J. Soc. Cosmet. Chem., 44, 347–371 (November/December 1993

Quantification and prevention of hair damage

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Received June 22, 1993. Presented at the Annual Scientific Seminar of the Society of Cosmetic Chemists, Baltimore, May 6–7, 1993.

Synopsis

Methods were established to evaluate primary chemical damage to hair from oxidative and reductive treatments. The effects of subsequent grooming treatments (combing, shampooing, and conditioning) were documented. Analytical methods used to evaluate hair damage included surface analysis through microfluorometry, scanning electron microscopy, and Wilhelmy balance wettability. Structural damage was evaluated by studies of dye diffusion, amino acid composition, mechanical properties, and fatigue behavior.

INTRODUCTION

Through efforts to improve appearance, hair may be exposed to damaging chemical and mechanical modifications. Once irreversible damage has occurred, other hair cosmetics are used to prevent further deterioration during subsequent grooming. For optimal product development, a quantitative assessment of hair damage is required so that the protective effects of hair care formulations can be established.

Over the last 25 years, much research has been done on hair damage from chemical treatments (bleaching and permanent waving) and grooming, including shampooing and combing. Beyak (1) established that both bleaching and perming can result in losses of up to 20% in mechanical properties. Robbins and Kelly (2,3) studied the amino acid composition of chemically altered hair and found changes from both bleaching and permanent waving.

Changes in hair properties from grooming have also been widely studied. The work has centered on microscopy and on wearing away the cuticular layer, which is five to ten scales thick (4). Cosmetic treatments, such as bleaching and perming, can be severe enough to damage or completely wear away the cuticle, as shown by Robinson (5). Normal grooming of hair, including combing, brushing, and shampooing, also produces damage that is progressive. This phenomenon was described in detail by Garcia *et al.* (6).

Most of the research has centered on damage from either chemical cosmetic treatments or from grooming practices. Chemical damage has been studied primarily by analyses of bulk fiber properties, and grooming damage has been viewed by microscopy of the fiber surface. An important but largely unexplored possibility is that one treatment might predispose hair to even greater damage from a second treatment, or conversely, that one treatment could alleviate the damaging effects of another.

The prime objective of an industry-wide research project at TRI is to explore methods of establishing the extent of damage from, among others, oxidative and reductive treatments. Damage to hair surfaces as a function of severity of these treatments has been measured using microfluorometry, scanning electron microscopy, and Wilhelmy balance wettability. Changes in hair structure, or bulk properties, have been quantified via dye diffusion studies, amino acid analysis, mechanical properties evaluations, and fatigue behavior. These analytical techniques are discussed, and the effects of subsequent grooming treatments (combing, shampooing, and conditioning) in causing and alleviating secondary mechanical damage are explored.

EXPERIMENTAL

HAIR TREATMENTS

Bleach treatments. Dark brown European hair from DeMeo Brothers Company, New York, was used. The segment near the root end, five inches long, was taken for use in this study. Bundles of hair were prepared, weighing 10 g each. The samples were rinsed extensively in deionized water.

Two types of bleach treatment were performed: 6% solution of H_2O_2, at pH 10.2, and a bleach creme, containing a persulfate with a higher peroxide concentration and lower pH. A higher pH was chosen for the 6% H_2O_2 treatment to achieve optimal bleaching effects. All 6% H_2O_2 treatments were done at 21°C with a liquid:fiber ratio of 50:1. Hair samples were bleached in 6% H_2O_2 for 30 minutes, 1 hour, and 4 hours, with fresh solution every hour. In an effort to concentrate treatment effects near the fiber surface, a treatment involving multiple exposures (ten) of short duration (2 min) was included. Exhaustive rinsing followed all treatments.

The 30 a minute wella bleach creme treatment was done at 21°C at a liquid ratio of 6:1. The bleach creme formulation contained 9% H_2O_2 at pH 8.6. Other contents of the bleach creme were ammonium persulfate, sodium silicate, sodium bicarbonate, EDTA, and Aerosil.

Perm treatments. Three criteria were used in establishing conditions for perming untreated and moderately bleached (4 hours, 6% H_2O_2) hair. These were 1) the use of an ammonium thioglycolate perm with peroxide neutralizer, 2) the formation of tight curls, and 3) simulation of salon treatments. The information given by Zviak (7) indicated that for untreated hair, 1.0 M thioglycolate at pH 9.5 would be appropriate, with 0.5 M thioglycolate at the same pH for the bleached hair sample. A hydrogen peroxide solution (3%) at pH 7.0 was used as the neutralizer.

Tresses of 0.5 g were secured on small perm rods (⅛″ diameter), using water mist and papers to moisten the hair lock. The rod-mounted tresses were soaked for 20 minutes at room temperature in a large excess of 1.0 M ammonium thioglycolate at pH 9.5 for previously untreated hair and in 0.5 M thioglycolate at pH 9.5 for moderately bleached hair. Rinsing for 25 minutes in running deionized water was followed by 10 minutes in 3% H_2O_2 at pH 7. After a ten-minute rinse under running water, the tresses were removed from the rods and rinsed for two more minutes, followed by blow drying. This cycle was repeated to produce tresses with one, two, and three perm treatments.

Grooming simulation treatments. We have simulated grooming processes by subjecting the hair to a number of cycles of combing, shampooing, shampooing plus combing, and shampooing plus conditioner treatment plus combing. Untreated hair and samples with two levels of oxidative damage were selected for evaluation. Each hair bundle was 13 cm long and contained about 1375 hairs.

Four grooming sequences were applied, as outlined in Table I. Each grooming sequence was performed on wet hair, and was repeated for ten cycles, each time after drying several hours under ambient conditions.

Combing was done by hand, with 25 strokes through each of the four sides of the hair bundle. The total time of combing was 1.25 minutes per 100 strokes. The standard "Ace" comb of brown nylon had 65 tines in 11 cm length. Wet hair was blotted between paper towels prior to combing.

Shampoo was applied to the wet hair swatch with a 1 cm^3 syringe and was massaged into the hair by hand for two minutes. The hair swatch was then rinsed for two minutes under running deionized (DI) water.

Conditioner (1 cm^3) was applied to wet hair and distributed manually for 30 seconds, then left on for 1.5 minutes, for a total exposure time of two minutes. The hair swatch was rinsed under running DI water for two minutes.

The experimental shampoo and conditioner samples were formulated by Colgate-Palmolive Company. Their compositions are shown in Table II.

Table I
Sample Identification

Bleach treatment	Grooming sequence	Code assignment
Untreated hair		
	None	U0
	Combing	U1
	Shampooing	U2
	Shampooing/combing	U3
	Shampooing/conditioning/combing	U4
10 × 2′ in 6% H_2O_2		
	None	2B0
	Combing	2B1
	Shampooing	2B2
	Shampooing/combing	2B3
	Shampooing/conditioning/combing	2B4
4 hours in 6% H_2O_2		
	None	4B0
	Combing	4B1
	Shampooing	4B2
	Shampooing/combing	4B3
	Shampooing/conditioning/combing	4B4

Table II
Shampoo and Conditioner Formulations

Shampoo		Conditioner	
Ingredient	%	Ingredient	%
ALS	12.0	Cetyl alcohol	3.5
CDEA	4.0	Germ II	0.5
Germ II	0.5	CTAC	0.5
NaH_2PO_4	0.3	DI H_2O	q.s.
DI H_2O	q.s.	(Conditioner base 358-2A)	
(Shampoo base 358-1A)			

Ten cycles of the assigned grooming sequence were applied to each hair swatch as shown in Table II. The order of swatches was randomly assigned and changed for each grooming cycle. The initial wetting of swatches was done in 100 ml beakers, and the samples were segregated by type so that shampoo or conditioner residues did not contact "combed only" samples. The comb was rinsed thoroughly between uses. Hair swatches were dried in air and evaluated using various techniques that will be described.

EVALUATION METHODS

The changes caused by bleaching, perming, and grooming were evaluated in terms of both surface and structural properties. Surface properties were evaluated by microfluorometry and SEM, and surface wettability by the Wilhelmy balance method. The structural or bulk properties evaluated were dye diffusion, amino acid composition (especially cysteic acid content), mechanical properties, and fatigue behavior.

Surface evaluations

Microfluorometry. Bleached hair samples were treated for ten minutes at room temperature in a 0.005% aqueous Rhodamine B solution brought to pH 3.3 with acetic acid, then rinsed for three seconds in distilled water. For the grooming studies, a treatment time of 90 seconds was used.

Cross-sectional and longitudinal microfluorometric studies were carried out using a Leitz MPV 1.1 microspectrophotometer with a PLOEMOPAK attachment. The PLOEMOPAK attachment contains filter blocks dedicated to various narrow and wide band ranges specific for excitation of molecules fluorescing at various wavelengths.

Scanning electron microscopy. A JSM-2 instrument (JOEL Company) was used for the determination of surface features. The samples were gold-coated to a thickness of approximately 80–100 Å.

Wettability. The Wilhelmy balance technique (8) was used to determine single-fiber wettability. A Cahn D200 microbalance was used, with water as the wetting liquid. The wettability scans were made in the with-scale direction, and 3 mm of the fiber surface were scanned at a speed of 3 μm/sec. Fiber perimeters were determined by measuring wetting behavior in hexadecane.

Evaluation of fiber structure

Dye diffusion studies. The diffusion behavior of a fluorescent dye into hair fiber cross sections was measured using microfluorometry. The samples were treated for 3–5.5 hours at 50°C in 0.1% uranin solution, rinsed, dried, embedded and cured, microtomed to 10 μm thickness, and scanned cross-sectionally at a wavelength of 540 nm, using an excitation wavelength range of 450–495 nm.

Amino acid analysis. The amino acid analysis was performed by Wella, AG, Darmstadt, on the untreated and bleached samples prepared at TRI/Princeton. Hair samples were hydrolyzed with 6 N HCl at 110°C for 24 hours. After multiple evaporations to dryness until the solution became neutral, a 5 μl aliquot was withdrawn for derivatization. A pre-column derivatization method reported by Bidlingmeyer *et al.* (9) was used. A 5 μl aliquot was finally injected into the chromatograph. A programmed elution procedure with variable mixtures was used for optimum separation.

Mechanical properties. Wet mechanical properties of single fibers were determined with an Instron tensile tester at a rate of extension of 40% per minute. Cross-sectional areas were assessed by use of an electronic vibroscope.

Fatigue behavior. Constant load fatiguing was carried out on an apparatus that accommodates 40 fibers in an impact-loading mode of fatiguing. The fatigue apparatus was described by Kamath *et al.* (10). Each 3 cm long fiber is mounted on a hook that is adjustable for fiber creep during the fatiguing procedure. A weight of 40 g is attached to the lower end of the fiber. The lower platform oscillates at approximately one cycle per second, and the fibers were fatigued for 100,000 cycles at 65% RH and 21°C. The weights mounted on the fibers clear the lower platform at its lowest position, thereby impact-loading the fibers. Each of the 40 positions has a microswitch counter that stops when the fiber fails. The conditions were the same for the bleached, permed, and groomed hair studies. A sample size of 60 replicates was used in each case. This type of fatiguing is known as constant load fatiguing rather than constant strain fatiguing. Strain levels in these measurements were well within the Hookean range.

RESULTS AND DISCUSSION

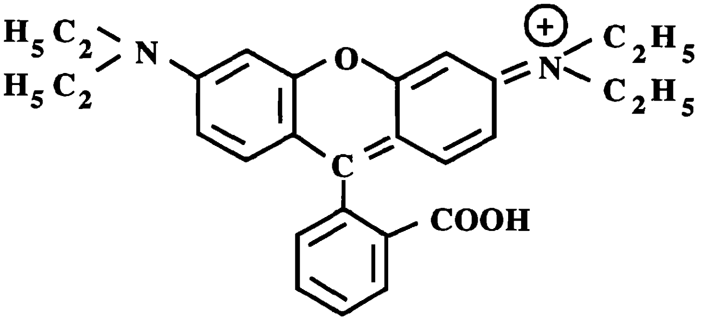
PRIMARY DAMAGE IN BLEACHED AND PERMED HAIR

Surface changes

Fiber surfaces of bleached hair were studied by microfluorometry and SEM. Wettability measurements were made on bleached hair and also on permed samples.

Microfluorometry. Previous work with the fluorescent tracer Rhodamine B (CI Basic Violet 10) suggested that this compound would be suitable for exploring aspects of oxidative damage of the fiber surface and the cuticular region. Rhodamine B is a cationic dye that would be expected to show interactions with the sulfonic acid groups produced by oxidative treatments of hair; the dye structure is shown in Figure 1.

Longitudinal views of characteristic filaments of the four bleach treatments with Rhodamine B are shown in Figure 2. Rhodamine B deposited at the scale edges of unbleached hair (Figure 2a), with the possibility of some slight penetration into either the endocuticle or the intercuticular cell membrane. Oxidation for one hour (Figure 2b)



Rhodamine B

Figure 1. Structure of Rhodamine B.

produced a significant increase in scale penetration and scale face deposition. This is much more pronounced after four hours of bleaching (Figure 2c), where the scale face appears to be extensively marked by the tracer. In the 30 minute bleach creme treatment, the scale faces show slightly less fluorescence intensity (FI) than in the four hour peroxide treatment.

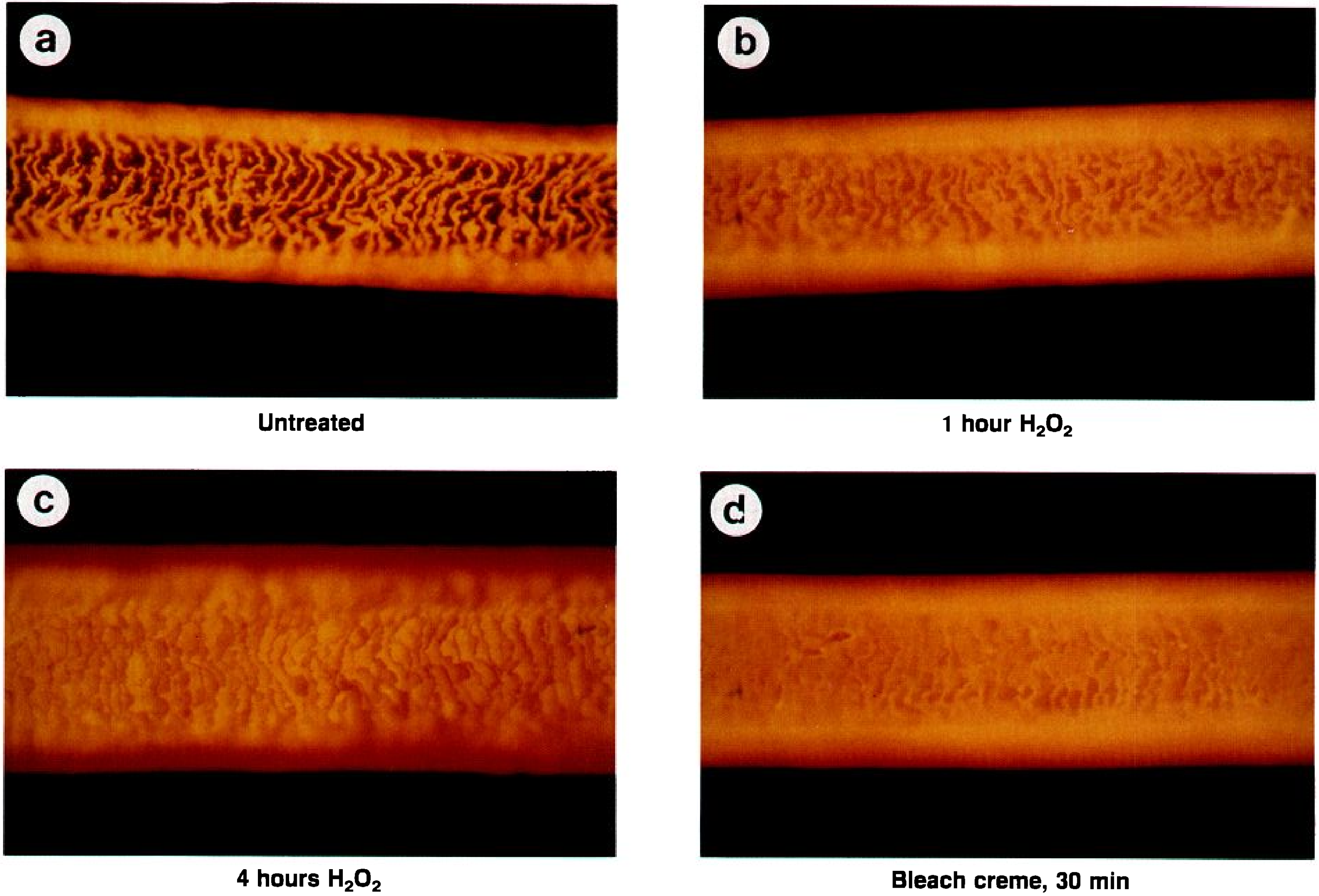
In order to quantify this behavior, longitudinal scans of fluorescence intensity were made along 2.2 mm of fiber surface, as seen in Figure 3. Fluorescence intensity levels were quite uniform in all samples. The outlining of scale edges in the untreated and the one hour hydrogen peroxide treated, and the extensive scale penetration, as shown for the four hour treated fiber, are clearly noticeable.

In Figure 4, average values of fluorescence intensity show a considerable increase as a result of oxidative damage. In general, the fluorescence intensity increased with increasing peroxide treatment times, and a major level of oxidative surface damage occurred already within one hour. The 30 minute bleach creme treatment produced essentially the same level of oxidative surface damage as the four hour 6% H_2O_2 treatment.

Scanning electron microscopy. When viewed by SEM, untreated and bleached hair showed a variety of features in their surface topography, as seen in Figure 5. Besides the normal cuticles of untreated fibers, loose and broken-off cuticle edges were observed. Fibers of all four categories displayed cuticles with holes in them, although hole formation was most extensive in bleached hair. Erosion of the cuticle face was observed after the four hour bleach treatment prior to subsequent combing. The bleach creme treatment produced the least topographical damage among the bleaching conditions we investigated.

Wettability. The surface of intact untreated hair is dominated by the hydrophobic epicuticle, while bleaching produces a hydrophilic hair fiber surface.

Figure 6 illustrates the factors involved in solid–liquid interactions. A hydrophilic fiber (a) shows a low contact angle (θ) with a hydrophilic liquid such as water, which has a surface tension σ_{LV} of $\sim$72 mN/m. This results in a concave meniscus at the fiber-liquid contact line and a positive wetting force, F_w. A hydrophobic fiber (b), such as the root end of an untreated hair fiber, forms an obtuse contact angle with water, resulting in a convex meniscus and a corresponding negative wetting force.



Untreated

1 hour H_2O_2

4 hours H_2O_2

Bleach creme, 30 min

Figure 2. Longitudinal views of unbleached and bleached hair fibers treated with Rhodamine B.

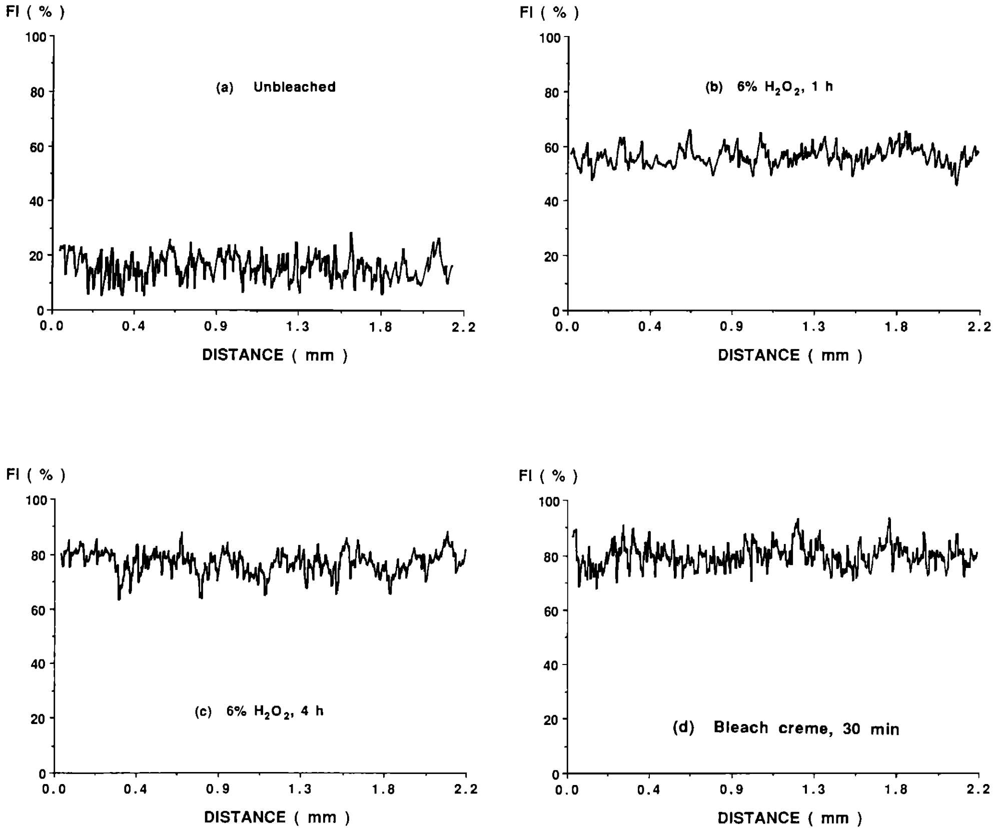


Figure 3. Longitudinal fluorescence intensity scans of unbleached and bleached hair fibers treated with Rhodamine B.

The wetting force is given by equation 1:

$$F_w = P\sigma_{LV} \cos\theta_a \tag{1}$$

where P is the fiber perimeter, σ_{LV} the liquid surface tension, and θ_a the advancing contact angle. The fiber perimeter is measured with hexadecane in a separate experiment, and the liquid surface tension is measured with a platinum wire.

Work of adhesion, W, used in this work as an index of surface energy, is defined in the present context as the work required to separate a solid/liquid system at the interface:

$$W = \sigma_{LV} (1 + \cos\theta_a) \tag{2}$$

Figure 7 shows the effects of various oxidative treatments on the wettability of hair fibers. The repeated short time treatment in 6% H_2O_2 (2′ × 10) and the bleach creme treatment are similar in their effects on water wettability, approaching surface energy levels close to that of the one hour treatment in 6% H_2O_2. The two minute bleach treatment repeated ten times has a total bleaching time of 20 minutes. Since the bleaching solution is most effective at the start of the bleaching treatment, and a fresh solution was used at each of the ten treatments, it seems reasonable that this sample would show greater change than one subjected to a single 30 minute bleach treatment. The bleach creme treated sample had a W value in agreement with other 9% H_2O_2

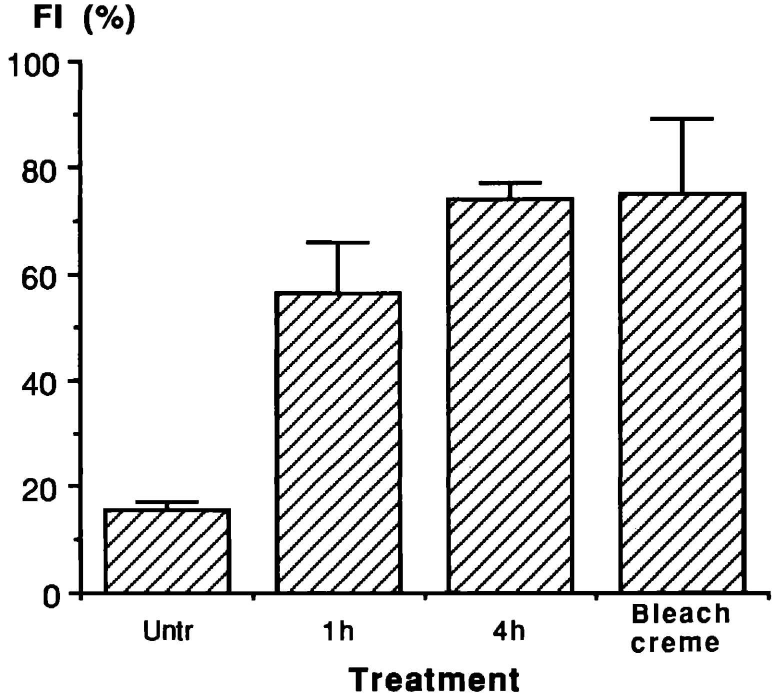


Figure 4. Average fluorescence intensity for five each of longitudinally scanned unbleached and bleached fibers treated with Rhodamine B.

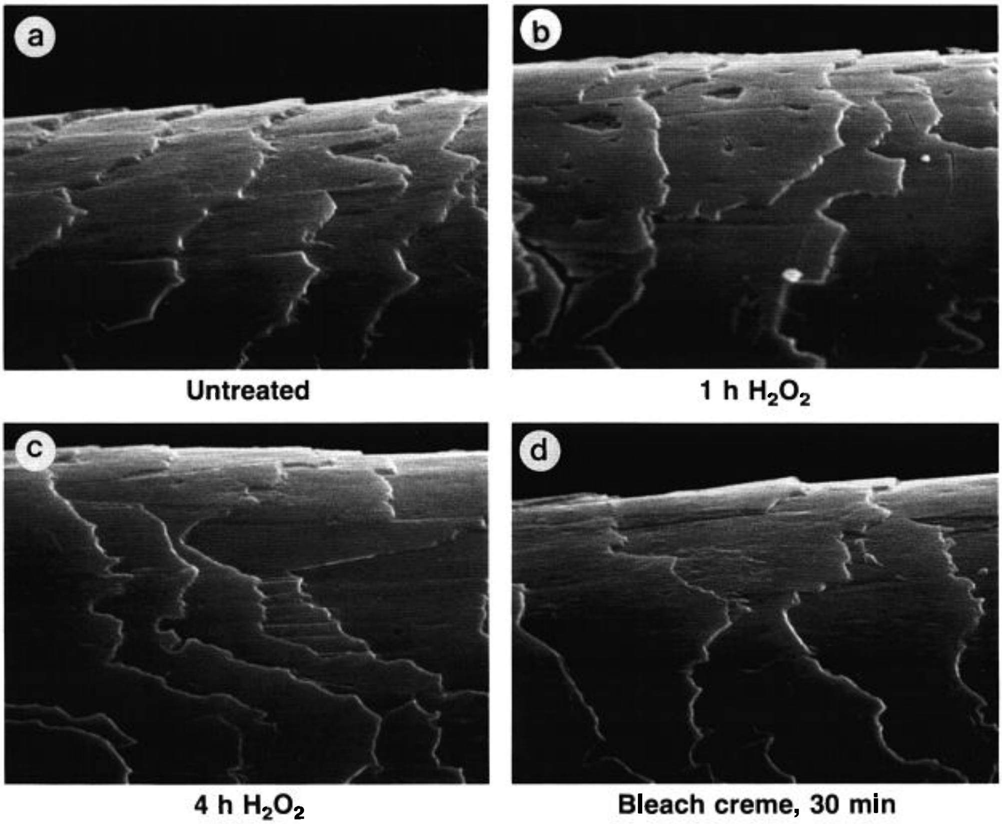
treatments done in our labs under similar conditions. Although the surface of the hair shows a relatively low level of wettability, we have seen that damage to the fiber interior is more extensive than one might expect from the observed change in surface properties.

We also studied the water wettability of unbleached and bleached hair permed one, two, and three times. In contrast to the increased wettability of bleached hair, after bleaching even repeated perm treatments did not produce a major increase in wettability. This observation was somewhat surprising since reductive scission of disulfide bonds leads to the formation of two hydrophilic sulfydryl groups that would be expected to produce an increase in the hydrophilicity of the hair fiber surface. In previous (8) studies of the effect of reduction without subsequent reoxidation (neutralization) on the wettability of hair, we observed that wettability increased rapidly and leveled off at W values of 85–90 mN/m.

This difference from the previously observed behavior must be attributed to the fact that the neutralization step (3% H_2O_2) following the perming apparently leads to extensive reformation of the original disulfide bonds in the surface regions of the hair. Although bond reformation with peroxide is known not to be complete, the surface sulfydryl groups are the most accessible to reformation and would be the first and most easily affected.

Structural changes

Dye diffusion. The rate of dye transport in keratin fibers is strongly affected by the nature of the fiber structure. Any decrease in the disulfide crosslink density in the matrix and



Untreated 1 h H_2O_2

4 h H_2O_2 Bleach creme, 30 min

Figure 5. SEMs of bleached hair, showing cuticle damage, hole formation, and abrasion effects.

introduction of highly hydrophilic sulfonic acid groups lead to an increase in swelling, and with it to higher transport rates. One way to characterize the effect of bleaching on hair structure is, therefore, to determine the change in diffusion of dyes into the hair fiber cross section. Diffusion studies were carried out using the strongly fluorescent molecule uranin, the sodium salt of fluorescein (CI Acid Yellow 73) shown in Figure 8.

The following treatment conditions were evaluated: one hour and four hours in 6% H_2O_2 and 30 minutes with bleach creme. Figure 9 shows micrographs of the cross sections of the dyed fibers and the corresponding cross-sectional scans that were used for the calculation of diffusion coefficients.

The ring dyeing of the cuticular region appears to be due to the rapid penetration of the dye solution into the intercellular regions or the endocuticular domains. Dye concentration profiles (which are not shown) in the cortex in the early stages of diffusion seem to indicate Fickian kinetics, as shown by the solutions of Fick's second equation for radial diffusion in a cylindrical geometry. A typical solution is given in equation 3 (11). The diffusion coefficients are calculated using the Bessel functions. Concentration-dependent coefficients will be obtained by this procedure; however, in this case, the concentration dependence of the diffusion coefficients seems to be negligible.

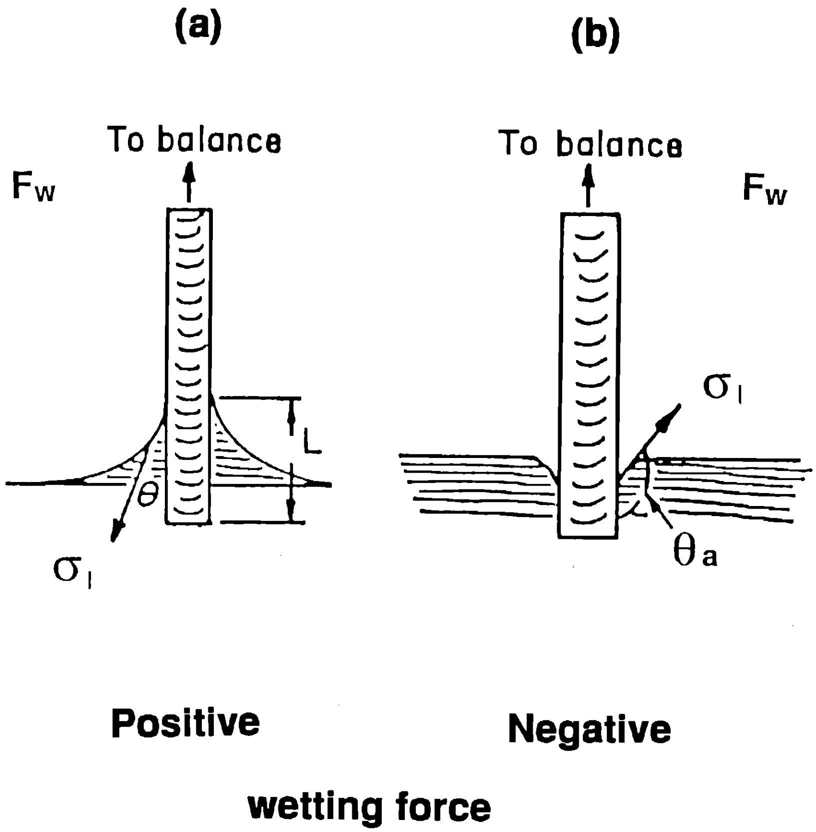


Figure 6. Fiber–liquid interactions, showing positive and negative wetting forces.

$$\frac{c}{c_0} = 1 - 2\sum_{n=1}^{\infty} \exp\left(\frac{-Dt}{a^2} \cdot \beta_n^2\right) \cdot \frac{J_0(r\beta_n/a)}{\beta_n J_i(\beta_n)} \tag{3}$$

Diffusion coefficients calculated at 0.1 intervals of normalized fluorescence intensity along the dye concentration profile are given in Table III for those categories for which diffusion gradients could be obtained under the chosen dyeing conditions. As seen in Figure 9, uranin diffusion into the hair after oxidation with the bleach creme is so fast that after 5.5 hours at 50°C, the fiber is completely penetrated, and the diffusion coefficient had to be determined after shorter dyeing times.

The overall effect of bleaching on the structure of the hair fiber is quite significant, as indicated by the change in diffusion coefficient. After one hour of treatment with 6% H_2O_2, diffusion rates into the cortex have already doubled, and extending the oxidation time to four hours produces only a marginal increase in diffusion rates, suggesting that most of the modification had occurred within one hour or less. The increase in the rate of dye diffusion could be due to a breakdown of the barrier function of the cuticle layers, or to a change in the structure of the cortex by decreasing the crosslink density in the

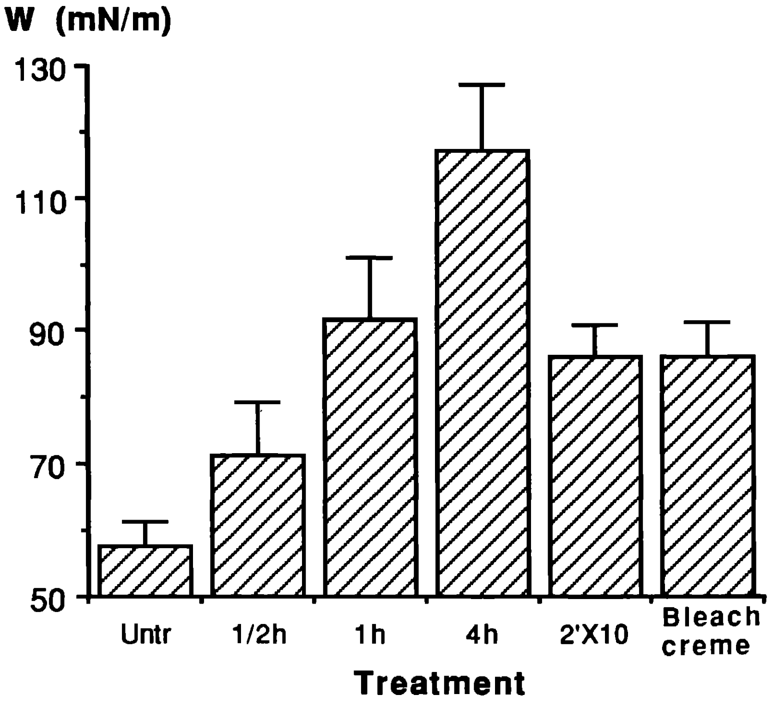
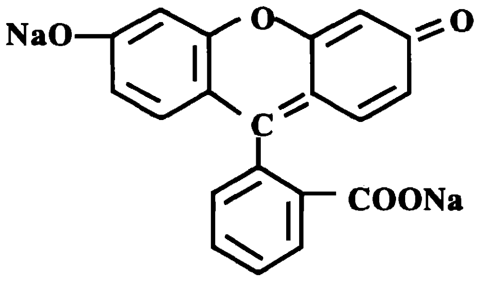


Figure 7. Comparison of average water wettabilities for bleached hair.



Uranin Na salt of fluorescein

Figure 8. Molecular structure of uranin used in dye diffusion studies.

matrix and increasing fiber swelling, or most likely to a combination of these two effects.

Amino acid analysis. Cysteic acid is the major product of cystine oxidation during the bleaching of hair, and so changes in cysteic acid content have been widely studied and reported in the literature. Usually, unbleached hair contains 25–40 μmoles/g of cysteic acid. When the hair is bleached, the cysteic acid content increases to 200–400 μmoles/g, and in severely bleached hair, up to 650 μmoles/g have been reported (12). A decrease of around 20% in tyrosine and methionine and of 10–15% in lysine and histidine has been reported by Robbins and Kelly (2).

The results of the amino acid analysis of the untreated and bleached hair reported in

Table III
Diffusion Coefficients of Uranin in Hair Fibers

Hair sample	$D(m^2/s \times 10^{-15})$
Untreated	3.59 ± 0.67*
1 hour (6% H_2O_2)	9.78 ± 3.67
4 hours (6% H_2O_2)	10.30 ± 0.87
0.5 hours (Bleach creme)	45.21 ± 28.66

* 95% confidence limits.

Table IV are limited to cysteic acid formation. In evaluating results, it is important to note the relatively low amount of fiber dissolved during acid hydrolysis for some of the samples. The cysteic acid values given in Table IV are based on the dissolved fraction of the fiber. Expressing the amino acid content in terms of mol % assumes that the undissolved keratin (not measured) has the same composition as the dissolved part, which is rather unlikely. In the case of hair bleached two minutes, ten times in 6% H_2O_2, only about half the fiber was dissolved and available for assay. For the other samples, dissolution was around 70%, which is considered "normal."

The most damaged sample, according to this technique of analysis, is the one bleached for four hours in 6% H_2O_2, which produced a level of cysteic acid of ~300 μmoles/g. A lower level of damage, in the range of 192 and 211 μmoles/g is found for the samples treated one hour in 6% H_2O_2 and with the bleach creme, respectively. All three results fall into the range of expected values for bleached hair, between 200 and 400 μmoles/g, although the results may be affected by the low percentage of dissolved fiber. The cysteic acid levels achieved in this series of bleached hair is considerably below that for severely bleached or frosted hair (~650 μmoles/g) (12). A decrease in tyrosine or methionine was not observed. The analysis did, however, detect a direct time dependence of damage in the series of hair samples bleached with 6% H_2O_2.

Mechanical properties

1. Bleached hair. The disruption of cystine crosslinks due to bleaching has a major influence on the wet tensile properties of hair. It is well established that in both hair and wool the disulfide bonds contribute largely to wet strength, while the dry strength of the fibers remains unaffected unless more than 60% of the cystine crosslinks have been broken (2). Dry mechanical properties appear to be more sensitive to peptide bond breakdown.

A summary of the effects of oxidative treatments on mechanical properties is given in Table V. The mechanical properties fall into two groups. The ultimate properties, involving measurements at the breaking point of the fibers, show significant differences from the untreated level only after the bleach creme treatment. This suggests that the other treatments cause only minor changes in these properties. However, the evidence obtained from the previously discussed analyses of structural change (dye diffusion and AA analysis) indicates that the 6% H_2O_2 treatments also cause considerable structural damage, suggesting that the trends shown in Table VI have some validity. The non-ultimate mechanical properties (initial modulus, yield stress, and 20% work) show that the four hour, 6% H_2O_2 treatment is indeed damaging, suggesting that mechanical properties that are not measured at the point of fiber failure are more sensitive to oxidative damage.

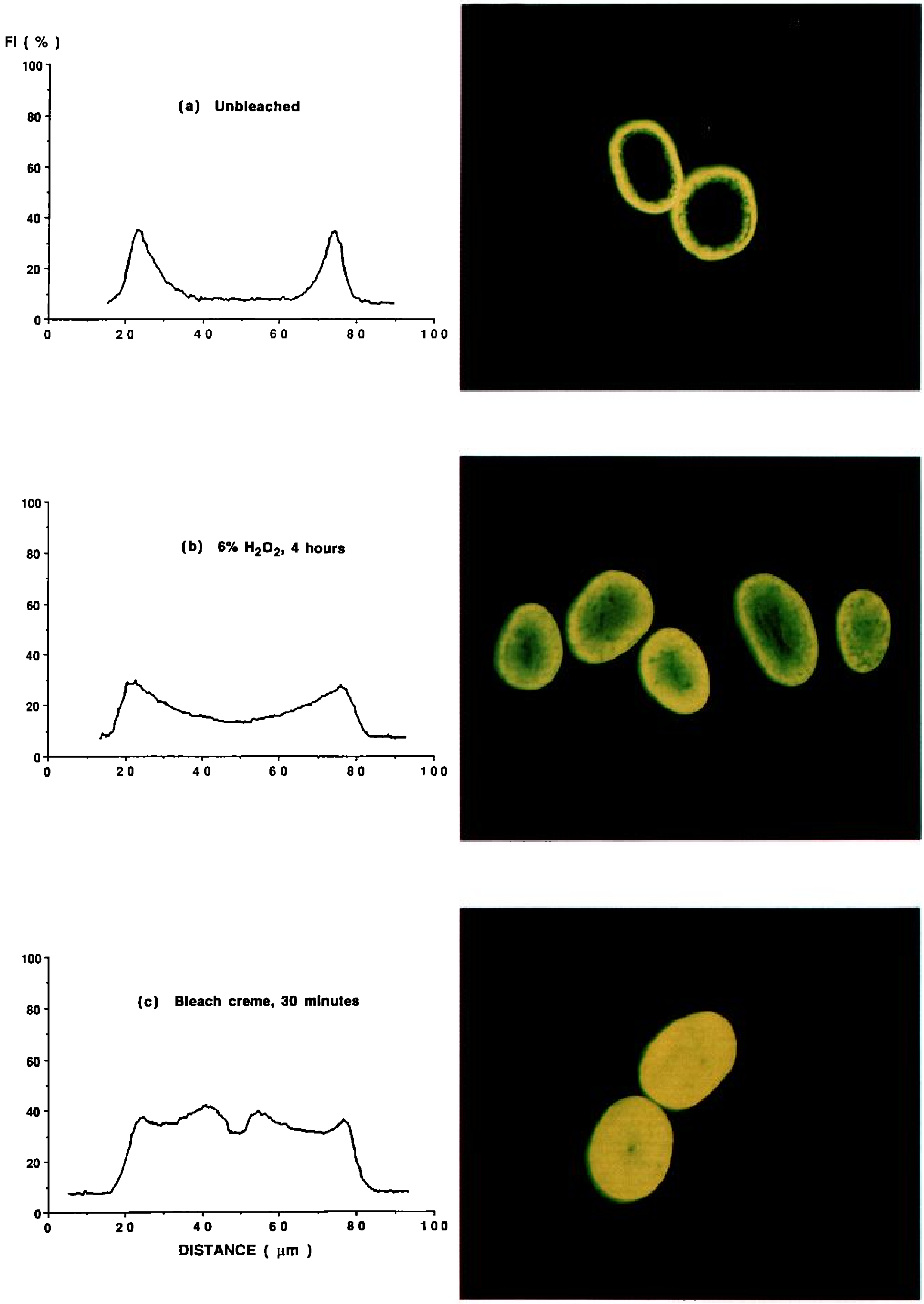


Figure 9. Micrographs of unbleached and bleached hair fiber cross sections dyed 5.5 h with 0.1% uranin and corresponding cross-sectional fluorescence intensity scans.

Table IV
Cysteic Acid Content of Bleached Human Hair

	Cysteic acid		Dissolved fiber
	(μmoles/g)	(mol %)	(%)
Untreated	n.d.*	n.d.*	70
6% H_2O_2			
2 min × 10	114	2.6	52
30 min	148	2.3	78
1 hour	192	3.4	67
4 hours	302	5.2	70
Bleach creme	211	3.7	68

* n.d., Not discernible; less than 40 μmoles/g cannot be detected by this method.

2. Permed hair. The mechanical properties of unbleached and moderately bleached hair (four hour, 6% H_2O_2) were reduced by the first and by each of two successive perm treatments (Table VI). Overall, the effects on the bleached hair sample were similar to those on the unbleached hair through each successive perming cycle. The only difference in the treatments was that the concentration of the thioglycolate solution was halved for bleached hair in accordance with the usual salon practice.

Although these surface properties were only slightly affected by the perming process, the bulk fiber properties were dramatically decreased by the perm treatments. In Figure 10, typical Instron load-extension curves are shown for unbleached and bleached hair. These are generalized curves with specific mechanical properties seen in Table VI. The size and area of the curves decrease with each successive perm treatment. The overall mechanical properties decrease accordingly. For bleached hair with repeated perm treatments, the loss of mechanical properties after one perm is even more dramatic, and by the third perm, the load-extension curve is greatly diminished. The loss of bulk properties is obviously not reflected in surface wettability, which is a reflection of the fact that the properties of the cuticle have little effect on the bulk properties of the hair fiber.

In general, the mechanical properties of both unbleached and bleached hair were reduced by repeated perm treatments. The major difference between unbleached and bleached hair was that the first perm treatment had a more profound effect on bleached hair. In fact, the level of first perm damage on bleached hair was similar by some measures to that produced by three perm treatments on unbleached hair.

Table V
Wet Mechanical Properties of Bleached Hair

Bleach treatment	Modulus (GN/m^2)	Yield stress ($GN/m^2 \times 10^{-2}$)	Work to extend 20% ($MJ/m^2 \times 10^{-1}$)	Breaking stress ($GN/m^2 \times 10^{-1}$)	Work to break (MJ/m^2)
Untreated	2.8 ± 0.23*	6.7 ± 0.76	4.4 ± 0.71	3.3 ± 0.31	2.6 ± 0.31
6% H_2O_2					
2′ × 10	2.6 ± 0.28	5.7 ± 0.79	3.8 ± 0.79	3.0 ± 0.32	2.3 ± 0.30
4 hrs	2.5 ± 0.23	4.9 ± 0.69	2.7 ± 0.27	2.8 ± 0.32	2.2 ± 0.32
Bleach creme	2.1 ± 0.02	—	2.8 ± 0.32	2.1 ± 0.23	1.7 ± 0.30

* 95% Confidence limits.

Table VI
Mechanical Properties of Bleached and Permed Hair

Bleach treatment	No. of perms	Modulus (GN/m^2)	Yield stress (GN/m^2 × 10^{-2})	Work to extend 20% (MJ/m^2 × 10^{-1})	Breaking stress (GN/m^2 × 10^{-1})	Work to break (MJ/m^2)
Unbleached	0	2.8 ± 0.23*	6.7 ± 0.76	4.4 ± 0.71	3.3 ± 0.31	2.6 ± 0.31
	1	2.4 ± 0.43	5.5 ± 0.89	3.0 ± 0.50	2.3 ± 0.43	1.4 ± 0.35
	2	1.5 ± 0.32	3.5 ± 0.95	2.0 ± 0.51	1.7 ± 0.41	0.91 ± 0.21
	3	0.76 ± 0.17	2.5 ± 0.66	2.7 ± 0.65	1.0 ± 0.22	0.69 ± 0.12
4 hour, 6% H_2O_2	0	2.5 ± 0.23	4.9 ± 0.69	2.7 ± 0.27	2.8 ± 0.32	2.2 ± 0.32
	1	1.5 ± 0.23	3.2 ± 0.54	1.7 ± 0.44	1.5 ± 0.29	0.88 ± 0.32
	2	1.1 ± 0.22	2.4 ± 0.59	1.5 ± 0.44	1.4 ± 0.24	0.76 ± 0.14
	3	0.52 ± 0.1	1.4 ± 0.38	1.8 ± 0.47	1.0 ± 0.22	0.72 ± 0.20

* 95% conficence limits.

Fatigue behavior. Hair is routinely exposed to mechanical stresses during combing and brushing, causing repeated low level extensions, mostly within the elastic limit of the fiber. Constant load fatiguing, described earlier, is used as an approximate simulation of the mechanical tensile damage caused by combing. Fatigue data are expressed as number of cycles to failure for a specimen at a given load. Such data can be presented in terms of cumulative failure probability, as given by equation 4.

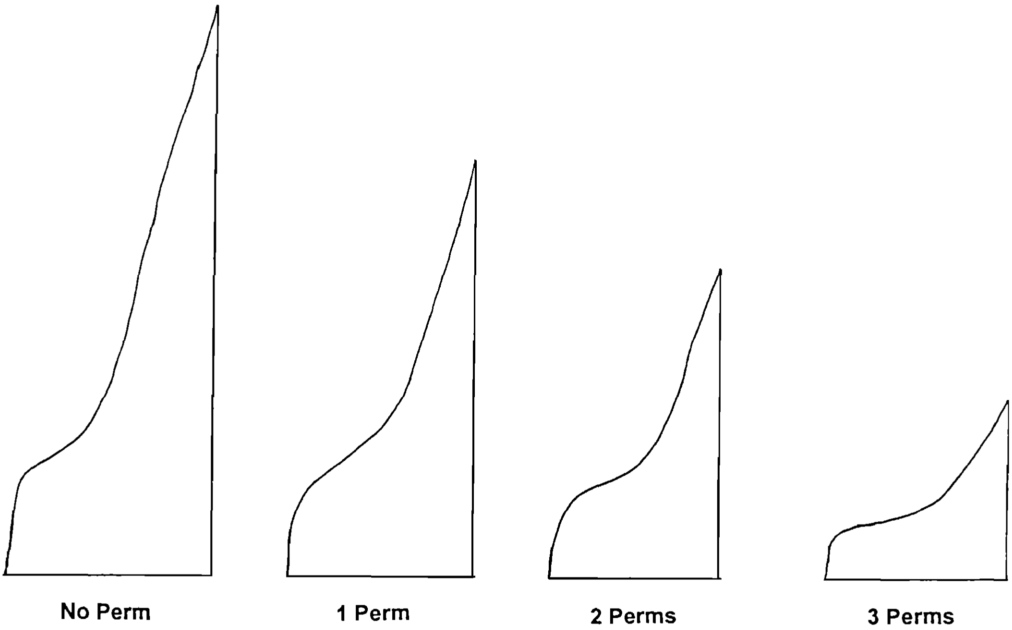
$$F(x) = A(x)^n \tag{4}$$

Where F(x) is the cumulative probability of failure, x is the number of cycles-to-failure, and A is a constant. The exponent n and fatigue half life (h_f), which is the number of cycles required for half the specimens to fail, can be used to characterize the damaging effects of grooming treatments on hair.

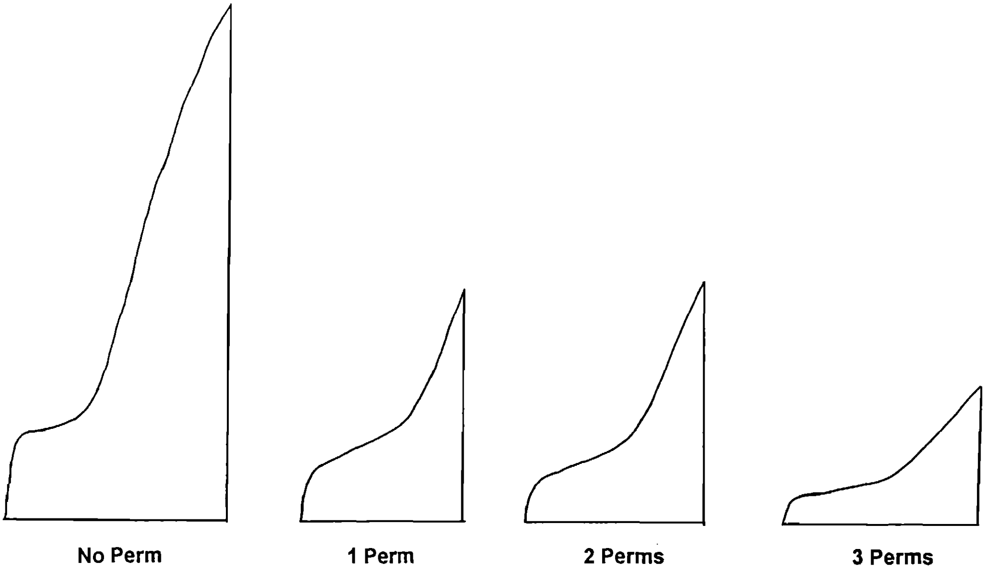
Typical logarithmic plots for unbleached hair after various numbers of perms are shown in Figure 11. The slope of these plots representing the exponent n and the fatigue half life are shown in Table VII. The usefulness of n and h_f in evaluating the damaging effect of a treatment or a combination of treatments is clear from Table VII. Reductions in slope and in fatigue half life indicate that the first perm has a greater damaging effect on bleached hair than on unbleached hair. A second perm brings about a precipitous drop in the fatigue half life, suggesting extensive damage. These parameters seem to become less sensitive with additional treatments as the fibers become progressively weaker. It should be noted that perming involved substantial bending effects as a result of winding on perm rods. This methodology shows promise for the evaluation of fiber damage by a combination of treatments. An attempt will be made to extend these studies to evaluate preventive treatments involving various hair care products.

SECONDARY DAMAGE FROM GROOMING OF BLEACHED HAIR

Changes in the nature and properties of the substrate are of primary concern in the manufacture or consumption of hair cosmetics. While appearance and manageability improvement are the initial goals of any modification of hair surface or structure, it must be kept in mind that such changes can lead to irreversible damage, and efforts must be made to achieve an optimum balance between desired effect and resulting damage.



Unbleached Hair



Bleached Hair

Figure 10. Force-extension curves for hair with repeated perm treatments.

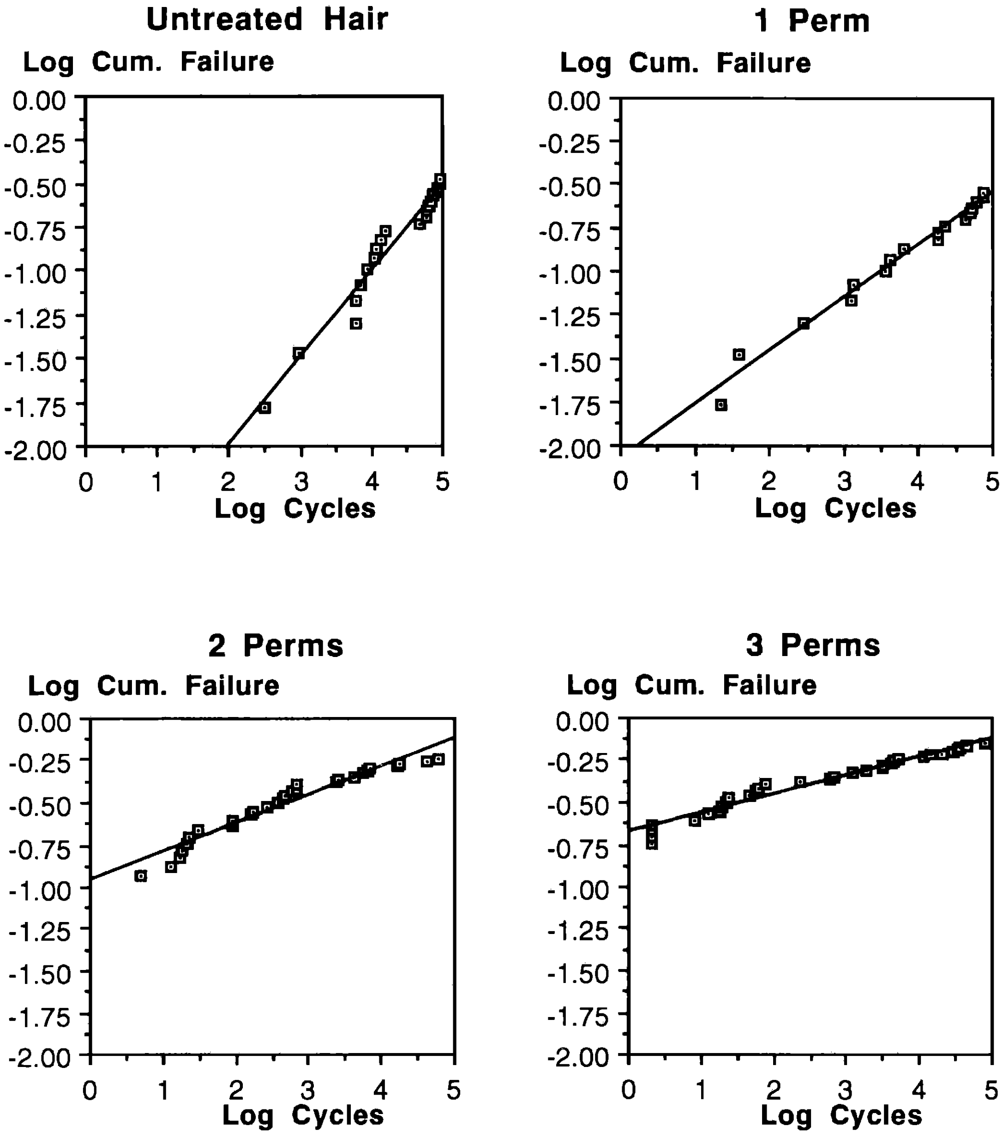


Figure 11. Fatigue lifetime data for untreated hair and three subsequent perm treatments.

Furthermore, the possibility must be considered that cosmetic treatments, especially those involving exposure to chemicals, leave the substrate more susceptible to further damage during subsequent grooming. Our goal was to establish whether subsequent grooming procedures caused secondary damage, and whether the inclusion of a conditioner could prevent or at least alleviate some of the mechanical or abrasive damage experienced during combing.

Surface changes

Microfluorometry. Our experience with the fluorescent tracer Rhodamine B in connection with hair fibers has shown that this molecule is a useful detector of damage to the

Table VII
Fatigue Behavior of Modified Hair (60 Specimens)

	Unbleached hair			Bleached hair		
No. of perms	h_f ($\times 10^3$)	Slope ($\times 10^{-1}$)	No. of survivors	h_f ($\times 10^3$)	Slope ($\times 10^{-1}$)	No. of survivors
0	*100+	5.0 ± 0.52	40	*100+	3.1 ± 0.22	39
1	*100+	3.1 ± 0.25	43	78	1.8 ± 0.17	27
2	6	1.7 ± 0.18	26	0.6	1.9 ± 0.23	16
3	3	1.1 ± 0.98	13	3	1.5 ± 0.12	13

* Indicates that at 100,000 cycles, fewer than half of the fibers broke.

cuticular region, especially to the scale face of the outermost cuticle. Since oxidative treatments produce sulfonic acid groups in hair fibers and Rhodamine B is a cationic dye, this fluorescent molecule is ideal for measuring the extent of oxidative damage. Longitudinal fluorescence intensity scans showed the expected major difference between the unbleached and bleached categories. However, differences due to grooming procedures within each of the three groups were slight and within the range of experimental error.

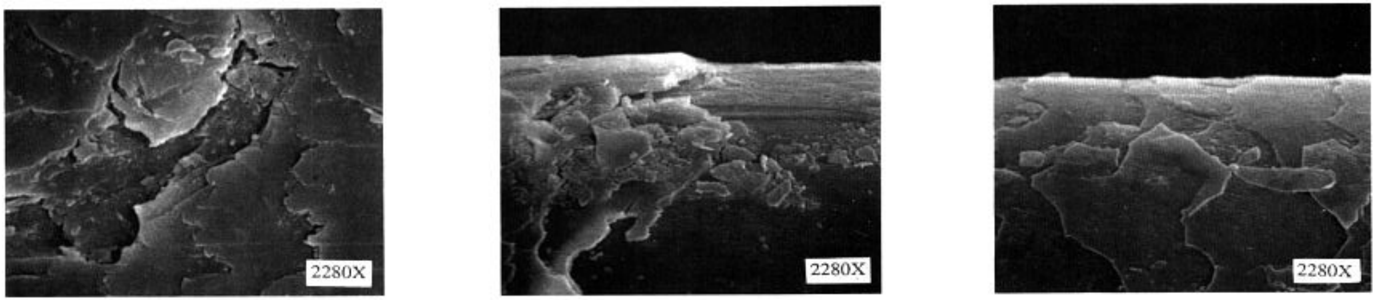
Scanning electron microscopy. Even unbleached hair appears to have suffered damage when repeated combing occurred without prior shampooing and conditioning. As seen in Figure 12, cracks, holes, and debris from broken-off cuticles are seen in practically all hair fibers subjected to the combing procedure.

Such damage due to combing is much more apparent in hair that had been bleached ten times for two minutes. Scales seem to become detached and brittle, resulting in fragmentation at the edges and deposition of the debris near the scale edge, as shown in Figure 12. Thinning of the surface cuticles, a characteristic feature in the four-hour oxidized hair, appears to be much more pronounced than in the 10 × 2′ bleached sample. The longer bleaching treatment, producing thinner and more swellable cuticle cells, may have rendered these fibers somewhat more pliable during the wet combing and thus less susceptible to damage.

The combination of shampooing and conditioning prior to combing appears to be responsible for less severe and less frequent damage to the surface cuticles of unbleached and bleached hair, as seen in Figure 12. As would be expected, the debris of the fractured cuticles has been removed during the shampooing, conditioning, and rinsing procedures. While cracks, holes, and broken-off cuticles are still present, they are definitely less frequent, and regions with intact cuticles are more common.

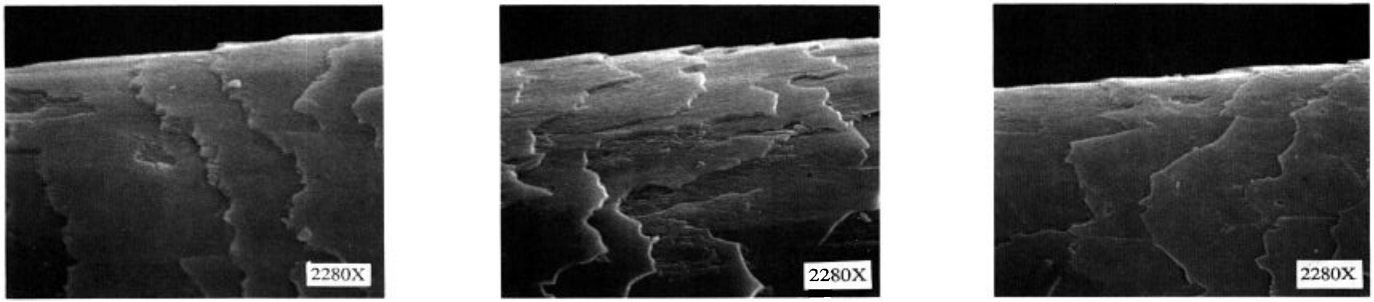
Shampooing and conditioning appears to result in the deposition of a protective layer of conditioners, rendering the hair fiber more manageable and less likely to fragment during subsequent combing. The shampooed/conditioned/combed hair fibers resembled the corresponding samples prior to the multiple grooming procedures.

Wettability. The effects of the various grooming procedures on the surface properties of hair were explored by determining the wettability of the fibers before and after the treatments. In evaluating changes in wettability, it has to be kept in mind that while mechanical abrasion is the major factor in combing by itself, shampooing and condi-



Unbleached 2′ × 10, H_2O_2 4 hours H_2O_2

Repeated combing



Unbleached 2′ × 10, H_2O_2 4 hours H_2O_2

Repeated shampooing, conditioning, and combing

Figure 12. SEMs showing typical appearance of unbleached and bleached hair after grooming.

tioning may modify the fiber surface due to deposition of surfactants and particularly of conditioners.

The effect of grooming on work of adhesion was established only on the sample bleached four hours in 6% H_2O_2. We chose this sample because we expected the most damaged hair to be most susceptible to secondary damage from subsequent grooming treatments.

Typical traces of work of adhesion along the distance scanned are shown in Figure 13. Besides differences in wettability, the traces show qualitative differences that are notable. The regularity and amplitude of "chatter" differ among the treatments, and these patterns were consistent among the samples of a given treatment. The traces for the combed only and the shampooed and combed samples are more irregular than for the ungroomed samples, which may indicate subtle physical surface changes. The chatter for samples that were shampooed, conditioned, and combed is extremely regular compared

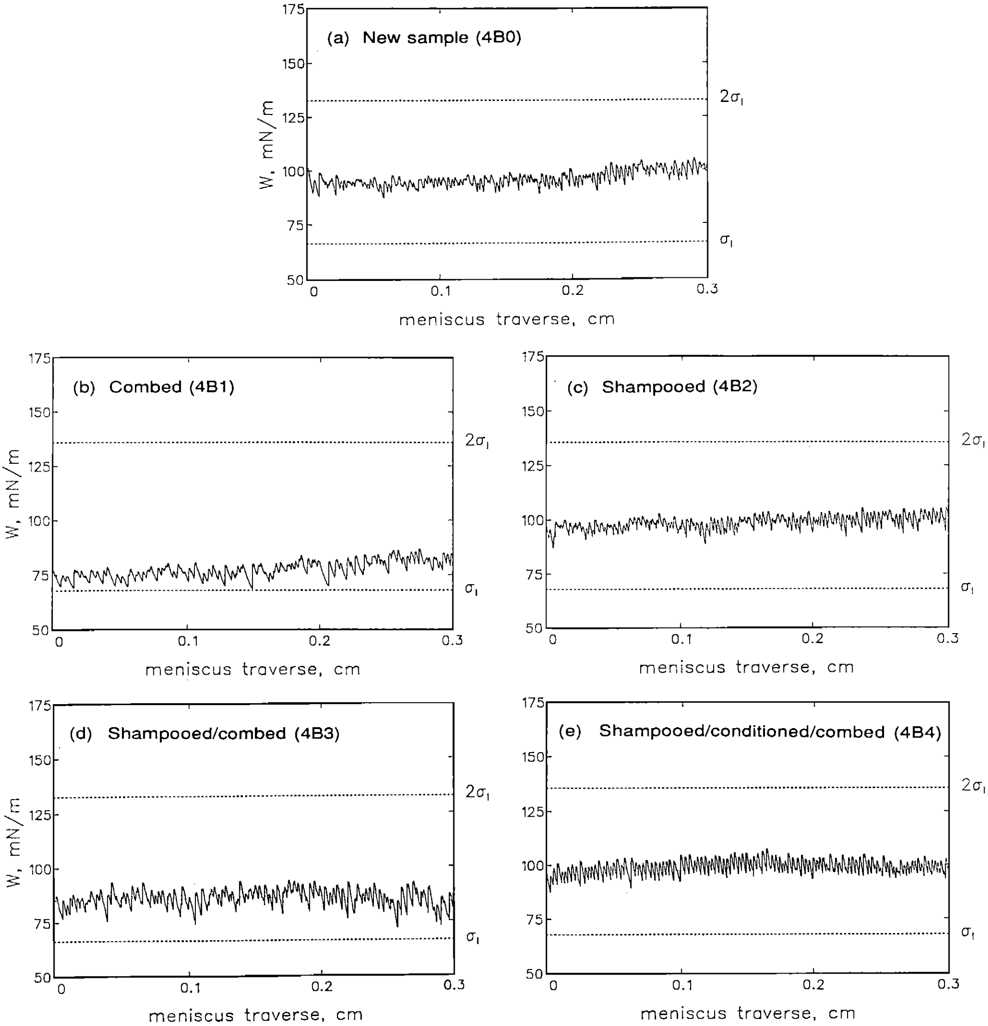


Figure 13. Water wettability of bleached hair before and after grooming sequences.

to any other group of samples. This suggests the deposition of conditioner–surfactant complexes on the fiber surface, which release surface-active compounds during the wettability scan (13).

Materials can accumulate on hair surfaces from a number of cosmetic applications and environmental sources; for example, conditioning polymers are deposited from shampoos and conditioner formulations. Previous studies at TRI on many different conditioning polymers have shown that most of the excess conditioner polymers rinse off in successive water immersions (14), although conditioner–surfactant complexes can lead to considerable buildup in multiple applications (15).

The average values of work of adhesion provide additional information about changes on the hair surface. Figure 14 shows the work of adhesion for the grooming sequences on the highly oxidized hair sample. As shown above, bleaching destroys the hydrophobicity of the untreated fiber surface, rendering it quite hydrophilic.

As seen for combing of these fibers, two of the combed samples, 4B1 (combed only), and 4B3 (shampooed and combed), significantly lowered the work of adhesion of the bleached control sample (4BO). Combing appears to produce a less hydrophilic fiber surface, which suggests abrasive removal of hydrophilic layers. The sample that was shampooed, conditioned, and combed shows a work of adhesion value only slightly lower than that of the uncombed samples, suggesting less of an effect from combing due to the presence of the conditioner.

Structural damage

Dye diffusion. Chemical and structural modifications due to bleaching were found to

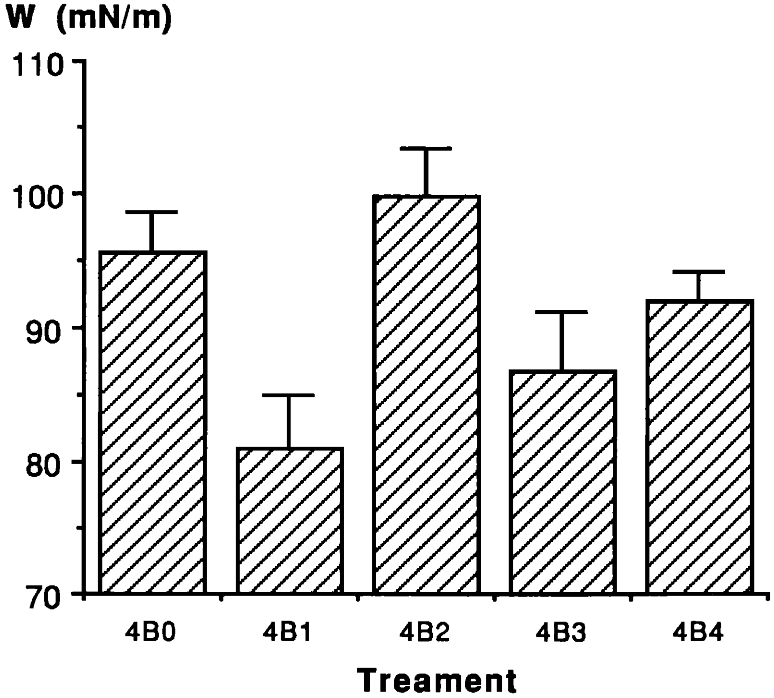


Figure 14. Work of adhesion for grooming sequences on hair bleached four hours in H_2O_2.

cause increases in the rates of diffusion of dyes into hair fibers in our previous work with uranin. However, cross-sectional fluorescence intensity profiles of groomed hair tagged with the fluorescent tracer showed similar diffusion patterns, indicating that subsequent grooming, for ten cycles or a total of 1,000 combing strokes, did not produce significant differences in diffusion rates for either the unbleached or the bleached samples.

Mechanical properties. Abrasive damage experienced during grooming would be expected to be restricted to the fiber cuticle and possibly lead to its total loss. It has recently been demonstrated (16) that oxidative cuticle damage even under quite severe conditions does not appear to cause a reduction in tensile properties, which supports the hypothesis that the tensile properties of human hair are primarily those of the cortex. In evaluating the original bleached hair, we observed that the nonultimate mechanical properties seem to be more sensitive to oxidative damage than the properties obtained at fiber failure. If damage from grooming sequences is indeed mainly a surface abrasion effect, we would not expect to see significant changes in mechanical properties. On the other hand, the shampoo treatments and intermittent stretching from combing may lead to structural weakening, which could be reflected in both the ultimate and nonultimate mechanical properties.

In general, the effects of grooming bleached hair were minor on the mechanical properties of modulus, breaking stress, and work to failure, as seen in Table VIII. The incorporation of conditioner into the grooming process had an alleviating effect on whatever damage was encountered during grooming.

Significant differences arose in the evaluation of 20% work and yield stress, however. Improvement in 20% work with the addition of conditioner was clear. In evaluating yield stress for unbleached and bleached hair, we found that shampooing and combing always was most damaging and that the incorporation of a conditioning step into the

Table VIII
Mechanical Properties of Groomed Hair

Treatment	Modulus (GN/m^2)	Yield stress (GN/m^2 × 10^{-2})	Work to extend 20% (MJ/m^2 × 10^{-1})	Breaking stress (GN/m^2 × 10^{-1})	Work to break (MJ/m^2)
U0	2.8 ± 0.23*	6.7 ± 0.76	4.4 ± 0.71	3.3 ± 0.31	2.6 ± 0.31
U1	2.8 ± 0.32	7.0 ± 0.86	—	2.4 ± 0.37	2.6 ± 0.37
U2	3.0 ± 0.41	7.0 ± 1.3	—	3.4 ± 0.64	2.5 ± 0.58
U3	2.9 ± 0.31	6.3 ± 0.76	—	3.2 ± 0.03	2.4 ± 0.30
U4	3.1 ± 0.45	6.6 ± 1.0	—	3.4 ± 0.46	2.4 ± 0.40
2B0	2.6 ± 0.28	5.7 ± 0.79	3.8 ± 0.79	3.0 ± 0.32	2.3 ± 0.30
2B1	2.2 ± 0.19	5.5 ± 0.55	—	2.7 ± 0.26	2.1 ± 0.29
2B2	2.5 ± 0.23	5.6 ± 0.80	—	2.7 ± 0.28	2.0 ± 0.31
2B3	2.6 ± 0.37	4.6 ± 0.62	—	2.7 ± 0.33	2.0 ± 0.26
2B4	2.7 ± 0.26	5.6 ± 0.51	—	2.9 ± 0.32	2.4 ± 0.46
4B0	2.5 ± 0.23	4.9 ± 0.69	2.7 ± 0.27	2.8 ± 0.32	2.2 ± 0.32
4B1	2.5 ± 0.29	5.0 ± 0.65	2.8 ± 0.32	2.9 ± 0.36	2.3 ± 0.34
4B2	2.6 ± 0.35	4.7 ± 0.74	2.7 ± 0.37	3.0 ± 0.41	2.3 ± 0.34
4B3	2.5 ± 0.23	4.6 ± 0.50	2.6 ± 0.24	2.8 ± 0.27	2.2 ± 0.28
4B4	2.9 ± 0.29	5.6 ± 0.66	3.1 ± 0.33	3.1 ± 0.32	2.6 ± 0.37

* 95% confidence limits.

sequence always alleviated that damage. In the case of the four hour bleach treatment, the improvement in yield stress after the application of conditioner resulted in values higher than those of the ungroomed sample.

SUMMARY

A variety of methods were combined to quantify the extent of primary damage from chemical changes introduced during oxidation of hair. Methods for detecting damage were chosen to evaluate surface or structural changes. Different levels of damage were achieved by changing the time of treatment in 6% H_2O_2 or the treatment process (hydrogen peroxide vs a commercial bleach creme).

Surface changes increased with peroxide treatment times. The four hour peroxide treatment resulted in the greatest surface damage. Surprisingly, the commercial bleach creme caused much less surface (by SEM and wettability analyses) than structural damage.

Although structural changes also increased with peroxide treatment time, some methods found the four hour peroxide treatment more damaging than the commercial bleach creme and others found the commercial product most damaging. Additional major structural damage was shown in successive perm treatments on unbleached and bleached hair.

We explored the possibility that oxidative damage, as experienced during bleaching of hair, leaves the fibers susceptible to secondary damage during subsequent grooming. Grooming processes were simulated by combing, shampooing, and conditioner treatments before combing.

We found that combing produced secondary damage and that conditioner use reduced or prevented the damaging effects of combing. Damage from combing was more severe in bleached than in unbleached hair. The application of conditioner after shampooing resulted in less damage in both bleached and unbleached hair.

Attempts to correlate the various damage analyses and to draw conclusions about the relative effects of surface and bulk damage are currently underway on an expanded data base and will be the subject of a subsequent paper.

ACKNOWLEDGMENTS

The work reported here was conducted as part of a project, *Analysis and Quantification of Hair Damage,* sponsored by a group of corporate TRI/Princeton participants. We acknowledge the contributions of our colleagues, Irene Bradford, Rudy Turner (deceased), and Chi Wang.

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