A Closer Look at the Complex Hydrophilic / Hydrophobic Interactions Forces at the Human Hair Surface

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Abstract. The complex chemical structure of the hair surface is far from being completely understood. Current understanding is based on Rivett’s model1 that was proposed to explain the macroscopic hydrophobic nature of the surface of natural hair. In this model covalently-linked fatty acids are chemically grafted to the amorphous protein (keratin) through a thio-ester linkage2,3. Nevertheless, experience like wetting and electrical properties of human hair surface4 shows that the complexity of the hair surface is not fully understand based on this model in literature. Recent studies in our laboratory show for the first time microscopic evidence of the heterogeneous physico-chemical character of the hair surface. By using Chemical Force Microscopy, the presence of hydrophobic and ionic species are detected and localized, before and after a cosmetic treatment (bleaching). Based on force curve analysis the mapping of the local distribution of hydrophilic and hydrophobic groups of hair surface is obtained. A discussion on a more plausible hair model and its implications will be presented based on these new results.

1. Introduction
The human hair is a complex structure; it has a unique physical and chemical composition, with a well characterised micro- and nano-structure. Knowledge of its surface properties is especially critical in hair care industry as many of the cosmetic actives and treatments have to interact on and through this interface. The hair’s surface area depends on the length and quantity of hair fibres but can reach easily ~6 m². In more detail, hair is a fibre 50 to 100 µm in diameter, which surface is formed by a large number of flat imprecated scales pointing outward from root to tip. Its structure can be divided into three parts: the cuticle, the cortex and the medulla in the central region. The cuticle, our interest, is formed of cells with a characteristic shape (flats square sheets of 0.5 ticks and 50 µm in length) that are at the origin of the surface scales. They contain keratin proteins, characterised by a high content of cystine, and amino acids rich on disulfide bonds and peptide bonds; (with an important presence of COOH and NH₂ chemical groups). To complete this brief description of the cuticle, it is important to know and understand the presence of an important lipid: 18-methyleicosanoic acid (18-MEA). The presence of such a lipid film covalently attached to the surface confers to the hair the hydrophobic character and, as recently discussed3, concomitant low friction. The role of (18-MEA) is still not fully understood, but its presence seems to be important for the protection of the surface of hair.

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In our study we present first evidences of the surface distribution of chemical groups involved in the hair surface structure, information that is essential for a correct modelling of its surface. Atomic Force Microscopy (AFM) was the technique of choice for this type of study and we used it to obtain the real topography of the hair. By using chemical modified tips (Chemical Force Microscopy), and in particular hydrophobic groups like CH3, we were able to map the surface adhesion interaction. Force-distance curves were measured at each point and the exhibited adhesion force extracted. An image (map) is formed that represents the distribution of a specific chemical affinity. In our study we used a proprietary repositioning technique that allows us to scan the same areas before and after a treatment. Because the hair fibre is very diverse from morphological point of view this approach is essential to obtain meaningful results. In this study we focused on chemical and physico-chemical hair surface modifications, before, during and after bleaching hair. Bleaching is a well known oxidation cosmetic treatment that increases the hydrophilic character of hair.

2. Materials and Methods

2.1. Atomic Force Microscopy

The measurements were done on a CPII Research AFM (Veeco Instruments, Dourdan, France) in contact mode on a buffer pH controlled medium. An optical microscope is use for selecting the area of interest and for repositioning, an example of these images is shown in figure 1(bottom).

Comparing with a previously recorded image it is relatively easy to locate the surface originally studied within ± 10 µm. A subsequent zoom allows us to look at exactly the same position.

2.1.1. Chemical Force Microscopy and Force – distance measurement.

In addition to the powerful imaging capabilities, AFM also provides us with a relatively new tool for measuring and mapping surfaces with very high spatial and force chemical resolution. The AFM chemical probes that we used are modified tips that have been coated by a thin layer of gold and reacted with thiol-terminated chain fatty acids (thiolisation). We used hydrophobic CH3 coated tips fixed to cantilever of nominal force constant of 0.5 N/m. The hair surface mapping is obtained from the analysis of the measured force-distance curves while approaching and separating tips and hair surface (up to a maximum loading force of 10 nN and at a scan speed frequency of 1 Hz). The probe is approached towards the surface, contact is made with controlled level of applied force and the tip is then retracted from the surface. The samples were imaged in contact mode, under ambient temperature (22 ± 2)°C in buffer conditions and pH control medium. The images were collected in a (256 x 256) matrix over typical area of (10 x 10 µm) subdivided into 25, then 100 zones.

2.2. Hair samples
Human hair of Caucasian origin was obtained from internal sources at L’Oreal. They were first cleaned, rinsed and dried using standard procedures\(^3\). First, the native natural hair surface was investigated, then the same areas were analyzed during and after a simplex bleaching treatment, which consist on application of H\(_2\)O\(_2\) (30 Volume) solution. The hair surface modifications were followed during 3 hours after treatment. The second study was performed with a more elaborated and representative of commercial cosmetic bleaching treatment. Finally the effect of a proprietary polyelectrolyte was studied.

3. Results and Discussion
A net morphological degradation of the hair surface was observed during the bleaching treatment, as we can notice in figure 2. After treatment, the surface is damaged (failure of scales), but we also notice the presence of superficial deposits due probably due to residues of formulation.

![Figure 2. Morphological degradation on hair surface, images obtained from the analysis of the same fiber before (natural) and after bleaching. Images obtained with electron scanning microscopy and sub micron scale with atomic force microscopy (area 10 x 10 µm). (Raw images, lines on the AFM imaged are scanning artefacts)](image)

This morphological degradation comes along with a modification of the physico-chemical properties of the surface. Figures 3 represent an example of high resolution adhesion maps obtained from the analysis of the same area of hair before (cf. fig.3a), after bleaching (fig.3b) and after a cosmetic polymer treatment (fig.3c). The colour scale (legend) quantifies the adhesion force (nN) and represents the local strength of the hydrophobic interaction.

![Figure 3. Adhesion mapping: Distribution of adhesion forces (F\(_{adh}\)) obtained from the analysis of the same hair area (10 x 10 µm), natural (a), and bleached (b) than after cosmetic polymer treatment (c). These results show that natural hair is globally a hydrophobic surface (90%) with an average measured adhesion force F\(_{adh}\) of ca. ~5.5nN, but it contains also very weakly adhesive zones with a rather hydrophilic character. These zones are mainly localized in the edge of scales, where those proteins are](image)
more exposed. After bleaching (cf. Fig.3b), there is dramatic decrease of the hydrophobic interaction on the investigated surface (up to an average $F_{adh}$ of ca. ~1.9 nN) exhibiting an hydrophilic character. However 25% of the surface remains still with hydrophobic character. After a cosmetic polymer treatment, the hair surface becomes again more hydrophobic. The morphological analysis of the surface shows that the most important hydrophobic area corresponds to polymer deposit, which interact strongly with the hydrophobic tip. The polymer restores the hydrophobic character of the hair surface and the average measured $F_{adh}$ increases to ca. ~6.2 nN. Bleaching is indeed a common hair treatment; and is well known to weaken the cell membrane complex and to oxidize cystine residues in the exocuticle. Bleaches hair becomes macroscopically hydrophilic and some recent studies suggest that bleaching is a complex phenomena with doesn’t consist on simply removing of 18-MEA.

Our results suggest that lipids form not so well defined layer on the hair surface, according scenario of heterogeneous ordered lipid layer proposed in previous studies of Luengo et al. These studies are helping us to understand better the distribution and availability of reactive groups at the hair outermost surface in the future and will be the object of a more detailed publication.

**Figure 4.** Different scenarios possibly taking place on the hair surface. 18-MEA repartition, model C is most probably the right reparation according to our results.

**4. Conclusion**

We used Chemical Force Microscopy to explore the physico – chemical properties of hair surface. The repositioning technique was used for the first time in order to evaluate, the distribution, localisation and eventual modification of hydrophobic groups, before and after bleaching process. We also show the impact of repairing cosmetic polymer treatment. Our results are very new and show for the first time the evidence of different chemical group’s effect at the hair surface and it’s evolution with bleaching treatment. Our results provide clearer experimental evidence for the heterogeneous ordered repartition of 18-methyleicosanoic lipid layer on hair surface and the consequent exposition of reactive sites underneath.

**References**

[1] A.P. Negri, H.J. Cornell, D.E. Rivett, Textile Res. Journal., 1997, 63, 199.
[2] Swift, J.A Human hair cuticle: Biologically conspired to the owner’s advantage, 1999J. Cosmet. Sci., 50 (1), 23-47.
[3] S. Breakspear, J. R. Smith, G. Luengo. 2005, J. of Structural Biology, 149, 235.
[4] V. Dupres, Dominique. Langevin, P. Guenounn, a. Checco, G. Luengo, F. Leroy. 2007, J. of Colloind and Interface Science, 306, 34.
[5] S. C.R. Robbins in Chemical and Physical behavior of human hair 4th edition.ed.Springer.
[6] Yorimoto, N., Naito, S. Physical and Chemical properties of integral lipids in hair cell membrane complex 1994, Inc Proc. Int. Symp. Fibre Sci. Technol, Yokohama, 215.
[7] Aleksander Noy, D. V. Veznov and Charles M. Lieber. 1997, Chemical Force Microscopy, Annu. Rev. Mater., 27, 381-421.
[8] Gustavo, S. Luengo, Philippe. Hallegot, Frederic. Leroy. 23rd IFSCC Congress 2004, Orlando, Florida, USA.