Journal of Photochemistry and Photobiology B: Biology 138 (2014) 172–181

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology B: Biology

journal homepage: www.elsevier.com/locate/jphotobiol

Yellowing and bleaching of grey hair caused by photo and thermal degradation

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ARTICLE INFO

Article history:
Received 31 January 2014
Received in revised form 16 May 2014
Accepted 25 May 2014
Available online 2 June 2014

Keywords:
Photo damage
Human hair
White hair
Hair colour
UV-light

ABSTRACT

Yellowing is an undesirable phenomenon that is common in people with white and grey hair. Because white hair has no melanin, the pigment responsible for hair colour, the effects of photodegradation are more visible in this type of hair. The origin of yellowing and its relation to photodegradation processes are not properly established, and many questions remain open in this field. In this work, the photodegradation of grey hair was investigated as a function of the wavelength of incident radiation, and its ultrastructure was determined, always comparing the results obtained for the white and black fibres present in grey hair with the results of white wool.

The results presented herein indicate that the photobehaviour of grey hair irradiated with a mercury lamp or with solar radiation is dependent on the wavelength range of the incident radiation and on the initial shade of yellow in the sample. Two types of grey hair were used: (1) blended grey hair (more yellow) and (2) grey hair from a single-donor (less yellow). After exposure to a full-spectrum mercury lamp for 200 h, the blended white hair turned less yellow (the yellow–blue difference, Db^* becomes negative, $Db^* = -6$), whereas the white hair from the single-donor turned slightly yellower ($Db^* = 2$). In contrast, VIS + IR irradiation resulted in bleaching in both types of hair, whereas a thermal treatment (at 81 °C) caused yellowing of both types of hair, resulting in a $Db^* = 3$ for blended white hair and $Db^* = 9$ for single-donor hair. The identity of the yellow chromophores was investigated by UV–Vis spectroscopy. The results obtained with this technique were contradictory, however, and it was not possible to obtain a simple correlation between the sample shade of yellow and the absorption spectra. In addition, the results are discussed in terms of the morphology differences between the pigmented and non-pigmented parts of grey hair, the yellowing and bleaching effects of grey hair, and the occurrence of dark-follow reactions.

1. Introduction

Research on protein photochemistry is important for understanding the degradation processes that occur as a consequence of light incidence on hair and for developing strategies to avoid such reactions. Solar radiation that reaches the earth's surface consists of three wavelength ranges: ultraviolet (UV), visible (Vis) and infrared (IR). Natural and synthetic polymers are susceptible to the damaging effects of sunlight. Although the UV range represents only 4–6% of the total spectrum of solar radiation, the energy associated with UV radiation is enough to break covalent bonds present in organic compounds [1,2]. Free radicals can be formed in these cleaving reactions, which will favour the occurrence of other free radical reactions, including protein damaging reactions [3].

It is well documented that hair, which is mainly composed of proteins (65–95% in weight) [4], is vulnerable to photodamaging [5,6]. However, the current literature about hair photodegradation is not conclusive with respect to white hair colour changes and the type of chromophores formed. Melanins, proteins and lipids are damaged after solar irradiation, resulting in complex photochemical reactions [7–9]. The main consequence of this process is colour modification [6,10] that depends on the natural colour of the hair and on the radiation range of exposure.

Hair proteins absorb radiation between 200 and 350 nm. Aromatic amino acids such as tryptophan, tyrosine and phenylalanine and the sulphur-containing amino acids cystine and methionine are UV-absorber chromophores that are present in keratin [4]. Melanins also absorb UV-radiation and are degraded or bleached

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http://dx.doi.org/10.1016/j.jphotobiol.2014.05.017
1011-1344/

during the process [11]. There are two types of melanins: the eumelanins (brown–black pigments) and the pheomelanins (red pigments) [12]. It is known that melanins, which are present in pigmented hair, prevent to some extent the colour change of hair due to light exposure. [13,14]. The absence of melanins in white hair is the reason why white hair is normally more prone to display the effects of photodegradation during light exposure than dark hair [10].

According to most of studies in this area, photodegradation results in yellowing of white hair and also wool after sun exposure [15,16]. Materials such as wood and paper of natural origin, and also synthetic polymers such as polyethylene are also known to become yellower after sun exposure [17]. A previous study by this research group [10], however, found a less predictable behaviour. White hair became less yellow when exposed to full-spectrum solar light but yellower when exposed to heat (at 50 °C). The photobleaching effect was also reported in wool exposed to visible (Vis) radiation, whereas yellowing occurred under UV exposure [18–20]. In the case of wool, the ratio of photobleaching to photoyellowing is directly related to the initial colour shade.

Published works concerning the presence of yellow chromophores on free amino acids after exposure to sun radiation have identified significant yellowing in tryptophan, tyrosine, histidine, phenylalanine, and cystine in solutions [21]. Tryptophan and tyrosine, in particular, are considered to be involved in photoyellowing, as the photo oxidation products of these amino acids were detected by fluorescence spectroscopy of wool after solar irradiation [21]. Our previous study with hair and free amino acids irradiated with a mercury lamp indicates that although a decrease in the tryptophan content of hair after lamp irradiation is observed, a direct correlation with hair yellowness cannot be achieved [10]. A limitation of the studies using free amino acids is that they may present a different behaviour when comparing the amino acids linked in the keratin structure. To overcome this problem, experiments based on the irradiation of wool fibres with a xenon lamp followed by the characterisation of the products of protein photodegradation were performed by Bryson and collaborators. Using a quasi-proteomic approach, these authors concluded that the photoproducts mainly originated from tryptophan and tyrosine [21].

The present paper contributes to the comprehension of the photoyellowing and photobleaching behaviour in white hair. Two types of hair were evaluated: blended grey hair and grey hair from a single-donor. These are composed of totally black fibres, totally white fibres or fibres that were partially white and partially black. The white regions of these two hair types were yellow before irradiation with UV, Vis and IR and a strong dependence of the result of the photodegradation process on the initial hair colour was noticed. Photoyellowing or photobleaching took place in each case, depending on the initial colour shadow and on the wavelength of incident light.

The morphology of untreated grey hair was also analysed by transmission electron microscopy to investigate the pre-existing differences present in white and black hair before photodegradation. Single partially black and partially white fibres from grey hair were used, so that the effect of genetic variability would not influence the final results. To our knowledge, this is the first study detailing the ultrastructure of a region of white hair in comparison with the morphology of a black region in the same hair fibre.

2. Experimental

2.1. Samples

Blended grey hair was purchased from De Meo Brothers Inc. (New York, USA). Grey hair was also collected from a male volunteer with no history of chemical treatments (called grey hair from single-donor along the text). Grey hair is a mixture of fibres with some that are totally white and totally black and some fibres that are partially white and partially black. White fibres were separated by hand, and samples weighing 0.5 g were used.

Prior to the experiments, the hair samples were washed with a 2.0% w/w sodium lauryl sulphate aqueous solution, according to the following steps: (1) hand-washing with 1 mL of the solution for 1 min, (2) rinsing with tap water at 40 °C for 30 s, (3) repetition of step (1) and (2) but with rinsing for 2 min, and (4) combing using a polypropylene comb. Then, the samples were dried at room temperature and stored in plastic bags.

All of the Merino wool used in the work was untreated and came from a single sheep. The wool closer to the sheep's body (more exposed to the body heat) was yellower, whereas the wool at the tips (farther from the body and more exposed to the sun) was less yellow. Samples were separated into yellow or white, cleaned with ethyl ether in a Soxhlet extractor for 8 h, dried at room temperature and stored in plastic bags.

2.2. Measurements of fibre diameter

The diameters of 35 partially white and partially black fibres from blended and single-donor grey hair were measured using two distinct devices: (1) a light microscope and (2) a micrometer. In both cases, the measurements were carried out in six distinct points in each fibre: three points on the white area and another three points on the black area. The diameter results, in each area, are thus an average of the three measurements in the 35 fibres (total of 105 values). When using the micrometer, the measuring points were randomly distributed along the white and the black areas of the fibre. In the case of the light microscope, images from the white and black areas of the fibre were obtained at distances of 2 cm, 4 cm and 6 cm far from the white–black boundary. The images were then imported to the Axio Vision SE Rel 4.9.1 Software (Carl Zeiss Company, Germany) and the diameters were measured.

2.3. Characterisation of the radiation sources

Direct sunlight and a mercury vapour lamp (OSRAM HQL 125 W, São Paulo, Brazil) were used as radiation sources. The lamp has an emission spectrum with strong lines at 367 nm (UV) and 406 nm, 438 nm, 548 nm and 580 nm (visible light), Fig. 1, in addition to emitting very low infrared (IR) radiation. Thus, it is very different from the continuous solar spectrum. The overall procedure for irradiation with the mercury vapour lamp is described elsewhere [6]. Measurements of light intensity from all of the sources were carried out with a radiometer (PMA 2100, Solar Light Co., USA), considering the dose incident on the samples. The distance source-sample and source-radiometer were the same. The intensity of sunlight was measured at noon in Campinas, Brazil (22°53′ S; 47°04′ W). The values of radiation intensity obtained for the mercury vapour lamp were 1.5 W m^{-2} (UVB), 26.0 W m^{-2} (UVA) and 70.0 W m^{-2} (Vis + IR), and for sunlight, they were 2.4 W m^{-2} (UVB), 32.0 W m^{-2} (UVA) and 658.0 W m^{-2} (Vis + IR).

The exposure times were calculated such that the daily doses of UV radiation from the lamp and sun were comparable. The intensities of visible radiation could not be equalised because the intensity emitted by the lamp is less than half of the sun emission.

2.4. Exposure to artificial radiation

One of the following exposure conditions were applied to the hair and wool samples: (1) exposure to Vis and IR only, using a common borosilicate glass (50 × 40 × 0.4 cm) covered with a polyester film to block the UV from the lamp full-spectrum and (2)