About photo-damage of human hair

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This paper reviews the current knowledge about human hair photodamage and the photodegradation mechanisms proposed in the literature. It is shown that there are still a number of questions without answer regarding this issue. For example, a better understanding of the hair structural changes caused by different radiation wavelengths is still lacking. We also find controversies about the effects of sun exposure on different hair types. Explanations to these questions are frequently sustained on the amount and type of melanin of each hair, but factors such as the absence of knowledge of melanin structure and of established methodologies to use in human hair studies make it difficult to reach a general agreement on these issues.

Introduction

It is well known that ultraviolet and visible radiations damage hair.[1–3] Sun radiation causes dryness, reduced strength, rough surface texture, loss of color, decreased luster, stiffness, brittleness and an overall dull, unhealthy appearance of the hair. However,

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compared to other research fields, little is known about the biochemical and photochemical changes caused in hair by radiation exposure. The published studies deal usually with measurements of the physical changes caused by radiation exposure, but do not explain the mechanism of hair photo-degradation.

On the other hand, the photochemical degradation of wool, a natural fiber that shows at various levels a series of similar features with human hair, has been extensively studied. If they are so similar, why is it so difficult to explain the hair photo-degradation mechanism? Part of the answer is that wool keratin studies are focused on the photo-yellowing of white wool, which contains no melanin. The melanins, which are the hair and wool pigments,[4] are especially important in the study of hair photo-degradation since these chromophores should provide some photochemical protection to hair proteins.[5] Unfortunately, the chemical structure of hair melanin is not yet known and there are still many difficulties in the study of these natural polymers.[6] The absence of this knowledge is a real obstacle for the establishment of a complete degradation mechanism, but this does not justify the current lacking of scientific studies about hair photo-damage. Quantitative data relating damage to hair type, proteins and color to the radiation wavelength is still missing and only a few works in the literature relate the effect of different ultraviolet wavelength ranges on hair properties or compare the emission intensity of an artificial UV source to sunlight.

Although being quite less important than the study of skin photo-damage, from the point of view of health risks, healthy hairs are associated not only with beauty but with overall self esteem. The huge growth of the market of cosmetics for hair may induce an increase in research, since one effect of the lack of knowledge is the empiric character associated with cosmetic formulations.[7] Formulating products to prevent radiation damages in hair is an important and difficult challenge of the current cosmetic industry, since the basic scientific knowledge is missing. For instance, a series of shampoos in the market are intended to avoid the photo-yellowing of white hairs. But to the best of our knowledge, it is not established that white hairs become yellower by photo-oxidation; for wool, it has been established that photo-yellowing and photo-bleaching are simultaneous events.[8]

A brief description of human hair

Robbins reported a complete description of the human hair morphology, composition and properties.[9] The fiber is composed mainly by keratins, a group of insoluble cystine-containing helicoidal protein complexes which account for 65–95% of the hair by weight. The remaining constituents are water, lipids, pigment, and trace elements.

The greatest mass of the hair shaft is in the cortex, in which crystallized α-keratin fibrils are responsible for hair's remarkable mechanical properties. These properties are dependent on time, temperature and humidity.[10] Melanin granules are located inside the cortex (about 3% by weight), whose type, size and quantity establish hair color.[11,12] Surrounding the cortex is the cuticle, a protective 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 damages.[13,14] Another component of hair fiber is the medulla, whose function is not well defined and generally comprises only a small percentage of the fiber mass. The medulla can be completely absent, or may be continuous or discontinuous along the fiber axis.

Optical properties

Human hair can be considered a two-component system regarding its interaction with visible and UV radiations. The keratins are transparent in the visible region of the light spectrum, but a few amino acids, tryptophan, cystine, tyrosine and histidine, interact with UV. Melanins, which are located only in the cortex, interact with both visible and UV radiations.

When UVB radiation hits the hair, it has to penetrate a layer of absorbing molecules of about 5 μm thickness (the cuticle), the intensity decreasing exponentially. The absorption spectrum of a Piedmont hair (a very clear-toned hair) can be taken as the keratin spectrum. A melanin absorption spectrum was obtained by Sarna and Sealy.[15] Melanin absorbs UVB, UVA and visible radiations, while keratin absorbs mainly UVB radiation. We showed elsewhere[16] that the extinction coefficient of melanin is about 70 times higher than that of keratin at 313 nm (UVB region). Also, the extinction coefficient keratin at 313 nm (UVB region) is about five times greater than at 363 nm (UVA region), whereas that of melanin is about the same at both wavelengths. At 436 nm (visible region), melanin absorbance is still high while keratin does not absorb. Roughly, this means that 97% of the hair mass absorbs mainly UVB radiation and 3% absorbs UVA, UVB and visible radiations.

Main effects of photo-degradation

If human hair is exposed to sun radiation over a prolonged period of time, it may be damaged in different ways.[17,18] In most cases, the amino acids of the cuticle are altered to a greater extent than those of the cortex because the outer layers of the fiber receive higher intensities of radiation.[9] This exposure can cause rupture and detachment of the external layers, resulting in splitting of the ends.

Signori[19] wrote a review about the interaction of human hair with visible and ultraviolet radiation. The author summarizes the current findings on this topic as follows: UVB, UVA and visible radiations cause hair photo-damage. Degradation of melanin granules (so-called photo-bleaching) is caused by visible radiation, with less contribution of UV radiation. On the other hand, UVB and UVA radiations attack hair proteins, with insignificant contribution of visible radiation. The photo-sensibility of light hair is greater than that of dark hair. This points to a better photo-protection of eumelanin compared to pheomelanin. Since melanin photo-protection is limited to the cortex, damage to cuticle amino acids is similar for both hair types. Concerning physical measurements correlated to strength and integrity of hair fiber, UV radiation decreases stress-to-break, Young's modulus (fiber strength) and the dynamic contact angle (hidrophobicity), and increases the wet-combing force, the copper uptake (negative sites in the fiber) and the transverse swelling of the hair fiber (index of the level of unaffected cross-linking of the protein matrix).

Ratnapandian *et al.*[20] studied the effect of humidity on the mechanical properties of hair exposed to UV radiation. They observed that greater damage happens when hair is exposed to very high or very low relative humidity (RH) and that the mechanical properties of hair are less affected when hair is exposed to 30% RH.

Ruetsch *et al.*[21] used microscopy techniques to check the extent of UV damage to hair microstructure and its physical properties. The authors observed that melanin granules remain undamaged after 700 h of UV irradiation, showing degradation only after exposure to hydrogen peroxide solution.

Photochemistry

Hair protein degradation is induced by wavelengths of 254–400 nm. As the cuticle protects the cortex, damages in this region generally occur after extensive damage to hair cuticle. These damages cause degradation of cystine; but the exact mechanism is not well known. Literature suggests that the photo-degradation of cystine occurs through the C–S fission pathway and is different from the chemical oxidation of cystine that proceeds mainly *via* the S–S fission route.[9]

There are two types of melanin, the brown–black pigments (eumelanins) and the less prevalent red pigments (pheomelanins). The chemical structures and molar masses of the melanins are not yet known,[22] 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.[23,24] Hair melanins provide some photochemical protection to hair proteins, especially at lower wavelengths, where both the pigments and the proteins absorb light,[1] 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 photo-sensitive amino acids in hair, preventing the transport of these free radicals into the keratin matrix.[25] However, in the process of protecting the hair proteins from light, the pigments are degraded or bleached.

UV radiation induces the formation of oxyradicals such as superoxide ($O_2^{\bullet-}$), and hydroxyl ($OH^{\bullet}$). These species have one unpaired electron in an outer orbital giving them a very powerful aptitude to react, especially with molecules having a double bond in their structure, such as unsaturated lipids.[26] Chemically, these changes are thought to be caused by UV light-induced oxidation of the sulfur-containing molecules within the hair shaft. Melanin has an intrinsic electron spin resonance (ESR) signal that increases significantly when irradiated with UV-visible light. In the presence of oxygen, superoxide is produced, which dismutates to hydrogen peroxide.[8] This leads to the formation of hydroxyl radicals in the presence of trace amounts of metal ions. Oxidation of the amide carbon of polypeptide chains also occurs, producing carbonyl groups.[27] This process has been studied extensively in wool, where it is known as photo-yellowing[28–32]

Davidson[33] reviewed the photochemistry of wool keratin. Similarly to human hair, the most apparent damages caused by ultraviolet and visible radiation are a color change and a weakening of the fiber. Depending on the spectral distribution of the sunlight, it either yellows or bleaches. Wool keratin also contains significant amounts of the aromatic amino acids, tryptophan, tyrosine and phenylalanine. These amino acids are the major chromophores in wool in the spectral range 250–310 nm and as such they are expected to play a significant part in its photodegradation upon exposure to sunlight. Furthermore, this fiber also loses its strength and bleaches at longer wavelengths, showing that these chromophores are photochemically active and important in the photodegradation of the protein. Most of these species are probably either thermal decomposition or photolysis products of the constituent amino acids of keratin. Free radicals have been observed by ESR spectrometry during the light-induced degradation of keratin. Carbon-centered radicals are formed with an action spectrum maximum of 285 nm, suggesting that they are primary photoproducts of aromatic amino acids.[34] Kinetics measurements indicate that there are at least three types of radicals produced at this wavelength. Stable sulfur-centered radicals are formed from irradiation of dry keratin in the absence of oxygen, but their ESR signals disappear in the presence of moist air. The presence of small amounts of metal ion induce the production of free radicals from irradiated keratin at wavelengths above 320 nm, apparently due to the formation of metal–protein complexes that absorb at higher wavelengths.[35]

Millington and Church[36] state that the variation of the wavelength of the incident radiation has a profound effect on both the photoproducts and the color of irradiated wool. Short wavelengths (<375 nm) cause the yellowing of wool, whereas longer wavelengths, particularly blue light (440–460 nm), result in photobleaching. These authors proposed a mechanism to explain the photo-yellowing of wool involving cystine, which can account for the observation of both oxidized sulfur species and thiol groups in the vibration spectra of irradiated wool. With this mechanism, the authors intended to improve another previous proposed wool photodegradation mechanism, which is based on the involvement of singlet molecular oxygen ($^1O_2$), formed from the reaction of excited triplet states tryptophan residues in the protein structure with ground state molecular oxygen. $^1O_2$ can then react with other amino acids in the keratin structure to form yellow products. However this mechanism is criticized because wool yellows far more rapidly when it is wet indicating that photo-oxidation mediated by singlet molecular oxygen it is not the main mechanism.

Open questions

As was emphasized by Signori,[19] the effect of the different wavelength ranges on hair properties is one of the main topics discussed in the literature, as well as the hair types more prone to hair photo-oxidation. Knowing this information is especially important to choose the correct filters to formulate hair sunscreens. We extensively discussed these two topics in a previous work,[16] using color changes and protein loss measurements to compare the effect of different wavelength exposure on various hair types. From hair spectra, obtained by diffuse reflectance spectrophotometry (DRS), we observed that each hair type shows a defined pattern of reflectance (Fig. 1), which changes substantially after hair irradiation. Both protein loss and color changes are dependent on hair type.

Concerning hair interaction with specific wavelengths, we showed that UVB radiation is the one mainly responsible for hair protein loss and that color changes are caused mainly by UVA radiation. A model to explain the interaction of human hair with light was developed, leading us to consider the hair cuticle as a natural absorber of UVB radiation. As also discussed, relating hair damages caused by UV exposure to the melanin type of each hair is not so simple. Hair types vary not only in

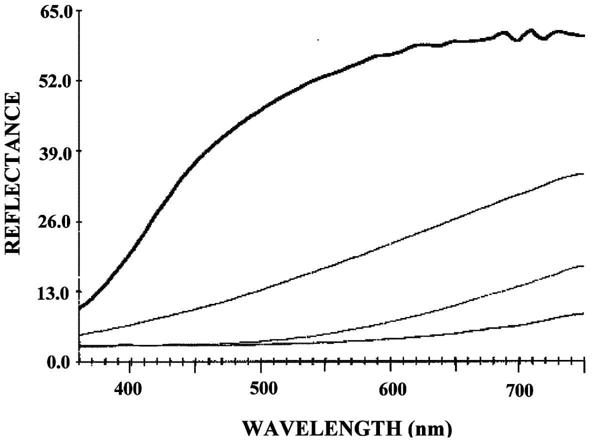

Fig. 1 Human hair diffuse reflectance spectra. From top: white, blond, brown and red hairs. Spectra change substantially when hair is exposed to sun radiation. Modifications are not attributable to melanin photodegradation only.

the composition of hair melanin. The total amount of amino acids more susceptible to photodegradation (tryptophan, cystine, tyrosine and histidine) depends on hair type. Male hairs have more cystine than female and, usually, dark hairs have more cystine than light hairs.[9] According to Bertazzo *et al.*,[37] the amount of tryptophan in dark-brown and black hair is greater than in blond hair. The highest trypthophan concentration is found in gray and white hair, indicating that tryptophan concentration in hair increases with age. Vincenci *et al.*[38] studied red hair, observing that the amounts of pheomelanin and eumelanin vary with sex, age and color shade. According to Borges *et al.*,[5] black hair contains more or less 99% eumelanin and 1% pheomelanin, dark-brown and blond hairs 95 and 5%, and red hair 67 and 33%. Although red hair contains a higher percentage of pheomelanin, the total amount of melanin in this hair is less than that of dark hairs and similar to that of blond hair.

It is also difficult to correlate *in vitro* studies of the melanin photochemical properties and the photodamage of human hair. Most studies of hair melanin degrade the protein matrix by exposing the hair to aggressive chemical procedures interfering with the isolation of natural pigments inducing transformation in the chemical composition of melanin pigment and associated protein.[39]

Although there is evidence that exposure to light induces the oxidative destruction of the hair proteins and the formation of free radicals, information is lacking about various other factors. Porosity, metal ions, and exogenous factors such as water hardness can influence the extent of oxygen radical production and photodegradation of hair.

As already mentioned, the absence of satisfactory knowledge of hair structure and most of all, hair variability, makes its study a difficult subject. This is worsened by the fact that there are no standard methodologies for experiments with human hair. The main parameters analyzed in the assessment of hair UV damages are color changes,[8,40] protein loss,[41,42] and changes of mechanical properties.[20,43] Alterations on hair shine are also a desired measurement.[44–46] The best methodology to use in these studies, as well as the number of replicates necessary to have statistically significant results, is still undefined.

The correlation between artificial and natural sunlight is another problem. Few authors relate the intensity of artificial sources with that emitted by the sun and when this is done, usually it is a direct correlation of the total energy emitted by the lamp to that of the sun. This can lead to contradicting data since hair proteins absorb at defined wavelengths.

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