS at 25°C and pH 9.0 for 15 min, then cross-sectioned, and finally dyed with methylene blue, is shown in Figure 6. The white human hair treated with CYS at 25°C and pH 9.0 for 5 min adsorbed the methylene blue into the cuticle, but the methylene blue almost was not adsorbed into the cortex at all. Also, interestingly, in the case of treating the white human hair with CYS for 15 min, the tendency for CYS to not penetrate the cortex remained the same. Also, we observed cuticle damage with optical microscopy when treating with TG at pH 9.0 for 15 min, but did not observe cuticle damage when treating with CYS at pH 9.0 for 15 min (Figs. 4 and 6).

From these experiments, the penetration of TG and TL into virgin human hair was dependent on the treatment time. On the other hand, the penetration of CYS into virgin human hair was independent of the treatment time.

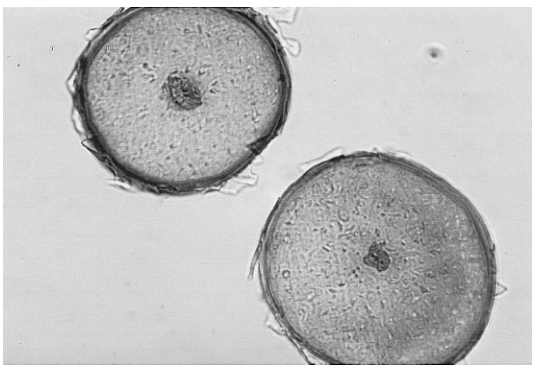

Figure 4 Photomicrograph of white human hair treated with TG at 25°C and pH 9.0 for 15 min, then cross-sectioned, and finally dyed with methylene blue.

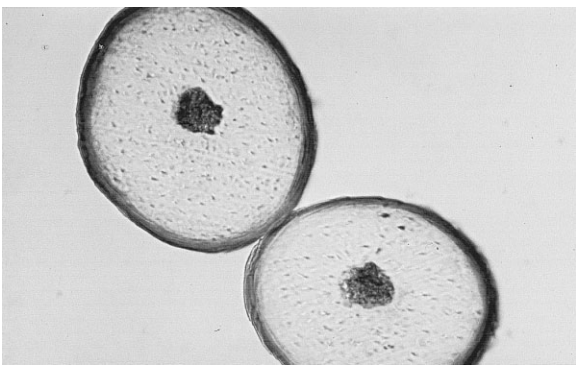

Figure 5 Photomicrograph of white human hair treated with CYS at 25°C and pH 9.0 for 5 min, then cross-sectioned, and finally dyed with methylene blue.

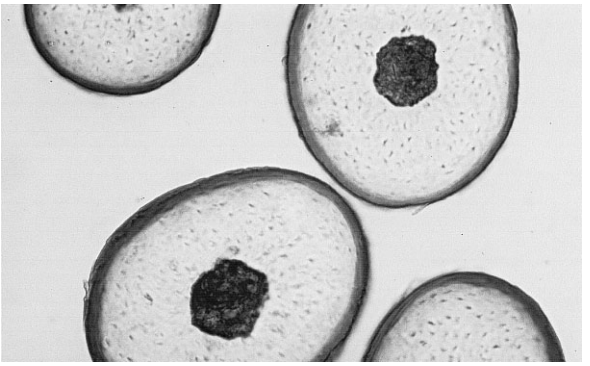

Figure 6 Photomicrograph of white human hair treated with CYS at 25°C and pH 9.0 for 15 min, then cross-sectioned, and finally dyed with methylene blue.

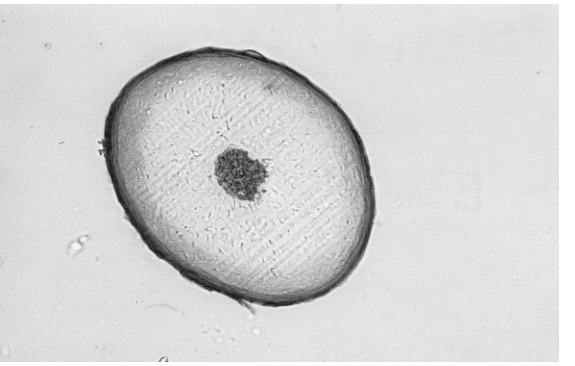

Figure 8 Photomicrograph of white human hair treated with TL at 25°C and pH 9.0 for 5 min, then cross-sectioned, and finally dyed with methylene blue.

The photomicrograph of the white human hair treated with TL at 25°C and pH 7.6 for 20 min, then cross-sectioned, and finally dyed with methylene blue is shown in Figure 7. The photomicrograph of the white human hair treated with TL at 25°C and pH 9.0 for 5 min, then cross-sectioned, and finally dyed with methylene blue is shown in Figure 8. Similarly, in the case of the white human hair treated with TG (Fig. 3), the white human hair treated with TL at 25°C and pH 7.6 for 20 min adsorbed the methylene blue through the cuticle and partially into the cortex. On the other hand, the white human hair treated with TL at 25°C and pH 9.0 for 5 min not only adsorbed the methylene blue through the cuticle and partially into the cortex, but also a sharp boundary line appeared. We observed that the occurrence of the sharp boundary line tended to increase when pH was raised (from pH 7.6 to 9.5).

Diffusion behavior of TG, TL, and CYS into human hair

Microspectrophotometry has been used to analyze the diffusion behavior of disperse dyes into various fibers.[13,16] Han et al.[14] reported that the diffusion coefficient of HC Red 3 (semipermanent hair dyes) into human hair was to the order of 10^{-10} cm^2/s by the same method.

In this study, the diffusion behavior of TG, TL, and CYS into virgin human hair was analyzed by combining microspectrophotometry and dyeing techniques. The diffusion patterns of reducing agents into human hair could not be determined by only microspectrophotometry, because the reducing agents did not have characteristic visible spectra. However, the diffusion patterns of reducing agents into human hair could be determined by combining microspectrophotometry and dyeing techniques.

The cross-sectional intensity scans at 664 and 430 nm of the white human hair treated with TG at 25°C for 5 min, then cross-sectioned, and finally dyed with methylene blue is shown in Figure 9. Methylene blue concentration, namely TG concentration, decreased from the fiber surface to cortex as shown by scanning.

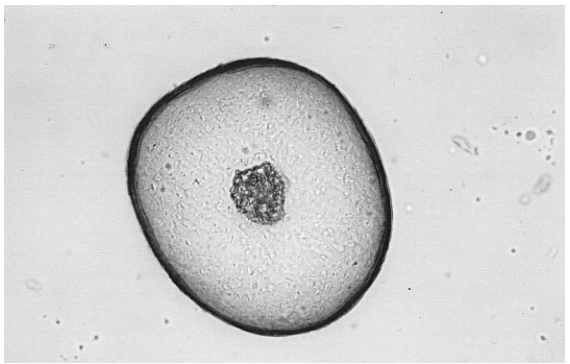

Figure 7 Photomicrograph of white human hair treated with TL at 25°C and pH 7.6 for 20 min, then cross-sectioned, and finally dyed with methylene blue.

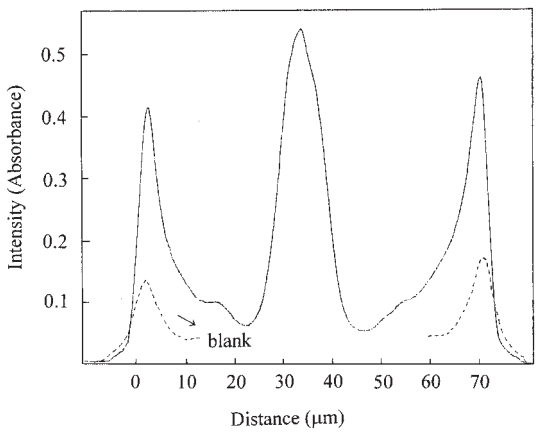

Figure 9 Cross-sectional intensity scans at 664 and 430 nm (blank) of white human hair treated with TG at 25°C and pH 9.0 for 5 min, then cross-sectioned, and finally dyed with methylene blue.

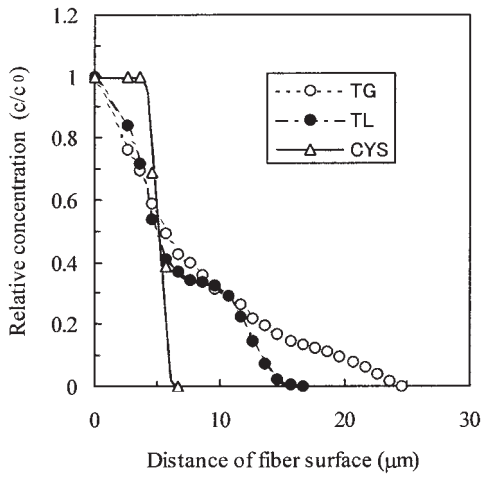

Figure 10 Relative concentration (c/c_0) profile of TG, TL, and CYS at 25°C and pH 9.0 for 5 min.

Also, the pseudopeak 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 scans at 430 nm (blank) from the cross-sectional intensity scan at 664 nm.

The relative concentration (c/c_0) profile of TG, TL, and CYS at 25°C and pH 9.0 for 5 min is shown in Figure 10. Here, it is c_0: TG concentration at fiber surface, c: TG concentration when distance from the fiber surface is x. The three different diffusion patterns from the three reducing agents were obtained. The diffusion pattern of TG comparatively showed Fickian type characteristics, while the diffusion pattern of CYS showed non-Fickian type characteristics and was absolutely different from the diffusion pattern of TG. This suggests that the free amino groups of CYS electrostatically interacted with the anionic ions of human hair, since the amino groups of CYS have a positive charge at pH 9.0. As shown in Figure 10, the diffusion area of CYS was observed ranging from the fiber surface to 6.65 μm below the fiber surface. Considering the fact that the cuticle region is about 5 μm (a sheet of cuticle is approximately 0.5 μm thick, and layers were overlapped with 5 to 10 sheets of cuticle[2,17]), CYS remained in the cuticle region of the virgin human hair, and CYS for the most part did not penetrate the cortex region. This experiment suggests the reason why virgin human hair treated with CYS was less damaged than the virgin human hair treated with TG is that CYS does not penetrate into the cortex region of the virgin human hair at pH 9.0.

The diffusion pattern of TL at pH 9.0 showed a combination of both types (Fickian and non-Fickian): the combination of both types occurs when overlapping the diffusion of the dispersed adsorption (TG) and the diffusion of the ionic adsorption (CYS). The relative concentration (c/c_0) profile of TL at varying pH values (7.6, 8.0, 9.0, and 9.5) and 25°C is shown in Figure 11. The diffusion pattern of TL at varying pH determined by our new method revealed a combination of both types (Fickian and non-Fickian) regardless of whether a sharp boundary line occurred, when observed using optical microscopy. On the other hand, here, the real diffusion pattern of TL at the same pH (mentioned above) could not be determined, since the two different diffusion patterns of TL were observed using optical microscopy. Therefore, we were successful in determining the real diffusion pattern of TL by our new method. The diffusion pattern of TL was different from that of CYS regardless of having an asymmetric carbon atom in both the TL and CYS molecule. This suggests that the diffusion pattern of CYS depends on the electrostatic interaction between the human hair and CYS rather than the molecular size of CYS.

From these experiments, we have concluded that the diffusion patterns of the three reducing agents in this study depended on the electrostatic interaction between the human hair and the reducing agents.

Determination of the apparent diffusion coefficient of TG

The interpretation for the diffusion coefficient of TG is complicated due to involvement of 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

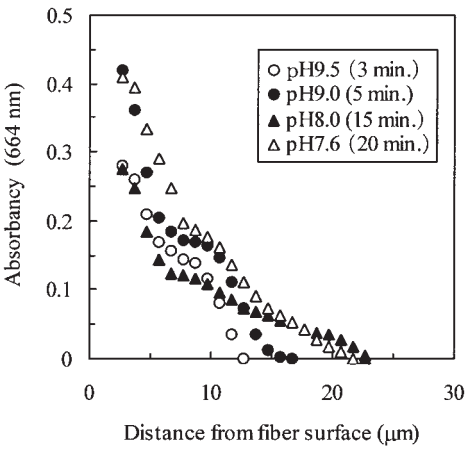

Figure 11 Relative concentration (c/c_0) profile of TL at varying pH values (7.6, 8.0, 9.0, and 9.5) and 25°C.

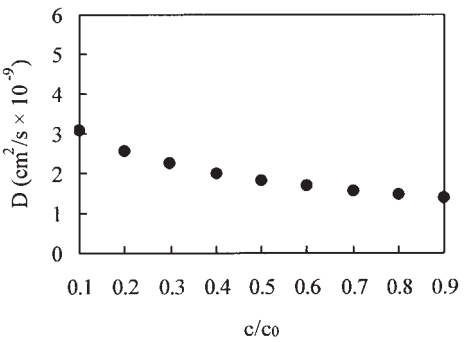

Figure 12 Apparent diffusion coefficient (D) of TG into human hair as a function of the relative concentration (c/c_0) calculated from the TG relative concentration profile (Fig. 10).

becomes a rate-determining step since the decrease in the reaction rate is more than the decrease in the diffusion rate.

In fact, the penetration of TG into human hair was quite different at pH 7.0 and 9.0 (Table I). Also, the diffusion pattern of TG comparatively showed Fickian type characteristics. In the case of this Fickian type pattern, the apparent diffusion coefficient at each concentration can be determined from the TG relative concentration profile using eq. (2), developed by Matano,[18,19] and eq. (3), developed by Karasawa et al.[19,20] 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 parameters.

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

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

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. 10) is shown in Figure 12. 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 II. The apparent diffusion coefficient of TG (23.6 $\times$ 10^{-10} cm^2/s) at pH 9.0 (treatment time: 5 min) increased about eight 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.

TABLE II
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.

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.

Setting ability and damage degree of the waved hair

In the previous section, we showed that the penetration of TG into human hair clearly increased by increasing the treatment time and by raising pH. In this study, the relationship between the penetration of TG and CYS into virgin human hair and the setting ability of the waved hair samples treated with TG and CYS were investigated. The waving efficiency of the waved hair samples treated with TG and CYS at 25°C is shown in Table III. Similarly, in the case of the penetration of TG into virgin 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 is the reason why TG diffuses gradually beyond the cuticle region and toward the inside of the cortex region along with the disconnection of the –SS– groups.[9] On the other hand, the penetration of CYS in virgin human hair was almost unchanged by increasing the treatment time (Table I, Figs. 5 and 6), but the waving efficiency of the waved hair samples treated with CYS nevertheless increased by increasing the treatment time. In a previous paper, we reported that the setting ability of the waved hair treated with TG

TABLE III
Waving Efficiency of the Waved Hair Samples at 25°C[a]

Reducing agent	pH	Waving efficiency (%)		
		3 min	5 min	15 min
TG	7.0	—	—	12.1
	9.0	22.8	48.4	79.1
CYS	9.0	—	10.2	44.0

[a] Kirby method.

TABLE IV
Tensile Strength of the Waved Single Fiber Measured at 25°C and 60% RH (n = 10)

Reducing agent[a]	Tensile strength[b] (N/fiber × 10^{-2})	Tensile strength[b] ($N/m^2 \times 10^8$)
Untreated	129 ± 20	3.17 ± 0.49
TG	97 ± 31	2.19 ± 0.44
CYS	111 ± 23	2.83 ± 0.72

[a] Treated with TG and CYS at pH 9.0 and 15 min.
[b] Mean ± standard division.

directly reflects the content of disconnected –SS– groups.[9] This suggests that the –SS– groups in the cuticle were gradually disconnected due to CYS remaining in the cuticle.

In the beauty treatment industry, it is widely known that waved hair is formed by the disconnection and reconnection of the disulfide (–SS–) groups, which exist in the matrix of the cortex. However, from this experiment, waved hair was clearly formed by the disconnection and reconnection of the disulfide (–SS–) groups, which exist in the cuticle region only.

Moreover, the damage degree of the waved hair samples treated with TG and CYS were compared. The tensile strength of the single waved fiber measured at 25°C and 60% RH is shown in Table IV. The tensile strength of the waved hair treated with CYS was strong compared with that of the waved hair treated with TG, indicating that the waved hair treated with CYS was less damaged than the hair treated with TG. These experiments indicate that the virgin human hair treated with CYS was less damaged as compared with the hair treated with TG, since CYS could not penetrate into the cortex region of the virgin human hair at pH 9.0.

CONCLUSION

We have developed a new method for analyzing the diffusion behavior of reducing agents into human hair. The three different diffusion patterns from the three reducing agents (TG, TL, and CYS) were obtained. The diffusion pattern of TG showed Fickian type characteristics, while CYS showed non-Fickian type characteristics. The diffusion pattern of TL showed a combination of both types (Fickian and non-Fickian). The apparent diffusion coefficient of TG into human hair at pH 9.0 was found to be 10^{-9} cm^2/s, whereas the apparent diffusion coefficient of TG into human hair at pH 7.0 was found to be 10^{-10} cm^2/s.

The relationship between the penetration of CYS into virgin human hair and the setting ability of the waved hair samples treated with CYS at 25°C were investigated. Waved hair was clearly formed by the disconnection and reconnection of the disulfide (–SS–) groups, which exist in the cuticle region only. Also, the tensile strength of the waved hair treated with CYS was strong compared with that of the waved hair treated with TG, indicating that the waved hair treated with CYS was less damaged than the hair treated with TG.

From these experiments, we have concluded that the diffusion patterns of the three reducing agents in this study depended on the electrostatic interaction between the human hair and the reducing agents.

We thank Mr. Isao Tabata and Ms. Shinobu Miyagawa of Fukui University for technical support.

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