Chemical Modification of Keratin Fibers Using 2-Iminothiorane Hydrochloride

A. Kuzuhara

Mandom Corporation, Central Research Laboratories, Osaka, Japan

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ABSTRACT: For the purpose of improving the properties of keratin fibers by chemical modification, we attempted to introduce new disulfide (–SS–) groups into hair using 2-iminothiorane hydrochloride (2-IT). After the evaluation of the setting ability of human hair, the waving permanence (66%) of our proposed permanent hair-setting process clearly improved compared with that of a conventional permanent hair-setting process (48%). Next, it became clear that new –SS– groups were created in the human hair samples as a result of introducing and then oxidizing new –SH groups. This –SS– content in the hair samples was estimated by employing FT-Raman spectroscopy. By examining the Raman bands of the treated and untreated hair, it was seen that each band of treated hair did not change, except for the increase of the –SS– groups. This suggests that hair damage does not occur as a result of the investigated treatment. From these experiments, the chemical modification of keratin fibers using 2-IT was clearly effective for a permanent hair-setting process. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3646–3651, 2003

Key words: fibers; 2-iminothiorane hydrochloride; –SS– groups; FT-Raman spectroscopy; modification

INTRODUCTION

Wool and hair fibers are mostly composed of keratin proteins. Wool and hair fibers characteristically have many disulfide (–SS–) groups compared with other natural protein fibers, and –SS– groups largely contribute to the structural stability and physical property of natural keratin fibers. Furthermore, existing permanent hair-setting processes, widely used in beauty salons, cause the inevitable disconnection and reconnection of –SS– groups. However, in the case of this setting process, hair damage is caused by the disconnecting of naturally existing –SS– groups, by the use of reducing agents such as thioglycolic acid and L-cysteine.[1,2]

Concerning the chemical modification of keratin fibers, many researchers[3–6] have aimed at improving the chemical and physical properties in wool. In previous studies,[7–10] we reported a new creaseproof finish for wool using 2-iminothiorane hydrochloride (2-IT), by introducing new –SS– groups, thus providing good wrinkle recovery and setting ability for wool fabrics. To improve the properties of keratin fibers by chemical modification, we attempted in this study to introduce new –SS– groups into hair using 2-IT and then evaluated the setting ability of the hair. Furthermore, we investigated the hair damage caused by the above treatment and estimated the new –SS– content in the hair by use of FT-Raman spectroscopy. As a result, the waving permanence of our proposed permanent hair-setting process was a great improvement over that of conventional permanent hair-setting processes without any hair damage. The chemical modification of natural keratin fibers using 2-IT was clearly effective for a permanent hair-setting process.

Correspondence to: A. Kuzuhara (kuzuhara-a@mandom.co.jp).

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EXPERIMENTAL

Materials

Virgin hair and virgin white hair as keratin fibers were purchased from Beaulax Co. (Tokyo, Japan) 2-Iminothiolane hydrochloride (2-IT), a protein crosslinking reagent,[11] was purchased from Sigma Chemical Co. (St. Louis, MO); ammonium thioglycolate (content: 50% thioglycolic acid solution), a reducing agent, was supplied by Sasaki Chemicals (Japan); sodium bromate (oxidizing reagent) and polyoxyethylene (10) octylphenyl ether (POEOFE) were purchased from Wako Pure Chemicals (Osaka, Japan).

Fiber modification and evaluation of setting ability

Waving efficiency and waving permanence were measured according to the Kirby method.[12] A bundled sample (20 pieces, 20 cm) of virgin straight hair, with uniform cuticle direction, was immersed in a solution

TABLE I
Conditions of the Waved Hair Samples

No.	Introducing–SH Groups → 2-IT (wt %)	Reduction → (6% thioglycolic acid)	Oxidation (6% sodium bromate)
1	0.2	U[a]	T
2	1.0	U	T
3	2.0	U	T
4	2.0	T[b]	T
5	U	T	U
6	U	T	T

[a] Untreated.
[b] Treated.

of 0.5 wt % sodium laurylsulfate at a hair : solution ratio of 1 : 60. The hair sample was soaked for 10 min at 50°C. Next, the hair sample was washed in distilled water and then dried in air. Conditions of the waved hair samples are presented in Table I.

Samples 1 and 3

Virgin straight hair was interlaced between two rows of pegs (diameter: 3 mm) without tension and held at each end with rubber bands. Next, the hair sample was immersed in a solution of 0.2 and 2.0 wt % 2-IT/0.5*M* phosphate buffer (pH 8.0) and 0.1 wt % POEOFE at a ratio of hair : solution = 1 : 76. The hair sample was soaked for 1 h at 50°C, continuously shaken, causing thiol (–SH) groups to be introduced into the hair sample. After being washed in distilled water, the hair sample was immersed in a solution of 6.0 wt % sodium bromate at a ratio of hair : solution = 1 : 266. The hair sample was soaked for 10 min at room temperature, resulting in new disulfide (–SS–) groups being created in the hair sample. After being washed in distilled water, the hair sample was slipped carefully out of the pegboard, and then set gently 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 eq. (1) (measuring procedure), presented in a later section.

Sample 2

Virgin straight hair was set using the pegboard under the same conditions as for Samples 1 and 3. Next, the hair sample was immersed in a solution of 1.0 wt % 2-IT/0.5*M* phosphate buffer (pH 8.0) and 0.1 wt % POEOFE at a ratio of hair : solution = 1 : 222. The hair sample was soaked for 1 h at 50°C, continuously shaken, resulting in thiol (–SH) groups being introduced into the hair sample. Next, the sample was washed in distilled water, after which it was immersed in a solution of 6.0 wt % sodium bromate at a ratio of hair : solution = 1 : 777. The hair sample was soaked for 10 min at room temperature, causing new disulfide (–SS–) groups to be created in the hair sample. Finally, finishing and measuring procedures were performed the same as for Samples 1 and 3.

Sample 4

Virgin straight hair was set using the pegboard under the same conditions as for Samples 1–3. Next, the hair sample was immersed in a solution of 2.0 wt % 2-IT/0.5*M* phosphate buffer (pH 8.0) and 0.1 wt % POEOFE at a ratio of hair : solution = 1 : 76. The hair sample was soaked for 1 h at 50°C, continuously shaken, resulting in thiol (–SH) groups being introduced into the hair sample. Next, the sample was washed in distilled water, after which it was immersed in a solution of 6.0 wt % thioglycolic acid (adjusted at pH 9.0 by ammonia water) at a ratio of hair : solution = 1 : 222. The wool sample was soaked for 10 min at room temperature, thus disconnecting the –SS– groups. After being washed in distilled water, the hair sample was immersed in a solution of 6.0 wt % sodium bromate at a ratio of wool : solution = 1 : 222. The hair sample was again soaked for 10 min at room temperature, causing new disulfide (–SS–) groups to be created in the hair sample. Finally, finishing and measuring procedures were performed the same as for previous samples.

Sample 5

Virgin straight hair was set using the pegboard under the same conditions as for Samples 1–4. Next, it was immersed in a solution of 6.0 wt % thioglycolic acid (adjusted at pH 9.0 by ammonia water) at a ratio of hair : solution = 1 : 777. The wool sample was soaked for 10 min at room temperature, thus disconnecting the –SS– groups (reduction process). Finally, finishing and measuring procedures were performed the same as for previous samples.

Sample 6

Virgin straight hair was set using the pegboard under the same conditions as for Samples 1–5. Next, the hair sample underwent the reduction process the same as for Sample 5. After being washed in distilled water, the hair sample was immersed in a solution of 6.0 wt % sodium bromate at a ratio of hair : solution = 1 : 777. The hair sample was again soaked for 10 min at room temperature, resulting in new disulfide (–SS–) groups being created in the hair sample. Finally, finishing and measuring procedures were performed the same as for previous samples.

Percentage waving efficiency (W.E.) was determined by the following equation:

$$\text{W.E. (\%)} = 100 - \left(\frac{B - A}{C - A} \times 100\right) \quad (1)$$

where A is the distance between five pegs on center (= constant = 24 mm); B is the length of a section of the waved hair (between the five pegs), after being removed from the pegboard; and C is the length of the section of the waved hair after it was removed from the pegboard and stretched (= constant = 70 mm).

Next, the hair samples, whose waving efficiency had been measured, were dried at room temperature for 24 h, after which they were immersed in distilled water at 60°C for 30 min. After that, the hair samples were set gently on a glass plate. Finally, the percentage waving permanence (W.P.) was estimated by eq. (2).

$$\text{W.P. (\%)} = \frac{\text{W.E. after treatment}}{\text{W.E. before treatment}} \times 100 \quad (2)$$

Methods

FT-Raman spectra

FT-Raman spectra of the hair samples were obtained using a Ramaonor T-64000 (Jobin Yvon, Longjumeau, France). The samples were excited with an argon laser operating at 514.5 nm and emitting 50 mW of optical power focused on the sample. The sampling geometry was 180°, and spectra were collected at 2.3 cm^{-1} resolution with a 1000-s scan. The cross-section samples were produced using white human hair, and a section of the hair 1 μm from the surface (spot diameter: 1 μm) was measured.

Ion chromatography

Sulfur (S) content in the white human hair was determined by ion chromatography. The absorption solution of the sample was produced by combustion in an oxygen flask. To be exact, 0.4 g of the sample covered with a paper holder was placed in a platinum cage and then combusted by an apparatus consisting of a flask (300 mL) with a ground stopper. Next, it was absorbed in a solution of 1.8 mmol Na_2CO_3 and 1.7 mmol $NaHCO_3$. After that, the absorption solution was allowed to flow through an ion chromatograph apparatus (DX-500; Dionex Corp., Sunnyvale, CA), and then SO_4^{2-} in the solution was measured. Finally, the SO_4^{2-} was converted into S.

RESULTS AND DISCUSSION

Setting ability of human hair

First, we compared the setting ability of our proposed permanent hair-setting process with that of an existing permanent hair-setting process.

TABLE II
Waving Efficiency and Waving Permanence of the Waved Hair Samples

No.	2-IT (wt %)	Waving efficiency (%)	Waving permanence (%)
1	0.2	44	35
2	1.0	65	56
3	2.0	70	66
4	2.0	77	67
5	—	30	0
6	—	67	48

Existing permanent hair-setting processes consist of both a reduction process and an oxidation process. Specifically, the hair is rolled up into rods, and then naturally existing –SS– groups in hair disconnect by use of reducing agents, such as thioglycolic acid or L-cysteine, for example (the reduction process). Next, the hair is washed in water. After that, –SH groups in hair reconnect by use of oxidation agents, such as sodium bromate or hydrogen peroxide, for example (the oxidation process). As a result, the waved hair is formed. Table II shows the waving efficiency (W.E.) and the waving permanence (W.P.) of hair (Sample 6) that underwent the reduction and oxidation processes, and hair (Sample 5) that only underwent the reduction process. The waving efficiency of the hair (Sample 5) that did not undergo the oxidation process was low, and the waving permanence of this sample was 0%. Specifically, when –SH groups in hair are not reconnected, wave permanence is not attained. Thus, the oxidation process plays an important role in the waving permanence in hair.

On the other hand, our proposed permanent hair-setting process is a method of introducing new –SS– groups in hair, and is different from the existing permanent hair-setting processes that involve disconnection and reconnection of –SS– groups. To be specific, the hair is rolled up into rods, and then new –SH groups are introduced in hair using 2-IT. Next, the hair is washed in water, after which –SH groups in the hair are reconnected using the oxidation agents. As a result, the waved hair is formed.

Table II shows the waving efficiency and the waving permanence of hair (Samples 1–3) by adjusting the –SS– content that was introduced by changing the 2-IT concentration from 0.2 to 2.0%. The waving efficiency and the waving permanence clearly improved with increasing 2-IT concentration. In particular, the waving permanence of Samples 2 and 3 (56–66%) improved greatly compared with that of a conventional permanent hair-setting process (Sample 5) (W.P. = 48%). Also, the waving efficiency of Sample 4 (W.E. = 77%), in which new –SH groups were introduced and reduced to disconnect from –SS– groups, and then

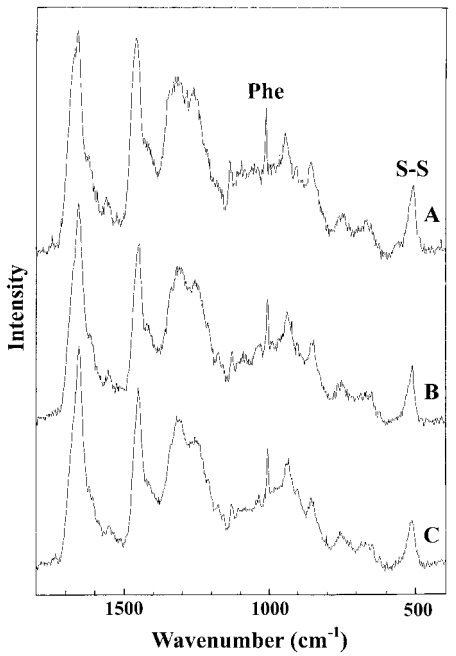

Figure 1 FT-Raman spectra of human hair: (A) untreated; (B) Sample 3; (C) Sample 4.

oxidized to make new –SS– groups, slightly improved compared with that of Sample 3 (W.E. = 70%). However, the waving permanence of Sample 4 (W.P. = 67%) scarcely different from that of Sample 3 (W.P. = 66%).

Structure of human hair

We investigated the structure of human hair after the introduction of new –SS– groups by use of FT-Raman spectroscopy. Hogg et al.[13] reported the structural change of wool fabrics that were subjected to hydrogen peroxide bleaching by use of FT-Raman spectroscopy. Jones et al.[14] investigated the photooxidation of wool using FT-Raman spectroscopy. According to these reports, the increasing signal intensity at 1040 cm^{-1}, assigned to the S—O vibration of cysteic acid, split and a shift of the peak assigned to –SS– groups was observed by resolution of –SS– groups. Also, Pande[15] reported that the FT-Raman technique is useful for the evaluation of hair damage.

The FT-Raman spectrum of untreated hair is shown in Figure 1(A). The peak assigned to the –SS– groups (the stretching vibration of the S—S bond) appear at 510 cm^{-1}. Sugeta et al.[16] reported that the S—S band at 508 cm^{-1} has a *gauche–gauche–gauche* (GGG) conformation and the S—S band at 523 cm^{-1} has a *trans–gauche–gauche* (TGG) conformation. Judging from the wavenumber of this peak, we believe that most of the –SS– groups in untreated hair have the GGG conformation. Because the distance between the polypeptide chain and the polypeptide chain of polypeptide surrounding the S—S bond is shortest in the case of GGG conformation, keratin fibers assume a compact structure. Also, data on the second structure (e.g., α-helix, β-pleated sheet, etc.) can be obtained from both the amide I and the amide III regions. The peak assigned to the α-helix appeared at 1655 cm^{-1} in the amide I region, and the peak assigned to the unordered phase appeared at 1250 cm^{-1} in the amide III region.

The FT-Raman spectrum of Sample 3, in which thiol (–SH) groups were introduced and then oxidized to make new –SS– groups, is shown in Figure 1(B). Also, the FT-Raman spectrum of Sample 4, in which –SH groups were introduced and reduced to disconnect from the –SS– groups, and oxidized to make new –SS– groups, is shown in Figure 1(C). Each of the bands of Sample 3 and Sample 4 was the same as that of the untreated hair sample. Also, the S—S band of Sample 3 appeared at 510 cm^{-1}, and had not broadened compared with that in the untreated hair sample. Meanwhile, the S—S band of Sample 4 was slightly broader than that of the untreated hair and Sample 3.

Disulfide content of human hair

Measurement by FT-Raman spectroscopy becomes a suitable way to obtain information on –SS– groups in keratin fibers. The disulfide (–SS–) contents of the treated hair samples were compared by FT-Raman spectroscopy. Normalization of Raman spectra of wool is often carried out based on the C—H peak at 1450 cm^{-1},[14] and the amide I peak at 1657 cm^{-1}.[17] The use of this band, however, is not appropriate because of the nature of the chemical modification. So, we chose the peak at 1003 cm^{-1}, which is assigned to phenylalanine (Phe), for normalization because the Phe peak is not influenced by the chemical modification.[8,9]

The ratio of the peak area of the S—S band (drawn baseline between 470 and 560 cm^{-1}), on the basis of the peak area of Phe (drawn baseline between 986 and 1020 cm^{-1}), was thought to be the standard of –SS– content. A comparison of values is shown in Table III. The ratio of the peak area (S—S band/Phe) of Sample 3, in which –SH groups were introduced and then oxidized to make new –SS– groups, was certainly increased compared with that of the untreated hair. Also, additional –SS– content on top of the naturally existing –SS– content in hair was estimated at about 10.0%. Moreover, the S (sulfur) content of the hair was determined by ion chromatography (Table III). The S content was 4.05% in untreated hair, and the cystein content that was converted into the S content was 15.2% in the untreated hair; the S content was 4.25% in Sample 2 and 4.38% in Sample 3. Additional S content on top of the naturally existing S content in hair was

TABLE III
Disulfide Content and S Content in the Hair Samples

No.	Peak area A: Phe[c]	Peak area B: S–S Band[d]	–SS–content[a] Ratio of peak area (B/A)	S content[b] (%)
Untreated	10.83	44.1	4.067	4.05
2	—	—	—	4.25
3	11.78	52.6	4.466	4.38
4	12.93	52.1	4.029	4.38

[a] Determined by FT-Raman spectroscopy.
[b] Determined by ion chromatography.
[c] Drawn baseline between 986 and 1020 cm^{-1}.
[d] Drawn baseline between 470 and 560 cm^{-1}.

estimated at 4.9% in Sample 2 and 8.1% in Sample 3, and the –SS– content in the hair was clearly increased by increasing the 2-IT concentration.

On the other hand, the ratio of the peak area of Sample 4, in which –SH groups were introduced and then reduced to disconnect from –SS– groups, and oxidized to make new –SS– groups, decreased about 10% compared with that of Sample 3, although the S content did not change.

The –SS– groups significantly contribute to the structural stability and physical property of natural keratin fibers. So, to improve the properties of keratin fibers by chemical modification, we attempted to introduce new –SS– groups into hair using 2-iminothiorane hydrochloride, and then to evaluate the setting ability of human hair (Table II). The waving efficiency and the waving permanence of hair (Samples 1–3), in which –SH groups were introduced and then oxidized to make new –SS– groups, clearly improved with increasing 2-IT concentrations. In particular, beyond 1.0 wt % 2-IT concentration, the waving permanence (56–66%) improved significantly compared with that of a conventional permanent hair-setting process (Sample 5) (48%). Also, by estimating the –SS– content in hair Sample 3 by use of FT-Raman spectroscopy, the –SS– content in hair Sample 3 had increased by about 10% compared with that in the untreated hair sample. In these experiments, it has became clear that –SS– groups are certainly introduced into hair by introducing –SH groups and then oxidizing them to make –SS– groups. Moreover, determination of the S content of the hair by ion chromatography (Table III) showed it to be 4.25% in Sample 2 and 4.38% in Sample 3; moreover, the –SS– content in the hair had increased by increasing the 2-IT concentration. That is, as the result of increasing –SS– content in the hair, the waving efficiency and the waving permanence of hair obviously increased. Furthermore, by examining the Raman bands of Sample 3 and the untreated hair sample, it was seen that each band of Sample 3 did not change, except for the increase of the –SS– groups. Also, the S—S band of Sample 3 appeared at 510 cm^{-1}, and did not broaden compared with that in the untreated hair sample. This suggests that most of the –SS– groups in Sample 3 have the GGG conformation, the same as that of the untreated hair sample. From this result, it became clear that the higher-order structure in the human hair does not change during this process.

From these experiments, hair damage evidently did not occur because our proposed permanent hair-setting process was able to introduce new –SS– groups into human hair without disconnecting naturally existing –SS– groups.

On the other hand, the –SS– content of Sample 4, in which –SH groups were introduced and then reduced to disconnect from –SS– groups, and oxidized to make new –SS– groups, decreased about 10% compared with that of Sample 3, although the S content did not change. This suggests that –SS– groups in the hair were destroyed by the reduction treatment. Tanaka et al.[18] reported that the degree of reconnection of –SS– groups by the reduction and the oxidation processes is about 90%. Our result was in good agreement with the above report. Also, Hogg et al.[13] reported that the S—S band broadens, and the structure of wool changes by subjecting it to hydrogen peroxide bleaching. Actually, the S—S band of Sample 4 is slightly broader than that of the untreated hair sample and Sample 3. This suggests that the structure of the polypeptide chain near the –SS– groups fell into disorder and was more porous.

CONCLUSIONS

The chemical modification of keratin fibers using 2-IT was clearly effective for a permanent hair-setting process. That is, the waving permanence of our proposed permanent hair-setting process is a great improvement over conventional permanent hair-setting processes. Also, it has become clear that hair in which new –SH groups were introduced and oxidized definitely created new –SS– groups in human hair, and the –SS– content in hair increased by increasing the 2-IT concentration. Moreover, it was seen that each Raman band of treated hair did not change, except for the increase of the –SS– groups.

From these experiments, it was demonstrated that hair damage did not occur because our proposed permanent hair-setting process was able to introduce new –SS– groups into human hair, without disconnecting naturally existing –SS– groups.

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