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Photodegradation of human hair

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Synopsis

The role of moisture in photolysis of hair was investigated in this research. Melanin-free Piedmont hair was exposed to simulated sunlight at different humidity levels. Changes in wet mechanical properties, swelling behavior, and IR spectrum were used to determine the degree of damage.

Weathering damages hair under all conditions of relative humidity during exposure, with exposure at 30% RH causing the least damage. A free-radical mechanism is used to explain the photolysis process.

INTRODUCTION

Hair is constantly subjected to repeated environmental assaults, commonly termed "weathering." Weathering occurs over a period of time, and the effects can be easily observed on long hair, with tip ends being more damaged than root ends. Hair lightening and dullness, weak and brittle tips, split ends, and an overall rough feel are a few of the obvious characteristics of damaged hair (1,2).

Damage to hair causes a reduction in tensile and fatigue properties (3). According to Robbins and Bahl (4) and Speakman *et al.* (5), the reduction is largely attributed to chemical damage to the protein chains, especially the S-S covalent crosslinks in cystine. The loss of crosslinks, in photochemical damage, alone will result in increased solvent swelling, although Wolfram (6) disagrees. He argues that crosslinking between amino acid residues would occur on irradiation and that these new crosslinks would limit solvent swelling in the case of keratin fibers.

According to the hair photolysis mechanism proposed by Tolgyesi (1), cystine, tyrosine, phenylalanine, and tryptophan residues absorb UV radiation, resulting in the formation of free radicals. Homolytic scission of disulfide bonds occurs. Melanin, the natural coloring matter in hair, provides partial protection to the hair fiber. It acts in a sacrificial manner, resulting in the lightening of hair color. Tolgyesi (1) explained that melanin, by its comprehensive system of double bonds and conjugated carbonyl groups, protects hair by scavenging free radicals generated by exposure to light. Wei (7) furthered the free-radical mechanism by showing that, all other factors being equal, the extent of photodamage is proportional to the square root of the amount of free-radical initiator present in the fiber. The mechanism assumed that the S-S group was the initiator, giving two –S· free radicals by homolytic scission.

Leroy *et al.* (8) and Dubief (9) investigated the role of moisture in the photobleaching of hair. Their research was limited to extreme RH levels, namely 5% and 88% only. Their data showed an increase in bleaching, measured as luminance, with exposure time, as shown in Figure 1. They also noted a greater loss in tensile properties, measured under deionized water, when hair was irradiated in the presence of moisture as per the 15%-stretching index shown in Figure 2. Also, a radiation dose of 10^5 J/cm^2 approximately equals an exposure period of 360 hours. Based on the concepts suggested by Wei, we hypothesize that moisture, in combination with trace minerals such as iron, is a source of free radicals in the presence of UV radiation. This leads to the notion that an increase in photodegradation will occur with increasing amounts of moisture during irradiation, up to a certain concentration.

This work tests the hypothesis by investigating the role of moisture in the photolysis of melanin-free human hair exposed to simulated solar radiation. Our objective is to characterize the damage in hair keratin as a function of RH during exposure to simulated solar radiation in air. The result is a better understanding of the photodegradation processes of hair keratin. Such knowledge may aid in formulating hair care products that minimize photolytic damage.

MATERIAL

Bleached hair was avoided because the bleaching process damages the fiber (10). Therefore approximately 6-in-long root ends of 18-in-long virgin, unaltered, naturally melanin-free, Piedmont hair samples, supplied by DeMeo Bros., New York, were used.

WEATHERING

About 120 individual Piedmont hair fibers (6-in-long) were mounted in a single layer

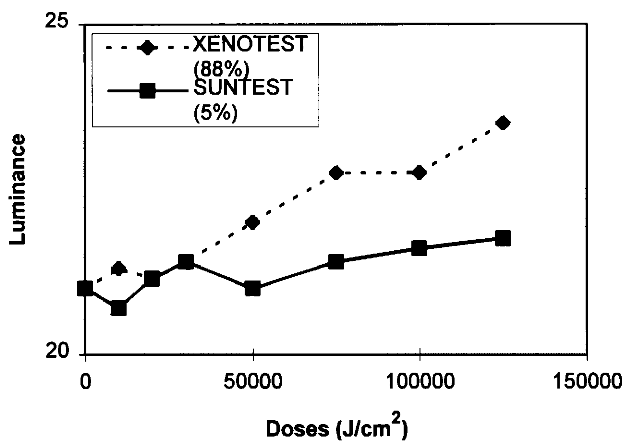

Figure 1. Bleaching of pigmented hair exposed at two RH levels (8).

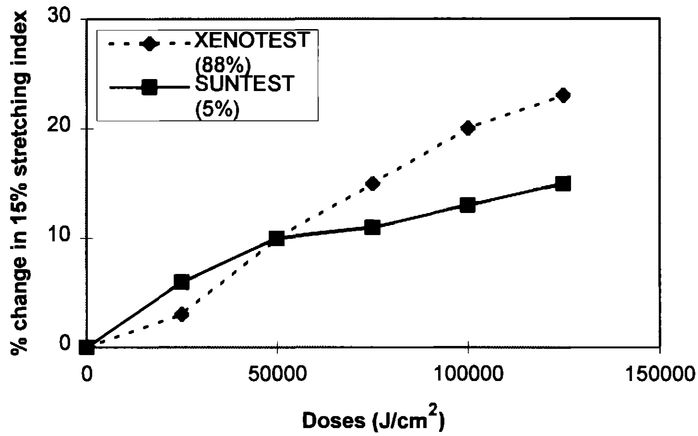

Figure 2. Changes in 15%-stretching index of pigmented hair exposed at two RH levels (8).

parallel to one another on plastic frames using double-sided tape. The mounted specimens were exposed to simulated solar radiation in the Atlas weatherometer at RH levels of 10, 20, 30, 50, and 70% for 100, 200, and 300 hours at 50°C.

The Atlas weatherometer uses a Xenon arc lamp to simulate the solar spectrum. Borosilicate filters were used to provide an "average" 45° Miami sunlight. The energy density at 340 nm was maintained at 0.3 W/m^2, resulting in a total energy density of 41.27 mW/cm^2. It should be noted that only about 10% of this energy was in the UV region and that the remaining energy was in the visible region of the solar spectrum. Automatic controllers maintained set temperature and humidity levels in the chamber (11).

TESTING

Three tests were employed to assess photodamage:
1. The difference in tensile properties between untreated and weathered hair was measured with the fibers totally immersed in deionized water.
2. Swelling tests were conducted on hair weathered for 300 hours, with an eye towards assessing changes in crosslink density as a function of RH during weathering.
3. The Fourier transform infrared/attenuated total reflection (FTIR/ATR) technique was used to assess surface damage of hair weathered for 300 hours at various RH levels.

TENSILE TESTS

A laser-scan micrometer supplied by Diastron Ltd., UK (Mitutoyo, model LS 3100) was used to measure the fiber cross-sectional area. The instrument employs a 1.0 mW 670-nm wavelength laser. The sample is placed in air, obstructing the laser beam, and rotated slowly by a motor. The resultant shadow falls on a sensor. The micrometer assimilates the data from the sensor and continuously measures the fiber diameter. The instrument has a precision of about 5 μm. The included LSMVB software analyzes the data from the micrometer, and identifies the minor and major axes of the fiber. From this data, the cross-sectional area is calculated assuming an elliptical cross section. The micrometer was calibrated using standard calibration wires of known cross-sectional area (12).

Test specimens for the laser-scan micrometer were prepared using a metal-tube sample-mounting system. This system uses a pair of hollow brass tubes with plastic sheaths on the inside and a stamping press (stock no. RS622-032) to crimp the fiber ends in the holders. The tubes are 1.4-cm long with an inner diameter of 0.1 cm and an outer diameter of 0.2 cm. The base of the press is a stainless steel template with a gauge length of 3.0 cm. The hair was threaded through two tubes, and the assembly was placed on the template. When crimped by mechanical pressure, a hair fiber is held securely by the crimped tubes. After measuring the cross-sectional area, the samples were directly transferred to the tensile tester.

Tensile tests were conducted in deionized water using a Diastron® miniature tensile tester. The miniature tensile tester autosampler, MTT 600 series, from Diastron Ltd., UK, has a sample holder with a capacity of one hundred (100) specimens. Each specimen can be wetted *in situ.* The degree of deformation and the rate of extension were preset. Data from each specimen were collected and transferred automatically to a personal computer using the MTTWIN software included with the instrument. The software was also used to calculate the tensile properties of the fibers (13).

Forty fibers per sample were tested, a number that earlier work has shown to be statistically acceptable (7). The sample length was 30 mm. The strain rate was 40%/min, that is, a crosshead speed of 12 mm/min was used. Samples were soaked for at least ten minutes to ensure complete wetting and saturation prior to tensile testing.

SWELLING TEST

Swelling was measured by determining the change in hair diameter in a 0.1 N solution of sodium hydroxide at room temperature (9). The "diameter" both dry and after swelling was measured using a Bausch & Lomb microscope fitted with a Digital Filar® eyepiece connected to a Microcode® meter from Boeckler Instruments. Hair fibers weathered for 300 hours at different humidity levels were tested.

FTIR/ATR ANALYSIS

The IR spectra of hair fibers exposed for 300 hours at different humidity levels were compared. IR spectra were obtained using a UMA 500 FTIR microscope from Bio-Rad. Samples were pressed between two optically matched diamond surfaces. The ATR (attenuated total reflectance) technique, with a depth of penetration of about 5 μm in hair, was employed.

The ATR technique involves bringing the fiber in contact with a germanium crystal designed for total internal reflection of the incident radiation. The reflected beam is altered by absorption by the sample surface in contact with the reflecting medium, and this alteration or attenuation is analyzed. Transmission spectroscopy was not used because the variation in hair sample diameter resulted in spectra unsuitable for comparison (14).

RESULTS AND DISCUSSION

TENSILE TEST RESULTS

A typical load-elongation curve obtained from the Diastron® tensile tester for an untreated Piedmont hair fiber, immersed in deionized water, is shown in Figure 3. The wet tensile properties of untreated Piedmont hair fibers are presented in Table 1. Table II shows the percent loss in properties of the hair fibers after exposure to simulated solar radiation at various levels of relative humidity. The data for work-to-20%-strain and stress-at-20%-strain shown in block A of Table II are graphed in Figures 4 and 5.

It is important to emphasize that significant differences in the mechanical properties will be observed only in the wet condition, where the contribution of hydrogen bonds to the mechanical properties is eliminated.

Effect of length of exposure. Damage occurs with exposure to simulated solar radiation and increases with duration of exposure, at all humidity levels, in agreement with the results obtained by Ratnapandian (3), Leroy *et al.* (8) and Dubief (9). As shown in block B of Table II, exposure for 100 hours results in about a 20% decrease in many properties, whereas a decrease approaching 50% is characteristic of fibers exposed for 300 hours.

On the other hand, the turnover point, which is the intersection of the yield and post-yield part of the load-elongation curve or the extension at which the β-keratin begins to play a significant load-bearing role, and extension-to-break data show an increase of about 10% (block C, Table II). This may be due to the increased mobility of molecular chains that results from the loss of disulfide crosslinks. The gains in these two properties do not compound with length of exposure. Exposure to UV radiation of many polymers causes embrittlement and the formation of new crosslinks, which may be the limiting factor, as suggested by Wolfram (6).

Effect of change in humidity. The tensile properties of hair fibers exposed to simulated sunlight for any given time period depends on the RH of the atmosphere during exposure. Contrary to the proposed hypothesis that photolytic damage will increase

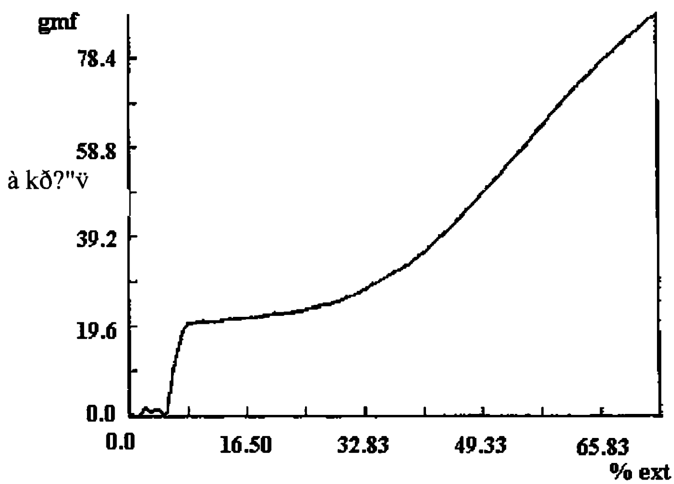

Figure 3. Typical load-elongation curve obtained for a single hair fiber on a Diastron® miniature tensile tester.

Table I
Wet Mechanical Properties of Untreated Piedmont Hair

Initial modulus (Gpa)	Work-to-20%-strain (MJm^{-2})	Work-to-break (MJm^{-2})	Stress-at-20%-strain (Gpa)
1.30	0.22	1.38	0.04
Stress-to-break (Gpa)	**Turnover strain (% extn)**	**Strain-to-break (% extn)**	**Post-yield modulus (Gpa)**
0.16	32.35	61.06	0.29

monotonically with an increase in ambient moisture during irradiation, damage appears to go through a minimum. A second-order polynomial regression indicates that this behavior is characteristic of most mechanical properties, as shown in Figures 4 and 5. Hair fibers exposed at 10% and 70% RH show similar losses—about a 47% loss for a 300-hour exposure period—whereas the loss is only about 30% for exposure at 30% RH for 300 hours. Wool, another keratin fiber, also photodegrades in sunlight, Holt (15) reported that wool undergoes a high degree of photo-tendering and photo-yellowing on being irradiated at low humidity levels or in the presence of moisture.

SWELLING RESULTS

The extent of transverse swelling in 0.1 N sodium hydroxide solution of Piedmont hair irradiated for 300 hours at various RH levels is shown in Figure 6. Hair fibers exposed at 50% RH show the maximum swelling, 74%.

Unlike the decreases in tensile properties, the extent of swelling goes through a maximum. Swelling increases with the loss of crosslinks (8,9). Hence, the results suggest that hair exposed a high and low humidity levels have a larger number of crosslinks compared to hair exposed at intermediate humidity. This interpretation is inconsistent with the trend seen in the wet mechanical properties. This suggests that the swelling is caused by the degraded protein residues in the fiber. At high and low humidity levels, the proteins are extensively degraded and the residues have a molecular weight small enough to let them diffuse out of the fiber during exposure or immersion in 0.1 N sodium hydroxide solution. For exposure at intermediate humidity levels, the extent of degradation is less and the residues are large enough to be retained. This will lead to osmotic swelling of the fiber. This explanation is consistent with the trend seen in the wet mechanical properties. Isolation and identification of the residues that are cleaved and diffuse out of the hair fiber might offer support for the theory suggested. However, the short protein chains might diffuse during irradiation, during immersion in sodium hydroxide solution, or both, thereby making the experiment contrived.

An alternative theory may be supported by the work of Wolfram (6), in which exposure caused formation of secondary crosslinks between protein residues, in addition to extensively damaging the fiber. The secondary crosslinks limited swelling without contributing significantly to the tensile properties. Exposure at low and high humidity levels favors crosslink formation as compared to exposure at intermediate levels. Hence, swelling passes through a maximum.

Table II
Loss (%) in Wet Mechanical Properties of Hair Exposed at Various RH

Block A

	Work-to-20%-extension				
Time/RH	10	20	30	50	70
100 h	26.98	12.56	11.16	17.67	22.79
200 h	38.60	28.84	18.60	22.79	32.09
300 h	46.98	29.30	34.42	25.12	46.51

	Stress-at-20%-strain				
Time/RH	10	20	30	50	70
100 h	22.73	11.36	11.36	13.64	20.45
200 h	38.64	27.27	18.18	18.18	29.55
300 h	47.73	27.27	31.82	22.73	43.18

Block B

	Initial modulus				
Time/RH	10	20	30	50	70
100 h	23.62	9.77	12.38	11.31	21.85
200 h	35.23	25.38	33.38	14.54	35.85
300 h	43.31	21.85	26.23	32.23	46.69

	Post-yield modulus				
Time/RH	10	20	30	50	70
100 h	17.42	9.76	42.51	17.77	39.37
200 h	24.04	20.91	50.52	12.89	55.05
300 h	32.06	25.78	47.39	35.54	60.63

	Work-to-break				
Time/RH	10	20	30	50	70
100 h	15.26	13.88	-2.02	19.02	19.09
200 h	31.02	29.21	4.05	13.81	7.66
300 h	41.43	24.15	11.71	13.88	23.14

	Stress-to-break				
Time/RH	10	20	30	50	70
100 h	25.79	19.50	27.67	25.79	33.33
200 h	34.59	32.08	32.08	20.75	44.03
300 h	44.65	29.56	35.85	32.70	49.06

Block C

	Turnover point				
Time/RH	10	20	30	50	70
100 h	-11.44	-4.40	-24.04	-5.28	-27.74
200 h	-9.94	-4.56	-24.66	-10.07	-40.51
300 h	-9.33	-9.12	-21.92	-13.40	-36.54

	Strain-to-break				
Time/RH	10	20	30	50	70
100 h	-11.28	-3.86	-23.23	-4.10	-28.49
200 h	-10.59	-4.11	-22.82	-9.42	-41.67
300 h	-10.67	-8.14	-31.24	-14.08	-43.14

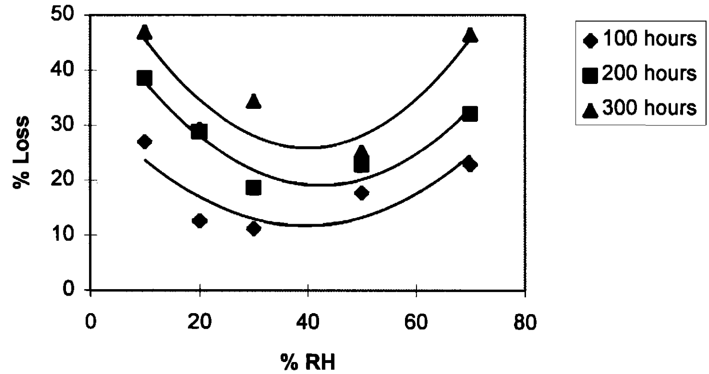

Figure 4. Reduction in work-to-20%-strain of Piedmont hair exposed to simulated solar radiation.

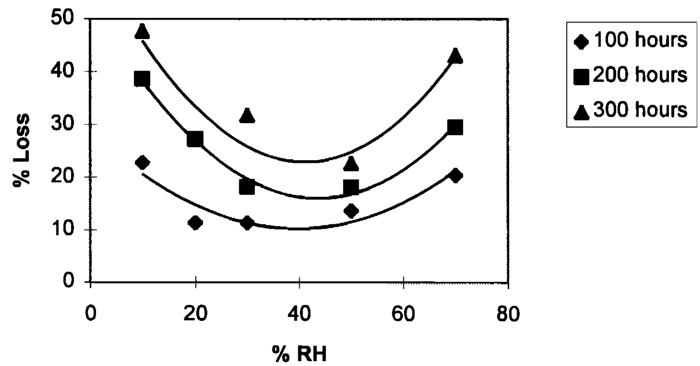

Figure 5. Reduction in stress-at-20%-strain of Piedmont hair exposed to simulated solar radiation.

ANALYSIS OF THE FTIR SPECTRUM

The FTIR/ATR spectra obtained from Piedmont hair exposed for 300 hours at different RH levels are shown in Figure 7. The spectra were normalized using the absorbance at 1513 cm^{-1} (peak 1), the amide-II band, allowing a semiquantitative comparison of the cystine oxide content. A listing of the different absorbance peaks is given in Table III (2).

The absorbances at 1042 cm^{-1} (peak 5) due to cysteic acid and at 1073 cm^{-1} (peak 4) due to cystine monoxide, the primary degradation products of the disulfide links, indicate that irradiation at 20% RH caused the least amount of degradation. These absorbances for fibers exposed to radiation at other RH levels are essentially invariant, as shown in Figure 7. Since the beam essentially penetrated only the cuticle, the results suggest that damage to the cuticle is nearly identical for irradiation under different conditions over similar duration of exposure. This concurs with the results reported by Hoting *et al.* (2). The low absorbances shown for exposure at 20% RH are probably due to experimental error. An important point to be noted is that cuticular damage, unless excessive, does not affect the tensile properties significantly (16). However, such damage is often the cause of crack initiation and fiber fracture.

ROLE OF MOISTURE IN HAIR PHOTOLYSIS

According to Arnaud (17), photolysis of hair proteins is caused by radiation with

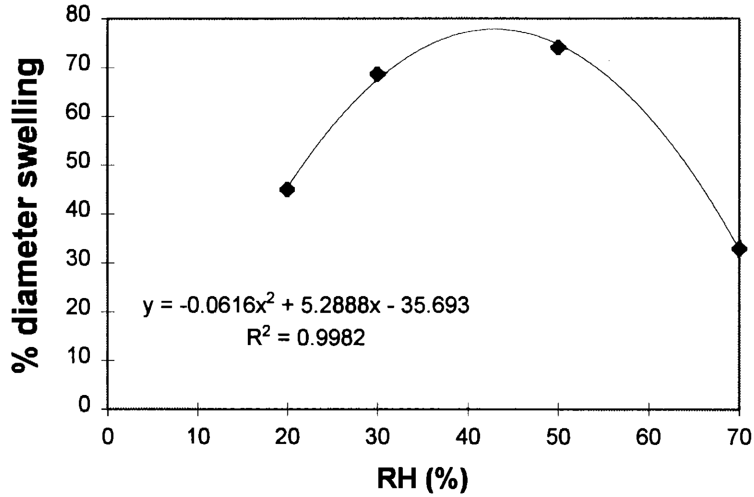

Figure 6. Diametral swelling of Piedmont hair exposed for 300 hours at different relative humidities.

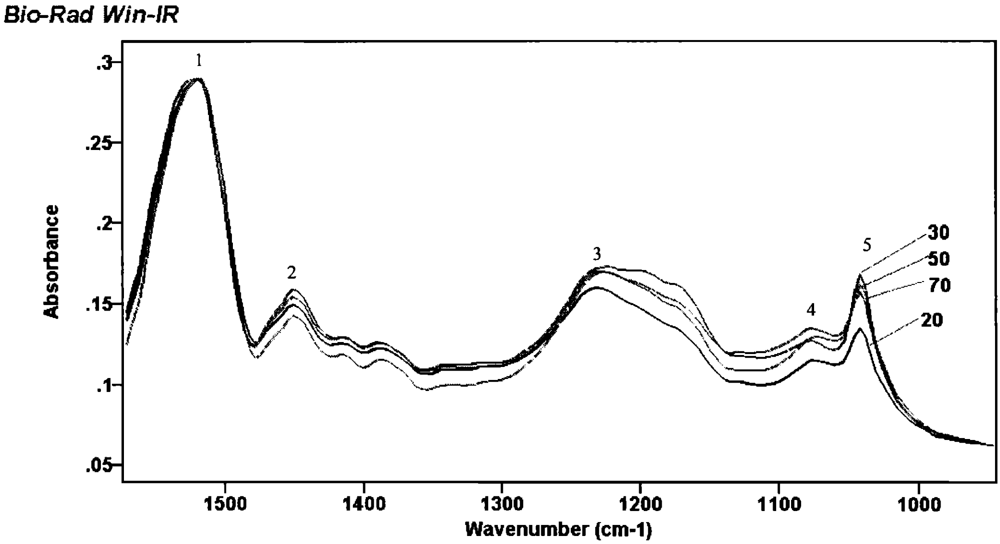

Figure 7. FTIR/ATR spectra for Piedmont hair exposed for 300 hours at different relative humidities.

wavelengths in the range of 254 to 350 nm. The absorption spectrum for Piedmont hair, shown in Figure 8, indicates this range to be the primary absorption region of unpigmented hair. Radiation of this wavelength can also initiate free radicals by Fenton's reaction involving iron, oxygen, and water. This is consistent with the suggestion that photolysis of hair keratin can follow the free-radical pathway as proposed by Tolgyesi (1) and Wei (7). A steady-state analysis suggests that the rate of photolysis of hair should vary with the square root of the concentration of the "initiator."

Assuming that hair contains small but uniform amounts of free-radical initiator (impurities) and that hair photolysis follows the proposed hypothesis, the damage will

Table III
Characteristic Bands in IR Spectra of Hair Fiber

Peak Number	Molecular group	Band (cm^{-1})
1	Amide-II	1513
2	CH	1449
3	Amide-III	1232
4	Cystine monoxide	1073
5	Cysteic acid	1042

Source: reference (2).

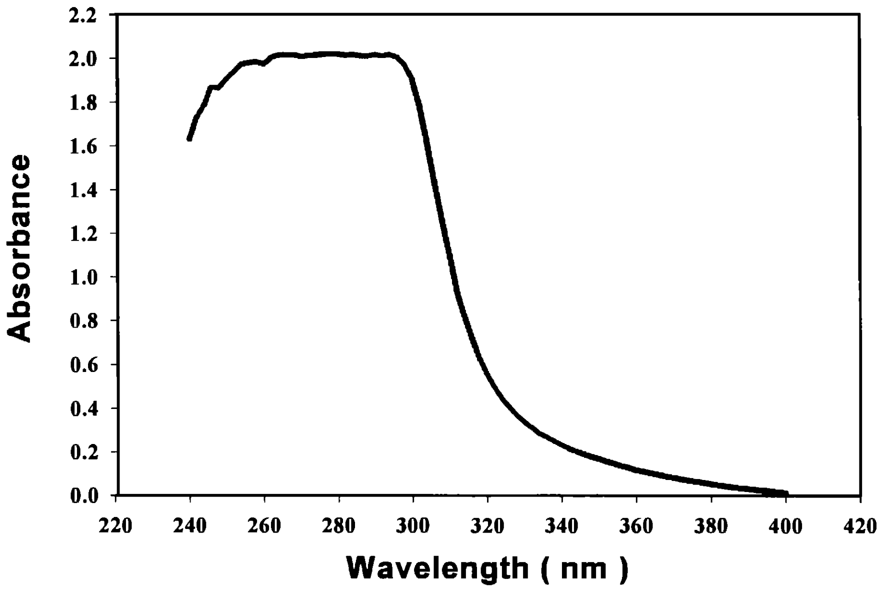

Figure 8. Absorption spectra of Piedmont hair.

increase as the ambient moisture level increases during irradiation. However, the changes in mechanical properties observed in this study, as functions of relative humidity, are related to the diffusibility of the radicals. At low humidity levels, the radicals cannot diffuse and terminate. Therefore, the number of radicals increases, causing extensive damage. Low-molecular-weight residues will diffuse out of these fibers when immersed in water. At intermediate RH levels the radicals can diffuse and terminate, thus limiting the number of radicals and the damage caused by them, as shown in Figures 4 and 5.

The details associated with the chemical interactions of moisture with hair keratin may be the keys to understanding the role of moisture in hair photolysis. According to Feughelman and Haly (18) the mobility of bound water in keratin increases with increasing moisture content. Water molecules associate more with each other than with keratin as the moisture content increases. Thus, at high RH levels the amount of loosely bound water in hair is large. The loosely bound water may act as a transfer agent for the free radicals as well as residues, thereby actively participating in the photolysis reaction. The removal of degraded protein residues exposes new protein segments to photolysis that accentuates the damage to the fiber.

The moisture itself may act as an additional source of free radicals. According to Walling (19), dissociation of water may be schematically represented as:

$$3H_2O \rightarrow H\cdot + \cdot OH + H_2O_2 + H_2 \text{ (+ perhaps other products).}$$

The peroxide can further dissociate into two radicals that can damage the fiber. The net result is a fiber damaged to an extent similar to that of fiber irradiated under low humidity conditions.

Some naturally occurring trace elements in hair may generate free radicals on irradiation (1). At low RH levels, there is minimal or no fiber swelling. Under such conditions, the free radicals have limited mobility. According to Walling (19), reduced free-radical mobility during condensation polymerization leads to polymerization in multiple directions instead of lengthwise chain propagation. This process is termed "popcorn polymerization," after the shape of the resulting polymeric structure. A similar depolymerizing reaction may be occurring in hair photolysis, leading to extensive local damage and loss of fiber mechanical properties.

The dual role of moisture explains the results obtained for work-to-20%-strain and work-to-break for fibers exposed at 30% RH. It also explains the changes in post-yield modulus and strain-to-break data with weathering at various humidity levels. At 70% RH, for example, low-level photolysis of the primary peptide bond may occur, leading to free movement of the molecular chains. New crosslinks may form at a later time.

The arguments presented above explain the current results satisfactorily, but in an indirect manner. They fall short of providing a definite proof of the exact mechanisms by which moisture affects photolysis of hair.

CONCLUSIONS

- Weathering damages hair at any given RH, the damage increasing with length of exposure. The wet mechanical properties of irradiated fibers decrease with extent of damage.
- Damage is more severe when hair is weathered at high or low RH. This is consistent with the results reported on wool weathered under similar conditions (15). The wet tensile properties of irradiated fibers are least affected when they are exposed at a RH of 30%.
- The free-radical mechanism for keratin photolysis proposed by Wei (7) has been used to explain the swelling and mechanical properties of irradiated fibers.
- Damage to the cuticle is not significantly affected by humidity during irradiation. This concurs with the work reported by Hoting *et al.* (2).

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