J. Cosmet. Sci., **61**, 1–12 (January/February 2010)

Reduction-induced surface modification of human hair

YASH K. KAMATH and SIGRID B. RUETSCH,
TRI/Princeton, PO Box 625, Princeton, NJ 08542.

Accepted for publication July 1, 2009.

Synopsis

A microfluorometric method has been developed to characterize lipid removal or "delipidation" of the human hair cuticula during light exposure and chemical grooming processes such as oxidation (bleaching) and reduction. In the case of photochemical and chemical oxidation, lipid removal ("delipidation" of the F-layer or lipid-layer) from the outer β-layer of the exposed scale faces and generation of cysteic acid groups occurs. This "delipidation," which ultimately results in "acidification" of the scale faces, leading to a change in surface chemistry from hydrophobic to hydrophilic, can be detected and quantified by microfluorometry by tagging, e.g., with the cationic fluorochrome Rhodamine B. In the case of reduction, similar tagging of the acid sites on the scale faces is possible, but this time, Rhodamine B reacts with the mixed disulfide containing a carboxyl group that will be ionized above a pH of about 4. In addition to this, we have shown by microfluorometric scanning that the negative charges generated in the cuticle surface can be used to bind low-molecular-weight quaternary conditioners. This process can be considered as "relipidation" or "refatting" of the scale faces. We have shown in earlier studies (1) that this entire process of oxidation-induced "delipidation" and subsequent "relipidation" of the acidic scale faces with a cationic conditioning molecule can also be reliably quantified by X-ray photoelectron spectroscopy (XPS). Furthermore, single-fiber wettability scanning using the Wilhelmy technique, which is highly sensitive to any changes in surface chemistry, is well-suited to detect and characterize treatment-induced changes in the chemical nature of the hair surface from hydrophobic to hydrophilic.

INTRODUCTION

In earlier publications (1,2), we discussed studies concerned with the characterization and quantification of damage done to the hair fiber by photochemical and cosmetic chemical oxidative processes. We hypothesized that the initial attack of these oxidative processes is on the outer (or upper) β-layer of the exposed surface cuticle cell. The outer β-layer consists of covalently bound lipids (also called the F-layer)—more specifically, the fatty acid 18-MEA (18-methyl eicosanoic acid) and cysteine residues, where the 18-MEA is presumably bound to the protein through thioester linkages. This covalently bound lipid layer, rich in 18-MEA gives a hydrophobic character to the hair fiber surface. The lipid layer is a rather chemically damage-resistant layer, except under alkaline conditions. On the other hand, removal or scission of the surface lipid layer

The current affiliation of Yash K. Kamath is Kamath Consulting, Inc.

(delipidation), as well as formation of acid groups (acidification) of the exposed scale faces, changes the originally hydrophobic nature of the scale faces and gives them hydrophilic properties.

Most of the information we have on the nature of lipids on the surface of hair originated from studies on wool. On the basis of persistence of hydrophobicity in wool after solvent extraction and mild scouring, Leeder and Rippon (3) concluded that the lipids left on the surface were covalently bound to the epicuticle. Evans *et al*. (4) and Kalkbrenner *et al*. (5) found that the covalently bound lipids can be released from the surface by treatment with potassium tert-Butoxide in tert-butanol. Negri *et al*. (6) found that chlorination released over 50% of the bound fatty acids, and these were mainly bound by thioester linkages. However, fatty acids bound by ester or amide linkages were cleaved only by hot aqueous treatments. The observation that acidic chlorine water is capable of releasing covalently bound fatty acids from the surface of hair is relevant to human hair, since the hair often encounters chlorine in the water of swimming pools. Wertz and Downing (7) approached the problem of lipids on the surface of human hair from the studies of lipids of mammalian epidermis. Their detailed analytical study of human hair showed that 18 MEA (C-21 ante-iso) forms only 40% of the covalently bound lipids.

In the current study we attempt to characterize and quantify changes in the surface chemistry of hair as a function of progressive reduction. Since surface chemistry is important from the point of view of the spreading of hair care products and the friction that affects the feel of hair, it would be important to characterize the surface of such chemically treated hair. As in earlier work (1,2), we again use the same microfluorometric technique with the help of the cationic fluorochrome Rhodamine B to detect the change in the surface chemistry of reduced hair. More specifically, we attempt to quantify and compare the level of photochemically and cosmetic-chemically (oxidation and reduction) induced breakdown of the thioester linkages, removal of the surface lipids (irrespective of their chemical composition), and formation of acid functionalities on the scale faces. In addition to microfluorometry, we attempt to measure this change in surface chemistry by XPS analysis and wettability scanning (8). The effect of delipidation of the hair surface on friction and the positive effect of depositing conditioners on such damaged hair have been presented in an earlier publication (9) and will not be pursued in this communication.

The concept of the microfluorometric approach used in this research is based on the fact that the intact lipid layer resists rapid adsorption of the cationic fluorochrome and is indicated by the low fluorescence intensity of the scale faces. On the other hand, removal of the lipid layer, and formation of a large number of acid groups on the exposed scale faces, enhances rapid adsorption of large amounts of cationic fluorochrome, resulting in the high fluorescence intensity of the scale faces.

Alternate methods, which are highly sensitive to changes in the surface chemistry of the scale faces, are single-fiber wettability scanning and XPS analysis. Wettability scanning, which is a measure of surface wettability, detects and measures changes in surface chemistry from hydrophobic to hydrophilic as a result of oxidation or reduction processes. XPS can establish treatment-induced changes in the concentration and chemical state of all detectable elements at a surface depth as shallow as 25Å. We use these techniques to confirm and support the results obtained by the microfluorometric approach.

EXPERIMENTAL

MATERIALS AND TECHNIQUES

(a) Unaltered hair samples. A tress of 14″-long, unaltered, European dark brown hair from DeMeo Bros., New York, was used for this study.

(b) Hair sample preparation. Eight inches of the root portions of individual hair fibers were taken and numbered 1 to 30. These root portions were then cut into six equal segments. Starting with the top section of each hair fiber, the segments were numbered 30, 15, 10, 5, 2, and 0 minutes.

(c) Reduction treatment. The numbered segments were then subjected to reduction with ~0.5 M ammonium thioglycolate (TGA at pH 9.4 with ammonium hydroxide) for 30, 15, 10, 5, and 2 minutes, while the bottom section (numbered "0") served as an unaltered, "not reduced" control. The reduced fiber segments were thoroughly rinsed in lukewarm running tap water for ten minutes and blotted between paper towels. The fiber segments were air-dried.

(d) Fluorochrome. A 0.020% aqueous solution of the cationic Rhodamine B (CI Basic Violet 10), (Aldrich Chemical Co., Milwaukee, WI) was used as labeling agent to highlight, characterize, and quantify the oxidative damage inflicted upon the scale surface (1).

(e) Tagging of the hair with Rhodamine B. The untreated and reduced hair fibers were treated for one minute with 0.020% aqueous Rhodamine B solution, actively rinsed for 15 seconds in warm running tap water, blotted between paper towels, blow-dried, and stored in the dark at ambient temperature.

(f) Instrumental settings for microfluorometric scanning. A Leitz MPV 1.1 microspectrophotometer (Ernst Leitz Wetzlar, GmbH, Wetzlar, Germany) with a Vertical Ploem Illuminator, a microfluorometry unit, was used for this study. Instrumental settings for the spectral and spatial (cross-sectional) microfluorometric measurements (scans) of the Rhodamine B-labeled unaltered and "reduced" hair fibers were as follows:

- Green excitation beam: 515-560 nm; KP = 580 nm; LP = 580 nm
- λ_m: 608 nm (filter: 37.5 mm)
- Objective: 40 X
- Accel. voltage: 1.2 kV
- Measuring sensor: (5×60) units^2 for spectral and distance (spatial) scans
- Scanning speed: 72 μm/s for distance scans (high-speed scans)

The dried, RB-tagged hair segments were mounted in parallel on microscope slides for spatial scanning. From the fluorescence emission spectrum of a Rhodamine B-tagged hair fiber (1), the wavelength of maximum fluorescence emission had been established at $\lambda_m \sim 608$ nm. All spatial scans were carried out at this wavelength under identical instrumental settings.

(g) Wettability scanning. Single-fiber wettability scanning was carried out using the Wilhelmy technique (8) (using our TRI/scan apparatus).

(h) XPS analysis. XPS analysis of the samples was done at an outside analytical facility for an appropriate number of hair fibers to assure confidence and reliability in the obtained results.

RESULTS AND DISCUSSION

BACKGROUND

In earlier work (9), we characterized and quantified the extent of cuticle cell ablation/abrasion and complete erosion along the human hair fiber caused by physical means. We demonstrated, with the help of a fluorochrome (Rhodamine B in this case), how everyday standard grooming practices severely damage the physical nature of the surface structures (the cuticula) of hair fibers (9). In other studies (1,2), we attempted to characterize and quantify photochemically and chemically induced oxidative damage to the outer β-layer on the exposed cuticle cell surface. These earlier studies have provided some interesting results, indicating distinctly different phases of hydrolysis-induced 18-MEA scission. The highlights of these studies will be briefly summarized for the ease of comparing the effects of photochemical and chemical oxidation of earlier studies with the effects of reduction on the outer β-layer of the exposed scale faces (our current research).

(a) Photochemical oxidation. Photochemical oxidation is apparently a "two-phase" process as clearly shown in Figure 1a showing the interfiber averages (~1200 data points per scan) of progressively UV-exposed segments of 30 different hair fibers. As can be seen in the plot, there are two distinct phases of photodegradation of the cuticula: (1) short-term light exposure, which is an initiation period of physical changes, especially at the scale edge (as observed in the SEM), preceding lipid removal on the scale faces, and (2) long-term light exposure, during which lipid scission (delipidation) and formation of acid functionalities (sulfonic acid groups) on the scale faces take place.

The kinetics of photodegradation, (see Figure 1a), may be explained as follows: The initial and rather constant fluorescence intensity (FI) of up to 48 hours suggests that this may be an induction period during which photodegradation is suppressed by free-radical generation in the sample. The source of these free radicals could be the ferrous iron in the hair that can generate free radicals by the well known Fenton's reaction. These free radicals (mainly OH and OOH) are very active and mobile and terminate faster than propagate free-radical chain reactions. When all the iron is converted to ferric iron, the internal source of free radicals is exhausted. This seems to occur by the end of 48 hours, after which time span the photochemical degradation reaction by direct photolysis of keratin takes over. In addition, free radicals generated by the high-energy photons in combination with water and oxygen may also contribute to overall photolysis. This strongly suggests that photochemical oxidation occurs through a free-radical mechanism, leading ultimately to negatively charged cysteic acid groups, which are tagged with RB.

(b) Chemical oxidation (bleaching). Bleaching with alkaline hydrogen peroxide, on the other hand, involves thioester hydrolysis at high pH, leading to delipidation, combined with some cystine disulfide cleavage. Both these reactions lead to formation of cysteic acid at the end, which adsorbs RB. This leads to a monotonic increase in fluorescence as shown in Figure 1b.

CURRENT STUDY: REDUCTION-INDUCED DAMAGE TO THE OUTER β-LAYER OF THE EXPOSED SCALE FACES

The present study again uses microfluorometry to establish how reduction with ammonium thioglycolate spontaneously initiates damage to the scale faces by attacking/breaking

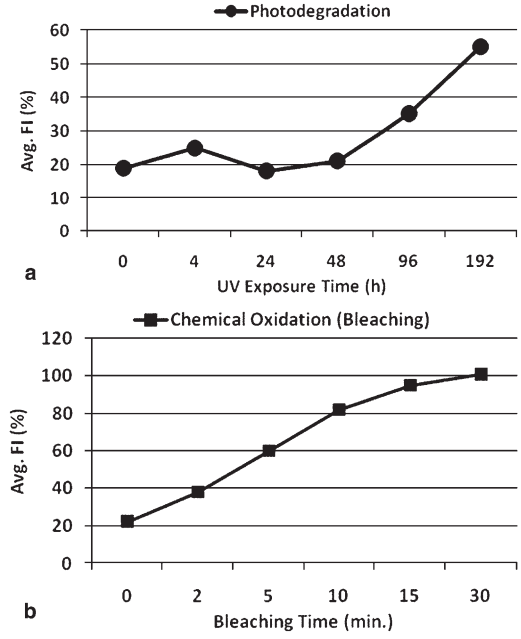

Figure 1. (a) Interfiber averages of fluorescence intensities of unexposed and progressively UV-exposed segments of 30 different hair fibers. (b) Interfiber averages of fluorescence intensities of unexposed and progressively chemically oxidized segments of 30 different hair fibers.

down the 18-MEA-containing lipid layer of the exposed cuticle surface. Again, the intact hydrophobic lipid domains on the exposed scale faces resist rapid adsorption of the cationic fluorochrome (indicated by low levels of fluorescence intensity of the scale faces). However, removal of the 18-MEA lipid layer from the scale faces leads to rapid adsorption of the cationic Rhodamine B, which is indicated by the high fluorescence intensity of the scale faces. We have shown (9) that cuticular damage increases from root to tip end, even in unaltered hair (indicated by increases in fluorescence intensity); therefore, studies of progressive reduction were again carried out along the same hair fibers. This eliminates additional problems due to fiber-to-fiber variation. Adjacent sections of relatively short segments of the root portion of the same hair fibers were exposed for increasing times to reduction with ammonium thioglycolate, (Figure 2).

Again, the tagging time of the reduced hair segments was kept short to limit the tagging process to adsorption and to prevent dye diffusion into the cuticula. Increased delipidation of the hair surface is indicated by high fluorescence intensity, as a result of dye uptake by acid functionalities on the scale faces.

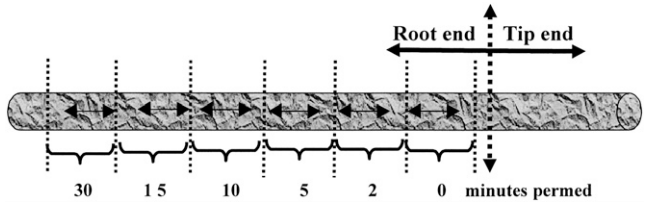

Figure 2. Designating specific fiber sections to reduction with ammonium thioglycolate.

Figure 3 compares the averaged fluorescence intensities of interfiber averages between progressively reduced and progressively bleached segments of 30 different hair fibers. A total of 1200 fluorescence intensity data points were measured along each of the six segments that were scanned for each of the 30 individual fibers of each set. As shown in Figure 3, the fluorescence intensity (which is proportional to dye uptake) of hair segments exposed to progressive reduction with ammonium thioglycolate increases much more rapidly during short treatment times than was observed in chemically oxidized hair. Damage to the scale faces occurs at a much faster rate during reduction than during chemical oxidation (see Figure 4) and photochemical oxidative processes (see Figure 2a). Under the experimental conditions used in this study, a larger number of disulfide groups is converted much more rapidly to R-SH by reduction, than to SOx by oxidative processes.

Also, in the case of reduction, thioester cleavage (on the exposed scale faces) takes place along with cystine disulfide reduction (in the bulk of the hair fiber). The concept is as follows:

Cystine disulfide reduction reaction (in the bulk of the hair fiber). The chemistry of reduction reactions, which occur in the bulk of the hair fiber, involves a two-step reaction of cystine disulfide reduction, and in the case of reduction of hair by ammonium thioglycolate, the two reversible reactions shown below in equations 1 and 2 are involved. In the first step, a mixed disulfide is formed as the intermediate, having a carboxyl group which is also negatively charged and capable of adsorbing the cationic fluorochrome RB. Sharply increasing FI right from the beginning suggests that these reactions occur initially at a faster rate (probably because of higher concentration of reactants). Then the mixed disulfide is used in the second step, and therefore its concentration goes down as the reaction progresses. Contrary to the commonly held notion that mixed disulfide is unstable, significant amounts of the mixed disulfide remain in the bulk of the reduced hair. This is why reduced hair swells more than oxidized hair.

$$K-S-S-K+\ RSH \rightleftarrows K-S-S-R+KSH \tag{1}$$

$$K-S-S-R+\ RSH \rightleftarrows R-S-S-R+KSH \tag{2}$$

Thioester cleavage (on the exposed scale faces). On the surface of the exposed scale faces, however, although reactions of similar nucleophilic substitutions occur, their outcome is different. This is shown by the two reactions shown in equations 3 and 4 below. The results obtained in this study strongly suggest that ammonium thioglycolate reacts with the

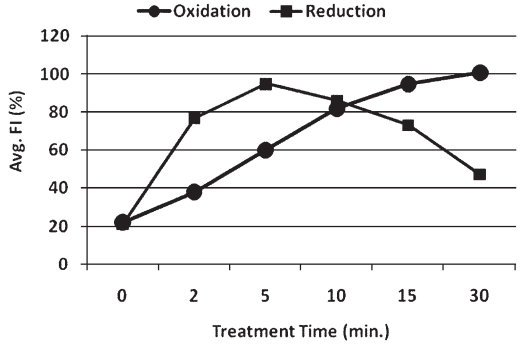

Figure 3. Comparisons of interfiber averages of fluorescence intensities (FI%) between progressively bleached and progressively reduced segments of 30 different hair fibers.

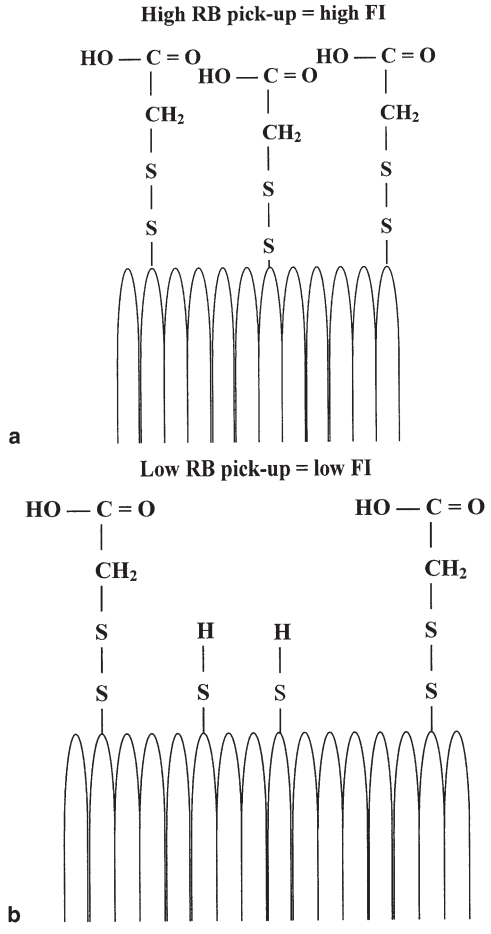

Figure 4. (a) Schematic of the appearance of the F-layer (lipid domains) on the scale faces during the initial stages of reduction. (b) Schematic of the appearance of the F-layer (lipid domains) on the scale faces after completion of the second step.

thioester group on the surface of the exposed cuticle face by a nucleophilic displacement (RS^- or OH^-), releasing 18-MEA (or other lipids) as shown in equation 3:

$$K-S-O-\overset{\overset{O}{\|}}{C}\wedge\wedge\wedge\wedge\wedge\wedge\wedge\wedge\wedge K- \underset{\underset{RS^{(-)}}{\uparrow}}{S} -\overset{\overset{O}{\|}}{C}\wedge\wedge\wedge\wedge\wedge\wedge\wedge\wedge\wedge \rightarrow K-S-S-R + 18\text{-MEA (or other lipid)} \quad (3)$$

The reaction is similar to the one involving a cystine disulfide functionality involving two steps, the second step being:

$$K-S-\underset{\underset{RS^{(-)}}{\uparrow}}{S}-R \rightleftarrows K-SH + R-S-S-R \quad (4)$$

The first step (equation 3) is unlikely to be a reversible reaction; the second step (equation 4) is probably reversible. In the initial stages (five minutes of reduction), the F-layer (lipid layer on the scale faces) will appear as shown in Figure 4a. After completion of the second step of reduction, the final appearance of the F-layer (lipid domains) on the scale faces will appear as shown in Figure 4b. It is important to point out again that this surface (exposed scale face) delipidation reaction has nothing to do with the reduction taking place in the bulk of the hair fiber by the conventional reversible two-step reaction mechanism.

The hair that has undergone these reduction reactions will have mainly –SH groups, and a small amount of SO_x^- groups (air-oxidized -SH groups), and in the case of reduction with ammonium thioglycolate, hair will also have the mixed disulfide K-S-S-R, which is a $-C-S-S-CH_2-COO^-$ group (depending on the pH). Also, it should be noted that at short reaction times (equation 1), the concentration of the mixed disulfide is high and decreases progressively with treatment time. Since the pH of the Rhodamine tagging solution is ~5.8, it is unlikely that the -SH group ionizes to $-S^-$ to form salt linkages with the quaternary nitrogen of the Rhodamine B. However, Rhodamine B can easily form a salt link with the $-COO^-$ of the mixed disulfide. This is the cause of such high fluorescence intensity at short reduction times when the concentration of the mixed disulfide with the $-C-S-S-CH_2-COO^-$ group is the highest.

Wettability as a measure of surface damage caused by reduction. We wanted to substantiate the fact that chemical oxidation shows progressive damage to the cuticle surface as a function of increasing treatment time, while in the case of the reduction reaction, the fluorescence intensity reaches a maximum by five minutes of reduction treatment and gradually decreases during longer exposure times.

Therefore, we used an alternate technique, which is well-suited to detect and characterize changes in the surface chemistry of the scale faces, namely, wettability scanning using the Wilhelmy technique (using our TRI/scan apparatus) (8). In this case, work of adhesion, which is a measure of surface wettability, was used to express changes in the surface chemistry of progressively oxidized and reduced hair fibers. The magnitude of the work of adhesion should reflect the increase in surface energy caused by oxidation and reduction processes, involving the removal of the lipid and creation of acid functionalities in the hair surface.

Work of adhesion is given by the expression

$$\sigma_{LV}(1+\cos\theta) \tag{5}$$

where cos θ is the contact angle and σ_{LV} is the surface tension of the wetting liquid. Studies at TRI using this technique, using water as the test liquid, have shown that the "work of adhesion" for the reduced hair increases much more rapidly and to a greater extent than that of oxidized hair (Figure 5). The results obtained in these earlier studies, using single-fiber wettability scanning, support the results obtained in our current research quite well. As can be seen in Figure 5, the progressively increasing hydrophilic nature of the scale faces, stemming from increased lipid scission by hydrolysis and progressive formation of acid groups on the scale faces, increases the work of adhesion of the hair fiber surface during chemical oxidation with hydrogen peroxide. However, in the case of reduction, a maximum of hydrophilicity is reached by six minutes of treatment,

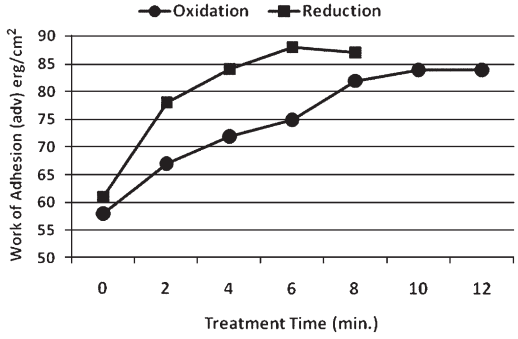

Figure 5. Effects of oxidation (alkaline H_2O_2) and reduction (NH_4OH thioglycolate) on hair fiber surface wettability (on the outer β-layer of the exposed scale faces).

after which a decrease is observed. These results obtained by single-fiber wettability scanning correspond well with the results of the microfluorometric studies.

"Relipidation" or "refatting" of the reduced hair surface with CETAB. In earlier oxidation studies, we had shown that after scission of the 18-MEA, the newly formed acid groups (acidification) on the scale faces can become "relipidized" or "refatted" by electrostatic bonding with a cationic conditioning molecule during subsequent treatment. In other words, the cationic conditioning molecule is used to replace the "lost" lipids on the scale faces. The same approach was used for reduced hair. Reduced hair fibers will also adsorb the low-molecular-weight cationic CETAB because of the negative charges generated on the hair surface during the reduction reaction.

Therefore, microfluorometry was again used to detect the resulting changes in the surface chemistry of the cuticula caused by reduction-induced delipidation and the subsequent relipidation/refatting with CETAB. Hair fibers that had been reduced for various times were treated for 15 minutes with a 0.5% aqueous CETAB solution, rinsed for 30 seconds in running water, and air-dried overnight at room temperature. The hair was then tagged for 60 seconds with a 0.020% aqueous Rhodamine B solution, rinsed for 15 seconds, and blow-dried at a moderate temperature. Microfluorometric scans were then carried out along the length of an appropriate number of these hair fibers. Comparisons between the interfiber averages of the fluorescence intensities of reduced/RB-tagged and reduced/CETAB-treated/RB-tagged hair segments are shown in Figure 6.

The averaged fluorescence intensity of the CETAB-treated controls and that of the CETAB-treated long-term-reduced hair segments are rather similar, suggesting that long-term-reduced hair treated with CETAB behaves in a manner similar to unaltered control hair with an intact lipid layer. This indicates a similar hydrophobic surface chemistry of the "long-term-reduced, CETAB-treated" hair stemming from the presence of a lipid-monolayer-like structure from CETAB molecules on the scale faces. Short-term-reduced/CETAB-treated hair segments still show a high fluorescence intensity; however, it is lower than the fluorescence of the comparable reduced hair segments without the CETAB treatment.

To explain the results of Figure 6, we again need to consider the chemistry of reduction reactions as explained in the equations above. Reduction of hair by ammonium thioglycolate involves these two reversible reactions and produces mainly –SH groups, a small

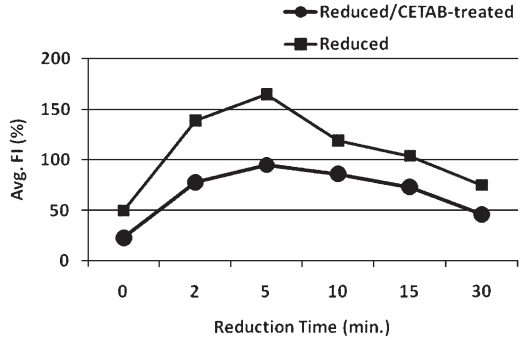

Figure 6. Interfiber averages of fluorescence intensities of "reduced" and "reduced and then CETAB-treated" hair segments, subsequently tagged with the cationic RB. The lower fluorescence intensity of "reduced (delipidized)," then CETAB-treated scale faces indicates a decrease in available sulfonic acid groups due to "relipidation reaction/refatting" with the cationic CETAB molecule.

amount of SO_x^- groups from air-oxidized -SH groups, and the mixed disulfide with $-C-S-S-CH_2-COO^-$ groups. It is shown again that the concentration of the mixed disulfide is highest at short reaction times (equation 1), and decreases progressively with reaction time. This is clearly seen in Figure 6.

When treated with CETAB, the cationic molecules will adsorb by salt links at the (air-oxidized -SH) SO_3^- and $-C-S-S-CH_2-COO^-$ groups of the reduced hair surface. The schematic representation in Figure 7 shows that what we envision might occur to the

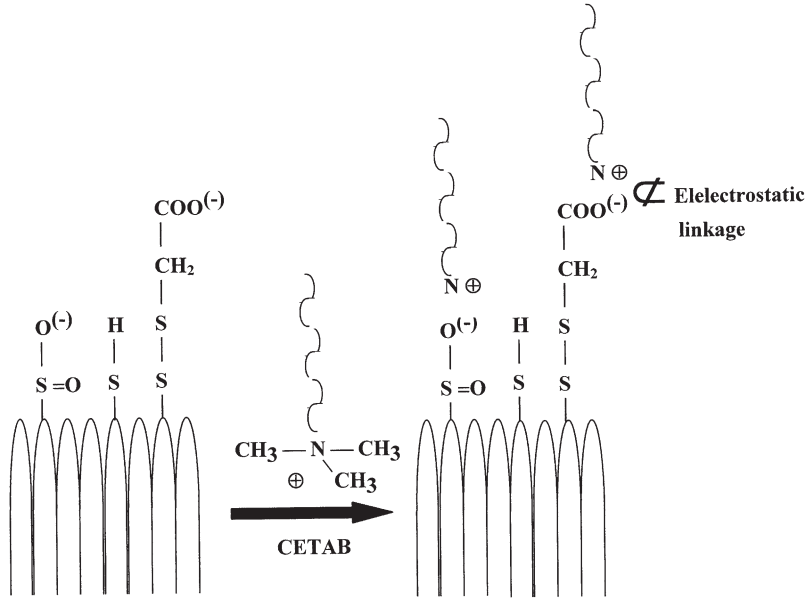

Figure 7. Schematic of what might occur to the outer β-layer of the exposed scale faces during reduction (delipidation) and subsequently during a "relipidation/refatting" treatment with the cationic conditioning molecule CETAB.

outer β-layer of the exposed scale faces during reduction (delipidation) and subsequently during treatment with the low-molecular-weight cationic conditioning molecule CETAB (relipidation or refatting).

X-ray photoelectron spectroscopy (XPS) as a measure of surface damage caused by reduction. To help explain and understand the changes in the surface chemistry of reduced hair samples, XPS was used as an additional technique. XPS was used to determine the concentration and chemical state of all detectable elements. In investigating changes in the surface chemistry of reduced hair samples, of special interest was, of course, the change in surface sulfur concentrations from sample to sample. For ease of comparison, the results of the XPS analysis of the hair categories investigated (unaltered and reduced) are shown in Table I.

Of special interest in these XPS analyses is the element sulfur. The sulfur listed is the total sulfur concentration on the scale faces of each specific hair category:

(a) The untreated hair had the least amount of sulfur (~0.3 atom%) among the hair categories. It is expected that most of the lipid layer (F-layer) on the hair surface is intact; however, low levels of damage to the surface lipids pre-exist.

(b) Figure 8 shows that for both the 5- and 30-minute reduced hair, the scale surface concentration of SO_x (SO_3^-) at ~168 - 169 eV is rather small (compared to photochemically oxidized hair), arising mainly from the air-oxidation of -SH. A tiny bump appears at a lower binding energy of ~164 eV on both light-exposed and reduced hair, and is probably a trace of C-S stemming from the amino acid cystine. For comparison, we have shown an XPS scan of UV-treated hair, showing the extreme delipidation UV radiation does to the exposed scale faces. It is clear that the mechanism of lipid removal is quite different between oxidative and reductive processes.

Table 1
Concentration† of Elements Detected (in atom%)

Hair sample	O	N	C	S
Unaltered	10.0	1.5	83.9	0.3
5-min reduced	14.3	0.8	77.6	0.6
30-min reduced	15.0	1.1	77.2	0.4

†Concentrations are normalized to 100%. XPS detection is ~0.1 atom%.

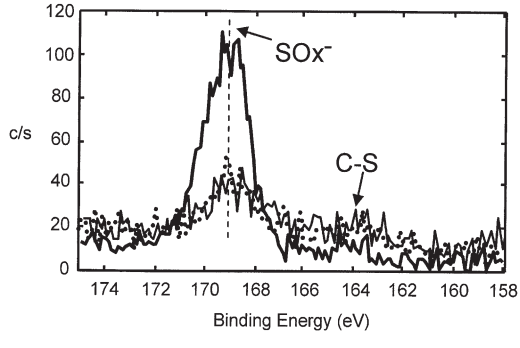

Figure 8. High-resolution spectra of the changes in SO_x^- and C-S concentrations on the surface of (–) 200-h light-exposed, and (–) 5-min- and (…) 30-min-reduced hair.

CONCLUSIONS

Microfluorometric scanning, single-fiber wettability scanning, and XPS analysis show rather similar results, in spite of their greatly varied applications. These techniques are highly sensitive to measuring changes in the surface chemistry of the scale faces. Short-term, rapid adsorption of the cationic fluorochrome and changed wetting properties are good indicators of changes in the chemical nature and surface wettability. Since XPS analysis is able to detect atomic species at the very surface of the scale faces, receiving signals from an escape depth as shallow as 25 Å, it appeared ideal to use this technique to characterize treatment-induced changes of the hair surface. Assuming that the upper β-layer is ~50 Å-thick, XPS detects the 18-MEA domains on the scale faces prior to oxidation or reduction, and the newly formed sulfur entities after removal of the fatty acid 18-MEA from the scale faces. The results of these analyses clearly indicate reduction-induced delipidation and acidification of the scale faces.

The reduced hair fibers show only very low concentrations of sulfur present as –SH. Sulfur present in the mixed disulfide is not registered because of its blockage with the $-CH_2-COOH$ group.

ACKNOWLEDGMENTS

This work was carried out with support from TRI sponsors of the international hair-care industry. The authors thank Ms. C. J. Dansizer for wettability measurements.

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