True porosity measurement of hair: A new way to study hair damage mechanisms

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Synopsis

This study employs a novel method, gas sorption (1), to quantify the porosity characteristics of hair by
determining total pore volume, adsorption pore-size distribution, and the surface area of damaged hair.
Damage mechanisms were studied by comparing the different pore volume and surface area resulting from
two different types of damage: chemical and UV. Hair color measurement and tensile strength, both
reflecting the changes in hair cortex, were also employed in this study. The results suggest that hair damage
caused by oxidative bleach and UV oxidation follows different pathways. Chemical damage (oxidative
bleach) nearly triples the hair surface area in the first minute of bleaching due to the increase in the number
of pores, followed by a sudden drop after 10 min of bleaching from smaller pores breaking down into larger
ones. In contrast, UV damage shows an immediate loss in surface area in the first 200 hr of exposure and
a gradual increase as exposure time continues.

INTRODUCTION

Many studies show that hair damage caused by chemical processes and UV exposure will result in increased hair swelling. Although much of the literature uses the terms "swelling" and "porosity" interchangeably, most of the methods developed to determine hair damage are geared toward measuring swelling rather than porosity. The techniques used to measure swelling include water uptake (2), hair diameter change (3), liquid retention (4), and a centrifuge method (5). There has been no study to date revealing the details of pore size, pore volume and surface area that precisely defines hair damage through the measurement of hair porosity. Gas sorption, the method we have developed recently, enables us to quantify the different porosity characteristics of damaged hair (1). Furthermore, we have undertaken research to study the damage mechanisms.

Bleaching and sun exposure (UV) are considered two major causes of oxidative hair damage. Several studies have concluded that chemical oxidation follows S–S fission, which generates two moles of cysteic acid (6,7), while photochemical oxidation of cystine follows the C–S scission pathway (8), where only one mole of cysteic acid is produced.

The work of Ruetsch *et al.* (8) also concluded that melanin granules remain physically almost intact even after long-term UV irradiation/humidification. On the other hand, chemical oxidation (bleach) results in solubilization of melanin granules and loss of hair color. Their study further proves that the hair cuticle cells show extensive "thinning" and eventually "fuse" to the underlying cuticle layer after hair is exposed to the cycling of UV irradiation and humidification.

Many investigations were also conducted to evaluate the deteriorated physical properties of damaged hair. The determination of the mechanical properties of degraded hair by bleaching and sun exposure illustrates that breaking strain and breaking stress are both affected by the two types of damage, but that chemical oxidation causes faster cortex degradation than photochemical oxidation (9). Several other analytical tools were also employed to examine hair damage, such as amino acid analysis, which exhibits a correlation between the amount of amino acids and bleaching time (10), and Fourier transform infrared spectroscopy (FT-IR), which utilizes the ratio of sulfonate bonds (S=O) with the amide III band (11) to express the degree of hair damage. However, the majority of the studies have been centered either on the change in chemical composition of hair or a change in the mechanical properties of hair. The objective of this paper is to understand the difference in damage mechanisms between UV and chemical damage from a porosity perspective. Tensile strength and colorimetry analyses were also utilized to correlate porosity results.

MATERIALS AND METHODS

BLEACHING AND UV DAMAGE TREATMENT

Virgin brown hair purchased from International Hair Importers Inc. was bleached by immersion in 6% hydrogen peroxide solution containing 1.7% ammonium hydroxide at 40 +/− 1°C for 1, 5, 10, 15, or 20 min.

UV EXPOSURE

A QUV Accelerated Weathering Tester (Q-Panel Lab Products) with a 340 UVA bulb emitting at 340-nm maximum was used. The energy dose of the irradiation was 450 J/cm^2. Hair tresses of 1.5 g, each arranged in a single layer, were exposed under UV light for 200, 400, and 1200 hr.

TENSILE STRENGTH

The diameters of forty hair strands randomly selected from each group of chemical- and UV-damaged hair were measured using a fiber dimensional analysis system (Mitutoyo, Model LSM 5000). The hair samples were placed in a DiaStron miniature tensile tester (Model 170/670) for the determination of tensile strength in a wet condition. The total work force, normalized with the hair diameter, was calculated by using DiaStron software (MTTWIN Application Software Version 5.0). The mean values obtained from 40 hair strands were analyzed using Tukey HSD statistical analysis to compare all the

testing pairs (ANOVA one-way analysis of variance from JMP statistical software, SAS Institute, Cary, NC).

HAIR COLOR MEASUREMENT

Color co-ordinate L, a, b values for a hair tress were measured using a Hunter colorimeter (LabScan XE), where "L" stands for lightness, "a" for color of green to red, and "b" for blue to yellow. The total color change of $\Delta E = [9*\Delta L^2 + \Delta a^2 + \Delta b^2]^{1/2}$ (12), in the case of hair damage by bleaching, was used to calculate the color difference between 0 min and 1 min bleaching or subsequently 1 min and 5 min, etc. The same calculation was also applied to UV damage. The total color change (ΔE) represents the color difference between 0 hr and 200 hr exposure, or 200 hr and 400 hr, until 1200 hr. We believe the ΔE value for color change in this calculation clearly displays the progressive change of hair color due to the progressive damage from both bleach and UV. In addition, color change in the blue-yellow index (Δb) or the light index (ΔL) was also included in the evaluation to further understand the degradation status of melanin granules after damage. The average taken from six measurements in each tested tress represents the values of ΔE, Δa, and ΔL.

GAS SORPTION

Nitrogen adsorption studies on hair samples after bleaching and UV damage were conducted using a Quantachrome Autosorb-1C instrument. Samples were cut in very fine pieces and then added to a sample cell where they were placed under vacuum at 145°C for 0.5 hr. Complete water removal is necessary to obtain accurate measurements, which is why 145°C was used. This value is based on the data collected from differential scanning calorimetry (DSC), in which a dehydration peak appears at about 125°C. A 5-pt BET (Brunauer-Emmett-Teller) surface area analysis was used for all samples. The total pore volume was collected at a P/P_0 of ~0.995. The pore size distribution curves are from the adsorption portion of the isotherm.

RESULT AND DISCUSSION

CHEMICAL DAMAGE

Tensile strength analysis. The cuticle and cortex are the two main morphological components in hair fibers. The cuticle is an important factor in torsional mechanical properties (13), but its contribution to bulk longitudinal mechanical strength is minor (14,15). The cortex constitutes the major part of the fiber mass of human hair and consists of elongated cortical cells, packed tightly and oriented parallel to the fiber axis. They contain microfibrils, which are composed of highly crystalline material, known as α-helical proteins. It is believed that the cortex is primarily responsible for the tensile properties of human hair (15). The oxidation of cystine due to bleach causes the disruption of crosslinks, which results in the reduced wet tensile strength. Under our specific bleaching treatment, the wet hair tensile strength (Figure 1) displays a significant decrease in breaking force (about 20%) after the first minute of bleaching and another decrease in breaking force after 10 min. The statistical analysis (Figure 2) shows
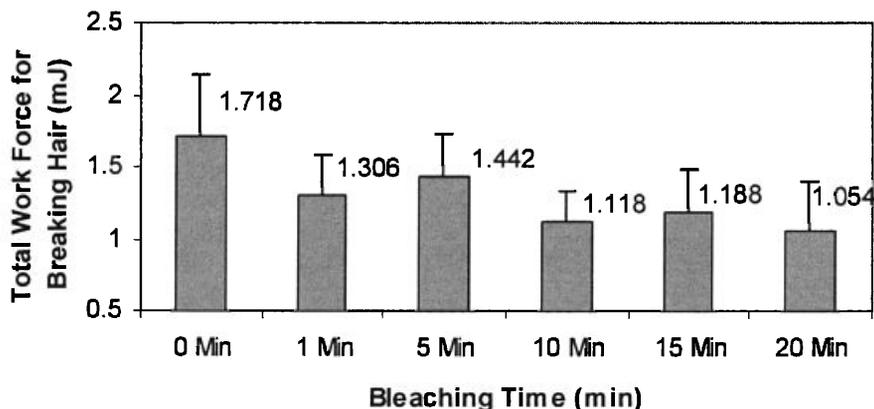
Figure 1. Tensile strength of bleached hair.
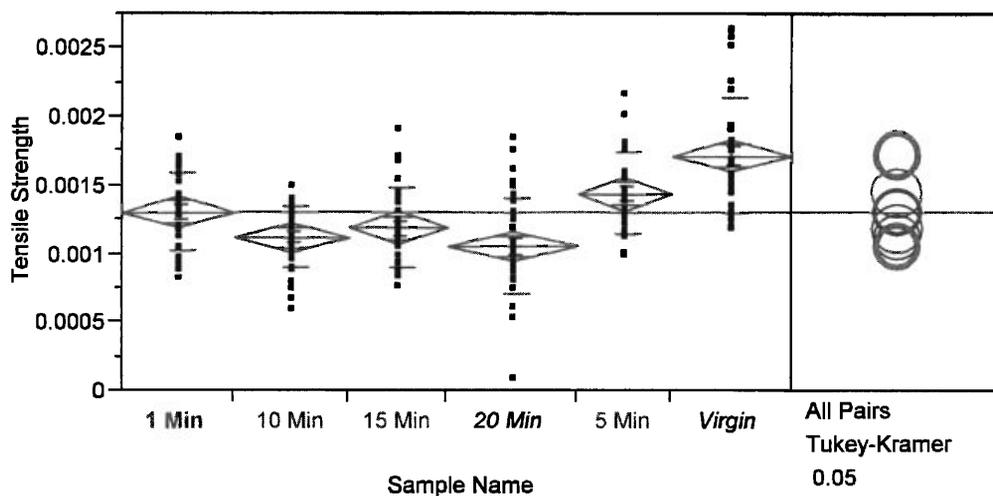
Figure 2. Statistical analysis for tensile strength measurement.

no difference between 1 min and 5 min of bleaching and also no difference between the pairs of 10 and 15, 10 and 20, and 15 and 20 min. It is understandable that the decrease in the wet tensile properties is primarily due to the degradation of disulfide bonds, but it is unclear why the change in tensile strength undergoes an immediate decrease in the first minute, and another after 10 min of bleaching time. Further analysis of color measurement and gas sorption was used to help find the answers.

Hair color measurement. Hair pigments are distributed within the cortex and medulla in ovoid or spherical granules, and are not normally found in the hair cuticle of scalp hair. The oxidative attack on hair not only causes the breakage of disulfide bonds in hair protein, but it also breaks down the melanins. Wolfram and co-workers (16,17) have investigated the oxidation of human hair with and without pigment. Their research concluded that hair with pigment consumes hydrogen peroxide at a measurably faster rate than hair without pigment, suggesting a faster reaction of peroxide with hair pigment than with hair protein. Based on that conclusion, the initial response of oxidative damage to hair fiber should be color change, under the assumption that the

Table I
Color Measurement of Bleached Hair

Bleaching time (min)	L	a	b	ΔE	Δb
0	38.2	6.1	15.9		
1	45.2	7.2	20.1	21.3	4.2
5	48.8	7.2	21.3	10.9	1.2
10	53.8	7.1	23.1	14.9	1.8
15	57.8	6.2	23.0	12.2	-0.1
20	58.8	6.1	23.2	2.9	0.2

peroxide is diffused into the hair cortex during the bleaching process. Table I and Figures 3 and 4 illustrate the color-change measurement of the bleached hair in the expression of total color change (ΔE) and the blue-yellow index (Δb).

It is clear from Figures 3 and 4 and Table I that the color change, like the tensile strength measurement previously discussed, also undergoes distinct decreases at 1 min and 10 min. The trend is more prominent in Figure 4, where significant changes are clearly shown at 1 min and 10 min, with almost no changes in the yellow index after 10 min. The loss of Δb over the bleaching time reflects the degradation of brown-black melanins (eumelanins), which are the principal pigments found in human hair. As we discussed previously, melanins reside within the hair cortex and medulla, and even after 1 min of bleaching, the peroxide has made its way to the cortex, as indicated by the significant color change. Since the cortex plays a dominant role in the tensile properties, it may also explain why the tensile strength shows a significant loss after 1 min of bleaching. It is important to understand that the pigment degradation by chemical means is a diffusion-controlled process, which appears to be rather fast in this case because 1 min of bleach time already imparts significant color change. However, the rate-controlling step in the process has not been determined due to the complex oxidation reactions of the many components in the hair (17).

It might be reasonable to assume that the second major change in color (10 min) could be due to further penetration of peroxide into the hair cortex after overcoming the initial slow rate of diffusion. The following gas-sorption analysis for the "true" porosity of bleach-damaged hair may give further insight.
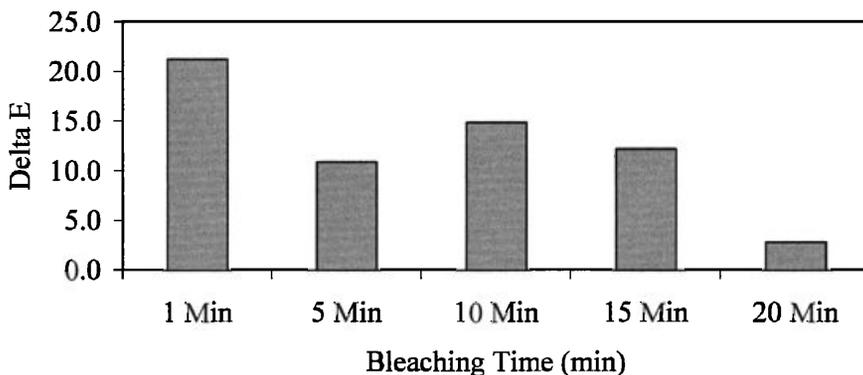
Figure 3. Measurement of total color change in bleached hair.
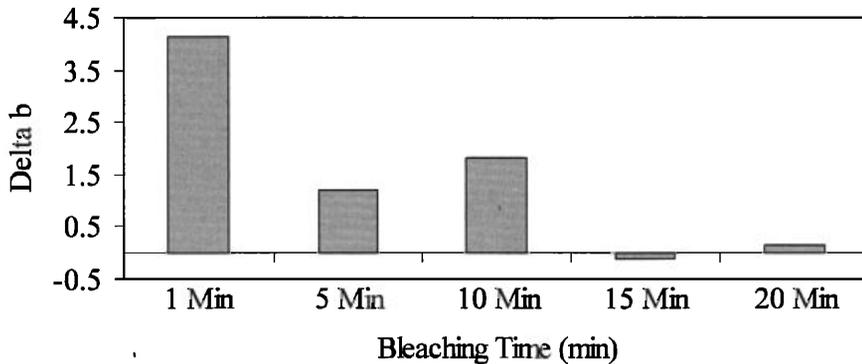
Figure 4. Measurement of yellow-index change in bleached hair.

Gas sorption. Gas sorption is a well-known technique used in the catalyst market to measure the surface area, pore volume, and pore size distribution of catalysts (18). These measurements are essential in the catalyst area in order to understand when a catalyst is spent and needs to be replaced due to the degradation of surface area and porosity.

Understanding how the porosity of hair changes with damage can be a real asset in determining what is causing the damage and what adverse effects it has on the hair. For this purpose, the authors have developed a new method using gas sorption to quantify the porosity characteristics of damaged hair (1). Nitrogen sorption can be used to measure the pore structure of hair up to *ca.* 100 nm. Water vapor sorption or mercury porosimetry would need to be used for pores > 100 nm. Based on the IUPAC definition, micropores are defined as pores < 2 nm, mesopores as pores 2 nm–50 nm, and macropores as pores > 50 nm. Nitrogen sorption can therefore be used to measure micropores, mesopores, and small macropores. Table II and Figures 5 and 6 show the surface area and total pore volume of bleached hair at different bleaching times.

These results are very interesting; after 1 min of bleaching, considerable increases in surface area (SA) and total pore volume (TPV) have occurred. The SA has nearly tripled and the TPV has increased by 30%. The SA and TPV increase slightly for the 5 min of bleaching time and then dramatically decrease for the 10 min of bleaching time, and are maintained for the most part through 20 min of bleaching. This is an indication that bleach does significant damage within 1 min of contact with hair and agrees with the findings of tensile strength and color change. After 5 min, the surface area goes up slightly compared to 1 min, indicating increased damage to the hair but less significant versus 0 min to 1 min. After 10 min of bleaching the surface area falls off significantly,

Table II
Surface Area (SA) and Total Pore Volume (TPV) at Different Bleaching Times

Bleaching time (min)	SA (m^2/g)	TPV (cc/g)
0 (Virgin hair)	0.40	0.000689
1	1.13	0.000991
5	1.17	0.001010
10	0.55	0.000785
15	0.49	0.000742
20	0.58	0.000778
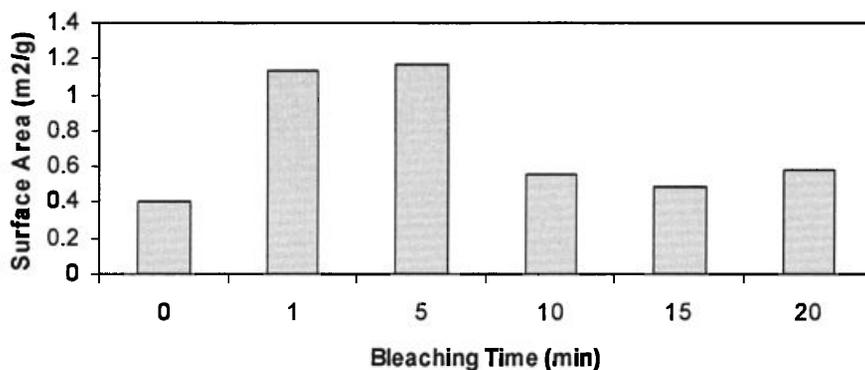
Figure 5. Surface area (m^2/g) of hair at bleaching times of 0, 1, 5, 10, 15, and 20 min.

indicating another notable change in the hair structure. Figure 7 depicts a rational explanation of the bleach damage to hair in terms of surface area.

The virgin hair has a set of pores that essentially triple (2.83 times) after 1 min of bleaching. The number of pores increases slightly after 5 min of bleaching. The next significant change happens after 10 min, in which the surface area decreases to almost that of the virgin hair. This might be due to the smaller pores breaking down into larger pores. The 15 min of bleaching time is just more of the smaller pores breaking down to form larger pores, while the 20 min of bleaching time gives a slightly higher surface area, possibly indicating penetration of the walls between the newly created larger pores.

UV DAMAGE

Tensile strength analysis. The fact that UV light can damage hair has been well established and studied (19). UV light degrades the amino acids of the hair fiber at the outer layer (cuticle) to a greater extent than the inter layer (cortex). The work of Ruetsch *et al.* from the Textile Research Institute (20) has shown microscopically that fusion reactions of UV irradiation happen more in the periphery of hair, where it receives higher intensities of radiation than at the core, providing the smooth break at the periphery and fractures toward the interior of hair following a multiple-step process. Also, a general concept mentioned above is that the hair cortex contributes largely to tensile strength, while cuticle shows little or minor influence. Robbins and co-workers (21) have studied the
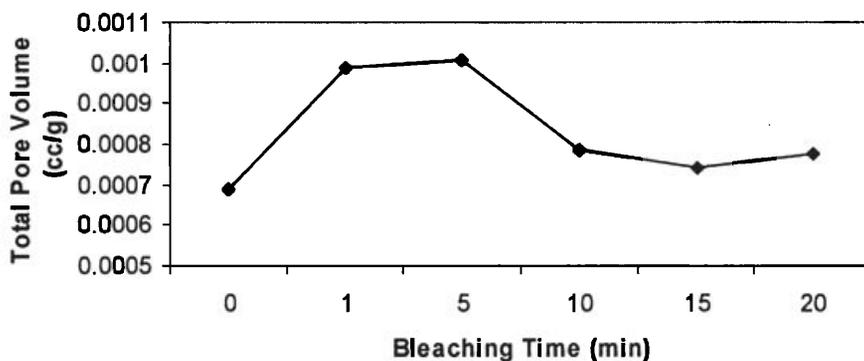
Figure 6. Total pore volume (cc/g) of hair at bleaching times of 0, 1, 5, 10, 15, and 20 min.
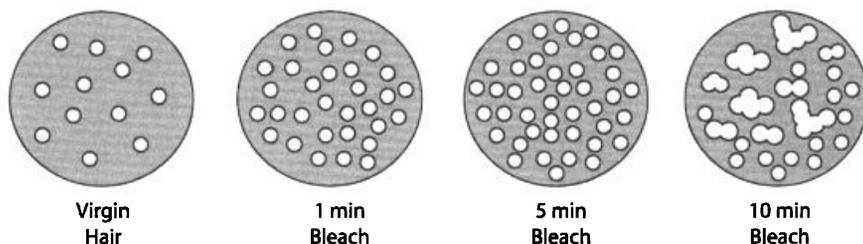
Figure 7. Illustration of bleaching damage mechanism.

correlation between cuticle damage and the tensile properties of hair fiber, and their work has focused on chemical damage and the resultant morphological changes shown by SEM.

Several other studies have proven that UV light decreases the wet tensile properties of hair (22). Figure 8 shows the results of our study that investigated the effect of UV exposure time on tensile strength. Over 40 hair fibers were used for each testing group to generate statistically sound data. The results are analyzed statistically in Figure 9. Figure 8 indicates that the tensile strength already shows a noticeable decrease after 200 hr of UV exposure, and it remains unchanged after 400 hours. Finally, there is another significant decrease after 1200 hr of exposure. The results illustrate that UV irradiation already attacks the hair cortex in a relatively short period of time, resulting in decreased tensile strength. However, much longer UV exposure times are needed to further damage the cortex after the initial damage occurs. Although the result agrees with other published studies—which proved that UV light decreases the wet tensile properties of hair [22]—more analysis is needed for further understanding of these physical changes from a mechanistic perspective. Color measurement and gas sorption were employed to provide insight into the process of UV damage.

Color measurement. Both hair proteins and pigment absorb UV light in the range of 254 to 350 nm. This unique nature helps hair protect itself from UV damage. However, in the process of protection from UV light, pigments are degraded and hair color is eventually "bleached." There are research papers published about the mechanisms of photochemical degradation of emuelanin (23). Since our main focus here is to understand at which exposure stage hair becomes significantly degraded, we measured the hair color
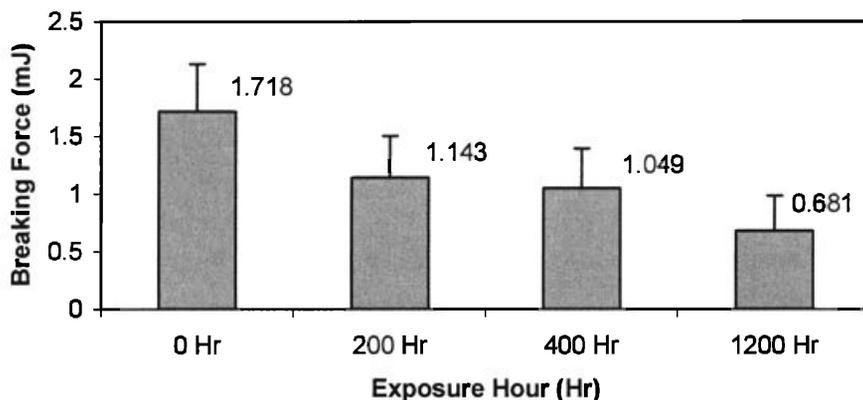
Figure 8. Tensile strength of UV-damaged hair.
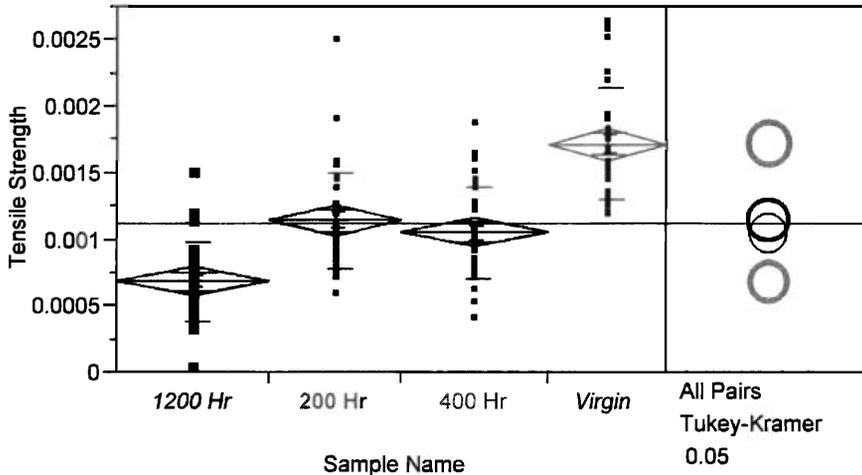
Figure 9. Statistical analysis of tensile strength of damaged hair.

at different UV exposure times. Figure 10 and 11 and Table III indicate that hair color becomes significantly lighter after 200 hr, and shows relatively small change after 400 hr. There is then a much larger change after 1200 hr. The results from color measurement correlate well with tensile strength analysis, which leads to the explanation that photodamage happens not only in the hair fiber periphery but also in the interior, even at 200 hr, and then damage seems to progress with a gradient to a lower level deeper inside, until reaching the stage where most of the peptide backbone has been oxidized. This explanation can be further supported by gas sorption analysis.

Gas sorption. The UV irradiation damage of hair gives a much different SA and TPV (Table IV) than oxidative bleached hair. Figures 12 and 13 show the surface area (m^2/g) and pore volume (cc/g) of hair versus UV irradiation times of 0, 200, 400, and 1200 hr.
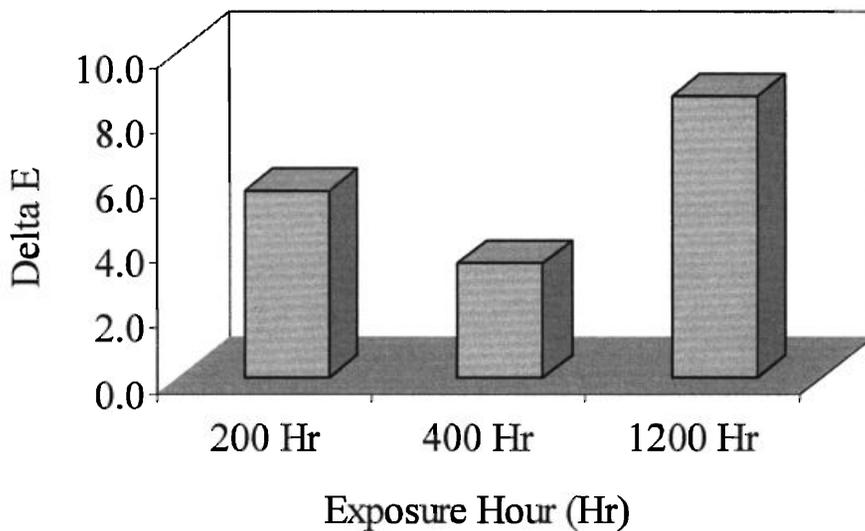
Figure 10. Total color change in UV-damaged hair.
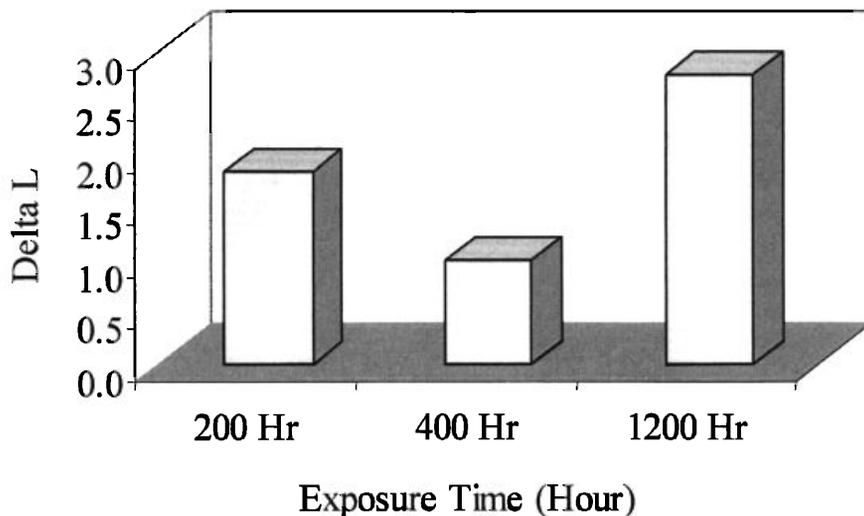
Figure 11. Lightness change in UV-damaged hair.

Table III
Hair Color Measurement of UV-Damaged Hair

UV Exposure time (hr)	L	a	b	ΔE	ΔL
0	39.22	6.45	16.73		
200	41.09	6.72	17.87	5.72	1.87
400	42.08	7.14	19.75	3.54	0.99
1200	44.85	7.20	21.96	8.61	2.78

Table IV
Surface Area and Pore Volume Versus UV Irradiation Times

UV Exposure (hr)	SA (m²/g)	TPV (cc/g)
0 (Virgin hair)	0.40	0.000689
200	0.22	0.000581
400	0.30	0.000651
1200	0.34	0.000729

With the bleaching shown in Table II, the SA increases significantly at 1 min. In contrast, after the first 200 hr of UV irradiation, the surface area decreases by almost half of that detected for the virgin hair. This proves that within the first 200 hr there is significant fusion of certain portions of the hair fiber that causes a loss in surface area. These findings agree with those found by Reutsch *et al.* using field emission scanning electron microscopy (FESEM) (20), in which UV irradiation damage leads to "fusion" of the surface cuticle edges. However, this is not the only thing happening during first 200 hr of exposure. Additional pores are also formed, which is supported by a loss of tensile strength. At continued UV irradiation to 400 hr, the surface area starts to increase, indicating that more new pores are generated or that the fused layer has been perforated to some extent to let nitrogen through. At 1200 hr of UV irradiation, the surface area increases again, indicating once again the increase in pores or the generation of more

openings through the fused layer. In agreement with the conclusions of Reutsch *et al.* (20), after long-term UV exposure, complete fusion of the cuticular sheath into a rigid, brittle unit occurs and may become susceptible to cracking, which in turn may lead to pores once restricted by the fused layer. The UV damage mechanism is illustrated in Figure 14.

For all the tests described above, we used the same source of hair for both chemical and UV damage in order to reduce the variables. We have found that BET results are
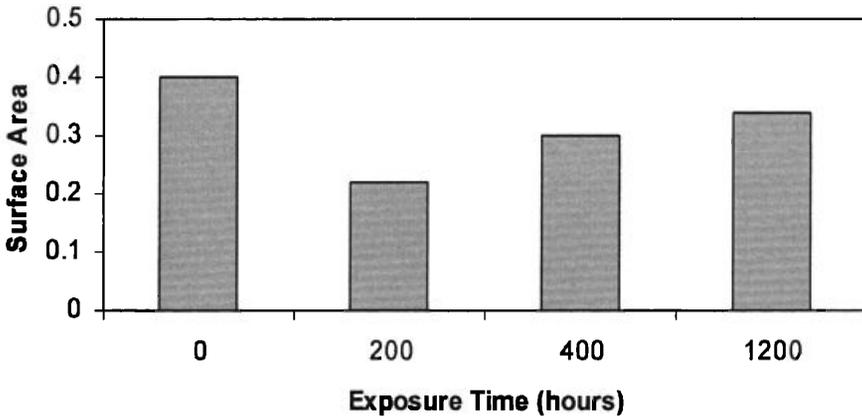
Figure 12. Surface area (m²/g) versus UV irradiation times of 0, 200, 400, and 1200 hr.
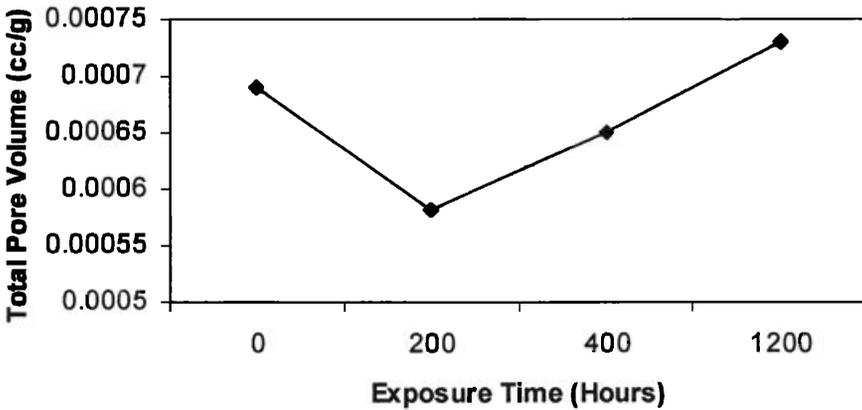
Figure 13. Pore volume (cc/g) versus UV irradiation times of 0, 200, 400, and 1200 hr.

No UV Irradiation   UV Irradiation 200 Hrs   UV Irradiation 1200 Hrs
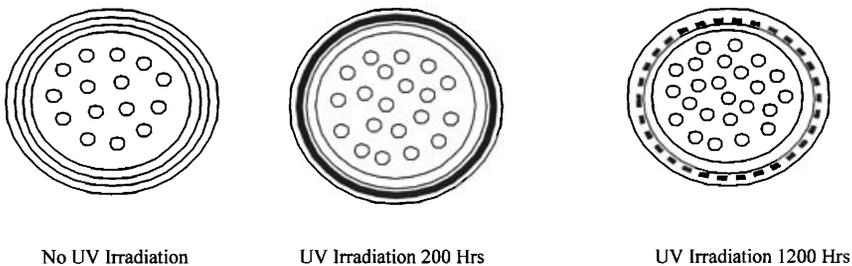
Figure 14. Illustration of UV damage mechanism.

reproducible if the hair source is the same and the conditions for the damage methods are consistent; otherwise, the surface area or pore volume could be very different for different batches of bleached hair samples. We have also found that the different parts of hair show different porosity: hair toward the root has much less porosity than the tip ends, which indicates that hair is more damaged in the tips due to abrasive combing. This finding shows the importance of consistently using the same location of hair when preparing BET samples in order to have valid comparison.

CONCLUSIONS

Our research has shown that hair damage by chemical and UV oxidation follows different pathways. These differences in physical changes were further explained by porosity measurements, which also reveal very different patterns for both damage types. Chemical damage (bleaching) nearly triples hair surface area in the first minute of bleaching due to the increase in the total pore volume. This is followed by a sudden drop in SA after 10 min of bleaching, suggesting that smaller pores break down into larger ones. This is in contrast to UV damage, which shows an immediate loss in surface area in the first 200 hr of exposure and a gradual increase as exposure time continues, which is most likely due to the fusion of cuticle cells followed by an increase in pores or cracks. The porosity analysis provides an insight into hair damage from a mechanistic perspective, and can be used as an effective tool for the study of hair repair or damage prevention.

ACKNOWLEDGMENTS

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