

Hair melanin content and photodamage

ANA CAROLINA SANTOS NOGUEIRA and INÉS JOEKES,
Chemistry Institute, State University of Campinas—UNICAMP, CP
6154, 13084-971, Campinas, SP, Brazil.

Synopsis

The aim of this study was to compare the susceptibility of hair with different melanin content (virgin white, blond and dark-brown) to photodegradation, evaluating changes on hair color and mechanical properties. Light exposure was carried out with a mercury-vapor lamp for up to 1800h. It was observed that color changes are different for each hair type and dependent on the wavelength range. Breaking elongation and breaking strength were affected in all hair types, mainly by UVB radiation. Results show that the melanin type and content of each hair is not the only parameter related to hair damages caused by sun exposure.

INTRODUCTION

The human hair fiber is composed mainly of keratins, a group of insoluble cystine-containing helicoidal protein complexes, which account for 65% to 95% of the hair by weight. The remaining constituents are water, lipids, pigments, and trace elements (1). The greatest mass of the hair shaft is the cortex, which is responsible for the mechanical properties of the fiber. These properties are dependent on time, temperature and humidity (2). Inside the cortex are also located the melanin granules (about 3% by weight). These are the hair pigments, whose type, size and quantity establish hair color. There are two types of melanin, the brown-black pigment (eumelanin) and the less prevalent red pigment (pheomelanin). The chemical structures and molar masses of the melanins are not yet known (3), mainly because they are highly insoluble materials of presumably high molar mass and are therefore difficult to separate from the other cellular components of the structures in which they occur (4,5). Surrounding the cortex is the cuticle, a layer of overlapping, keratinized scales, which can account for 10% of the hair fiber by weight and has the role of protecting the fiber against environmental and chemical damage (6,7). As the cuticle protects the cortex, damage in the cortex generally occurs after extensive damage to hair cuticle.

It is well known that solar radiation causes dryness, reduced strength, rough surface texture, loss of color, decreased luster, stiffness, brittleness and an overall dull, unheal appearance of the hair. These damages cause degradation of cystine, but the exact mechanism is not well known (8). Hair melanins provide some photochemical protection

Address all correspondence to Inés Joekes.

to hair proteins, especially at lower wavelengths, where both the pigments and the proteins absorb light, by absorbing and filtering the impinging radiation and subsequently dissipating this energy as heat. Their high absorption capacity can be explained in terms of their extensive system of conjugate carbonyl groups and double bonds. This not only captures a large fraction of the radiation but also immobilizes many of the free radicals formed upon the absorption of the UV radiation by the photo-sensitive amino acids in hair, preventing the transport of these free radicals into the keratin matrix. However, in the process of protecting the hair proteins from light, the pigments are degraded or bleached (9–11).

Contradictions are still found in the literature about the effect of specific wavelength ranges of the solar radiation on hair properties and the sensibility of different hair types to photodegradation. Authors generally attribute hair damage to the total ultraviolet range of the solar spectrum and relate the photo-sensibility of light and dark hair to the hair melanin type. The aim of this work was to quantify and compare the effect of different UV wavelength ranges on the mechanical properties and color of hair with different melanin content. In this way, we hope to improve knowledge on the interactions of human hair with solar radiation.

MATERIALS AND METHODS

HAIR SAMPLES

Tresses of (blended) virgin dark-brown and blond hair from De Meo Brothers Inc. (New York, USA) and virgin white hair from a volunteer were used. Each tress, weighing 2.0 g and approximately 20-cm in length, was washed two times with 2.0% w/w sodium lauryl sulfate aqueous solution, as follows: (a) hand-washing with 1 mL of the solution for 1 min; (b) rinsing with 40°C water for 1 min; (c) wet combing four times using a polypropylene comb. Afterwards, they were dried at room temperature, combed and stored.

RADIATION EXPOSURE

Sun exposure was simulated by irradiation with a mercury vapor lamp (OSRAM HQL 125W, São Paulo, Brazil). Full or UVB filtered radiation conditions were used as described in a previous work (12). The tresses were irradiated for 448 and 1792 h at 30 ± 2 °C and 50 ± 2 % RH. The values of radiation intensity obtained for the mercury-vapor lamp were 1.5 ± 0.5 W/m² (UVB), 26.0 ± 1.0 W/m² (UVA) and 70.0 ± 1.0 W/m² (visible plus infrared radiations), summing a total radiation intensity of 97.5 ± 1.0 W/m². This value is around seven times smaller than that measured for the sun (692.0 ± 1.0 W/m²). Considering that 1h sun exposure is “equivalent” to 7-h lamp exposure and 4 h of sun exposure per day, in this work we have simulated 16 and 64 sun exposure days.

COLOR CHANGES

Changes in the hair color were measured by diffuse reflectance spectrophotometry (DRS),

performed using a spectrophotometer (GretagMacbeth Color-eye® 2180UV, New York, USA). The instrument configuration used was the same as previously described (12). Spectra provided values of coordinates L^* (color lightness), a^* (redness, if positive or greenness, if negative), b^* (yellowness, if positive or blueness, if negative) from the CIELAB system of equations. From these, the color difference parameters, DL^* (lightness difference: lighter if positive, darker if negative), Da^* (red-green difference: redder if positive, greener if negative), Db^* (yellow-blue difference: yellowish if positive, bluer if negative) and DE^* (total color difference: $[(DL^*)^2 + (Da^*)^2 + (Db^*)^2]^{1/2}$) were calculated. Measurements were done keeping the same sample region and turning the hair sample in the instrument sample holder. Ten diffuse reflectance measurements were done for each sample. The internal reference was the average of a set of 10 measurements from control samples. Prior to reflectance measurements, the samples were conditioned at $50 \pm 5\%$ RH and $25 \pm 2^\circ\text{C}$ for 24 h.

MECHANICAL PROPERTIES

Stress/strain curves were obtained from 40 fibers (5.0 cm length, 24 h conditioning at $25 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ RH) of each sample using a universal test machine (EMIC DL 2000, São José dos Pinhais, Brazil) with a 10 N load cell operating at 10 mm/min constant speed. The diameter of each fiber was measured after conditioning using a micrometer (Mitutoyo Ltd., São Paulo, Brazil).

RESULTS AND DISCUSSION

COLOR CHANGES

Figure 1 shows the average values of the lightness difference parameter (DL^*) for the hair samples obtained after 16 and 64 days of 'sun exposure' (4 h exposure per day). As

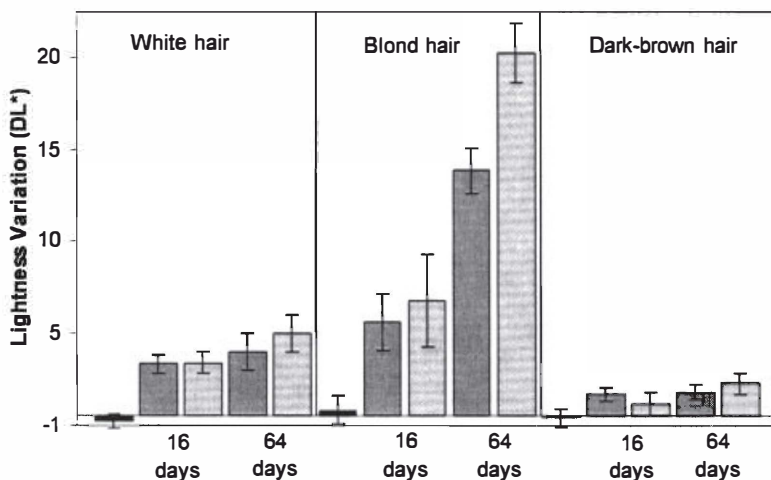


Figure 1. Average values of the lightness difference parameter (DL^*) for white, blond and dark-brown hair obtained after 16 and 64 days of simulated sun exposure, considering 4 h exposure per day. Ten color measurements on each sample. ■ UV exposed. □ UVA exposed. ■ Unexposed.

expected, every hair became lighter after exposure. This change was more pronounced when UVB was cut out of the radiation system. Blond hair showed the greatest change, followed by white and dark-brown hair, respectively. Figure 2 shows the average results obtained for the yellow-blue difference parameter (Db^*). Blond hair turns yellower after UV exposure, but not after UVB filtered radiation exposure. Dark-brown hair turns yellow after both UV and UVB filtered radiation exposure. Surprisingly, white hair turns less yellow after both UV and UVB filtered radiation exposure. Figure 3 shows the average results obtained for the red-green difference parameter (Da^*). Dark-brown hair became redder after both exposure conditions. Blond and white hair showed an opposite trend, turning less red. Figure 4 shows the total color variation (DE^*) obtained to the different hair type. Blond hair showed the greatest change, with DE^* values on the order of 6.0 and 20.0 after 16 and 64 days of exposure, respectively. Total color difference values of about 3.0 for dark-brown and 10.0 for white hair were measured after exposure. Results show that hair color changes are mainly affected by UVA radiation in every hair type.

According to Borges *et al.* (13), the total amount of melanin (eumelanin + pheomelanin) in blond and red hairs is about 2.5 mg/g hair, in dark-brown hair 5.2 mg/g hair and in black hair 7.2 mg/g hair. As expected, we observe that the hair color change increased with the decrease in melanin content. On the other hand, the observation of color changes on white hair (without melanin) after irradiation shows that the melanin type and content of each hair is not the only parameter related to hair damage caused by sun exposure. Keratin is also photosensitive. Among the keratin amino acids, tryptophan, cystine, tyrosine and histidine are more susceptible to photo-degradation. The total amount of these amino acids depends on hair type. Male hairs have more cystine than female and, usually, dark hairs have more cystine than light hairs (8). According to Bertazzo *et al.* (14), the amount of tryptophan in dark-brown and black hair is greater than in blond hair. The highest tryptophan concentration is found in gray and white hair, indicating that tryptophan concentration in hair increases with age. Vincenci *et al.*

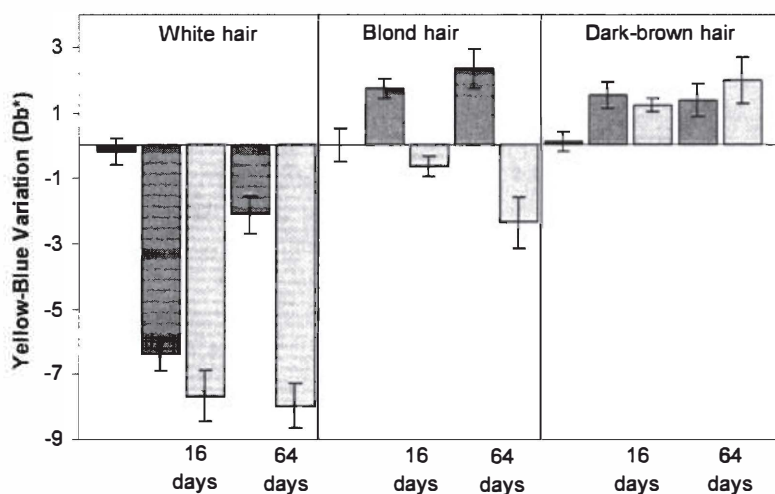


Figure 2. Average values of the yellow-blue difference parameter (Db^*) for white, blond and dark-brown hair obtained after 16 and 64 days of simulated sun exposure, considering 4 h exposure per day. Ten color measurements on each sample. ■ UV exposed. □ UVA exposed. ■ Unexposed.

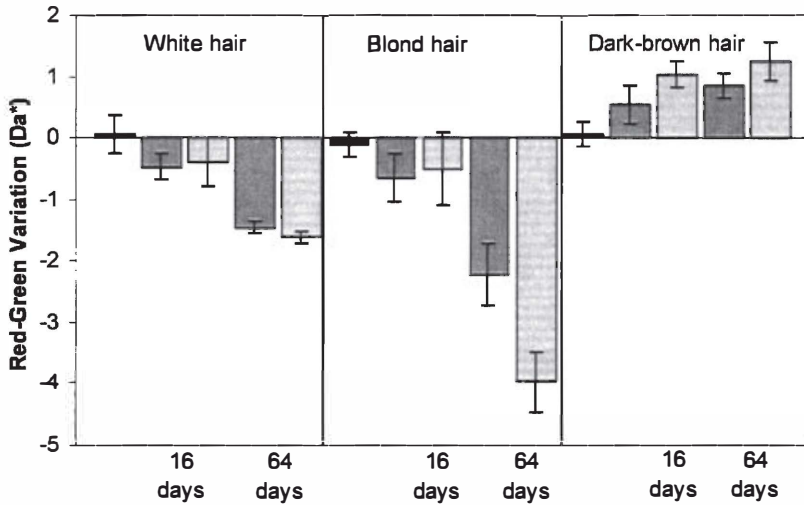


Figure 3. Average values of the red-green difference parameter (Da^*) obtained for white, blond and dark-brown hair after 16 and 64 days of simulated sun exposure, considering 4 h exposure per day. Ten color measurements on each sample. ■ UV exposed. □ UVA exposed. ■ Unexposed.

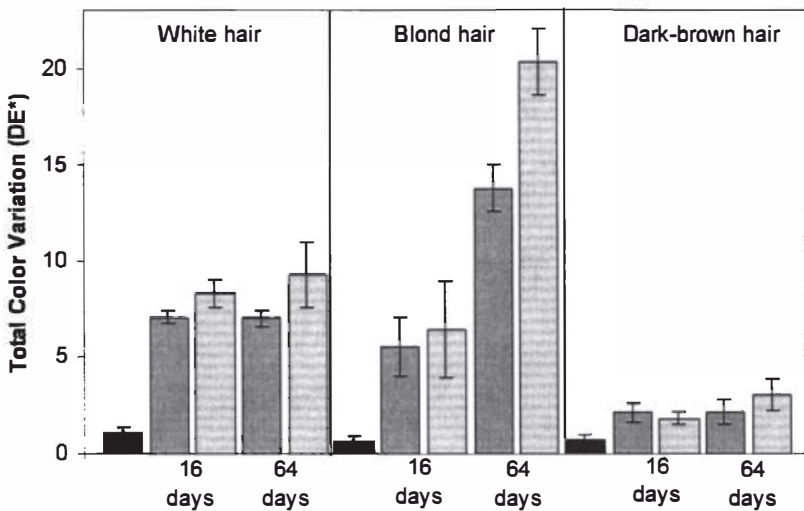


Figure 4. Average values of the total color difference parameter (DE^*) for white, blond and dark-brown hair obtained after 16 and 64 days of simulated sun exposure, considering 4 h exposure per day. Ten color measurements on each sample. ■ UV exposed. □ UVA exposed. ■ Unexposed.

(15) studied red hair, observing that the amounts of pheomelanin and eumelanin vary with sex, age and color shade. In this way, it must be assumed that color changes are related not only to melanin photodegradation but also to protein photodegradation, in a way that is difficult to account by now.

MECHANICAL PROPERTIES

Figures 5 and 6 show, respectively, the breaking strength and breaking elongation data

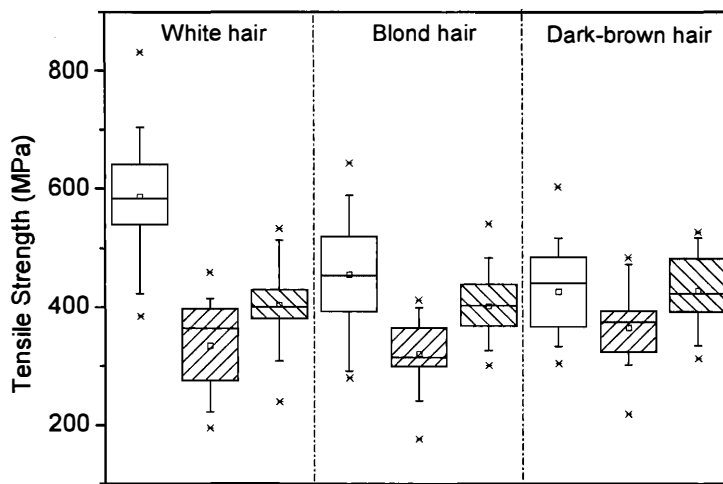


Figure 5. Breaking tensile strength data for hair samples after 64 days of simulated sun exposure, considering 4 h exposure per day. The values are the average of 40 hair fibers measurements from each hair sample. ▨ UV exposed. ▩ UVA exposed. □ Unexposed.

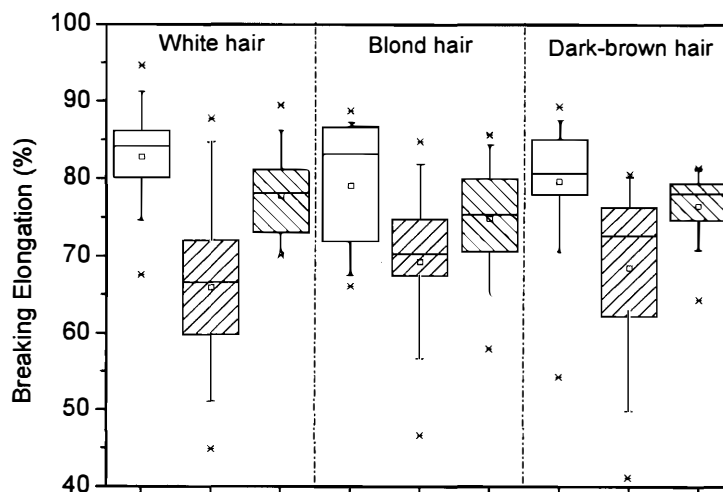


Figure 6. Breaking elongation data for hair samples after 64 days of simulated sun exposure, considering 4 h exposure per day. The values are the average of 40 hair fibers measurements from each hair sample. ▨ UV exposed. ▩ UVA exposed. □ Unexposed.

for hair exposed to different wavelength ranges. Both parameters were affected in all hair types, mainly by UVB radiation. A reduction of circa 7% and 15% was observed on breaking elongation in all hair types after UVA and UV exposure, respectively. Concerning breaking strength, a more pronounced reduction was observed on white hair, followed by blond and dark-brown hair, respectively. The same trend was found when UVB radiation was filtered. In this case, a smaller reduction on breaking strength was observed, indicating that changes in the α -keratin crystals of hair are mainly related to that range of the solar spectrum.

CONCLUSIONS

It was observed that changes in the hair mechanical properties are mainly related to the UVB range of the solar spectrum and that UVA radiation is the one responsible for color changes, disregarding the hair type. Color changes depend on hair type, being more pronounced for light colored hairs. Although lightening every hair type is the main effect of radiation, significant variations in all color parameters are observed after lamp irradiation. The susceptibility of different hair to photodegradation is not only related to the melanin type and content of each hair, though also with the overall hair fiber structure.

ACKNOWLEDGMENTS

The authors thank FAPESP (Grants 01/14161-9 and 04/13066-0), CNPq, CAPES and Cognis Brasil Ltda. for financial support.

REFERENCES

- (1) C. R. Robbins and R. J. Crawford, Cuticle damages and the tensile properties of human hair, *J. Cosmet. Sci.*, **42**, 59–67 (1991).
- (2) P. Zuidema, L. E. Govaert, F. P. T. Baaijens, P. A. J. Ackermans, and S. Asvadi, The influence of humidity on the viscoelastic behaviour of human hair, *Biorheol.*, **40**, 431–439 (2003).
- (3) W. L. Cheun, The chemical structure of melanin, *Pigment Cell Res.*, **17**, 422–424 (2004).
- (4) G. Prota, *Melanins and Melanogenesis* (Academic Press, London, 1992).
- (5) P. Z. Margalith, *Pigment Microbiology* (Chapman and Hall, London, 1992).
- (6) Z. D. Draelos, The biology of hair care, *Dermatol. Clinics*, **18**, 651–658 (2000).
- (7) S. B. Ruetsch, Y. Kamath, and H. Weigmann, “Photodegradation of Human Hair: A Microscopy Study,” in *Sun Protection in Man*, P. U. Giacomoni, Ed. (Elsevier, Amsterdam, 2001), pp. 175–205.
- (8) C. R. Robbins, *Chemical and Physical Behavior of Human Hair* (Springer-Verlag, New York, 2002).
- (9) C. M. Pande and J. Jachowicz, Hair photodamage: Measurement and prevention, *J. Soc. Cosmet. Chem.*, **44**, 109–122 (1993).
- (10) E. Tolgyesi, Weathering of hair, *Cosmet. Toiletr.*, **98**, 29–33 (1983).
- (11) S. Ratnapandian, S. B. Warner, and Y. K. Kamath, Photodegradation of human hair, *J. Cosmet. Sci.*, **49**, 309–320 (1998).
- (12) A. C. S. Nogueira and I. Joekes, Hair color changes and protein damage caused by ultraviolet radiation, *J. Photochem. Photobiol. B: Biol.*, **74**(2–3), 109–117 (2004).
- (13) C. R. Borges, J. C. Roberts, D. G. Wilkins, and D. E. Rollins, Relation of melanin degradation products to actual melanin content: Application to human hair, *Anal. Biochem.*, **290**, 116–125 (2001).
- (14) A. Bertazzo, M. Biasiolo, C. V. L. Costa, E. C. Stefani, and G. Allegri, Tryptophan in human hair: Correlation with pigmentation, *Il Farmaco*, **55**, 521–525 (2000).
- (15) M. R. Vincensi, M. d’Ischia, A. Napolitano, E. M. Procaccini, G. Riccio, G. Monfrecola, P. Santoianni, and G. Prota, Phaeomelanin versus eumelanin as a chemical indicator of ultraviolet sensitivity in fair-skinned subjects at high risk for melanoma: A pilot study, *Melanoma Res.*, **8**, 53–58 (1998).