



Contribution ID: 41

Type: Oral

## Impact of lipids present at the hair bio-interface on the structure of adsorbed polymer-surfactant systems

Thursday, 18 July 2024 09:50 (20 minutes)

The hair fiber surface is normally hydrophobic as it is covered by a layer of different lipids. The most abundant lipid is 18-methyleicosanoic acid (18-MEA), which has a characteristic antepenultimate methyl branch whose role is still under study. Processes such as bleaching can damage the hair fiber, removing the lipid layer by hydrolytic and oxidative processes. The loss of lipids exposes the underlying keratins, rich in cysteine which readily oxidizes to cysteic acid and makes the surface hydrophilic, modifying its tribology. This completely changes how the hair fiber interacts with haircare products. Despite all the research in the area, details on this complex system are still missing at the molecular level and they are crucial for the cosmetic industry whose current challenge is to improve the sustainability of their formulations without compromising their performance. This study aims at defining the role of hydrophobicity and specifically of the 18-MEA methyl branch on the interaction properties of hair. Neutron Reflectometry (NR) is used as it can give information about hierarchical adsorption from mixtures. Biomimetic hair surfaces are used in this study which are produced by functionalizing gold surfaces with thiol terminated 18-MEA, its straight-chain analogue eicosanoic acid (EA), or a sulfonate-terminated alkane that mimics the cysteic acid moiety. Mixed 18-MEA/sulfonate surfaces are also investigated, to explore the effect of intermediate hydrophobicity. Adsorption of an anionic surfactant (Sodium dodecyl sulfate (SDS)) and a cationic polysaccharide (Chitosan) system is studied by NR and complemented by Quartz-Crystal Microbalance (QCM) and Atomic Force Microscopy (AFM) measurements. Results show differences in the adsorption behavior on the various biomimetic surfaces, that can be rationalized considering the involved molecular structures. For example, a 1:100 mixture of Chitosan and SDS adsorbs on an undamaged hair model as a monolayer of SDS followed by a thick (ca. 10 nm), highly hydrated (>90%) layer of Chitosan, while it adsorbs as a complex on the damaged hair model. This adds important knowledge on the influence of the hair surface on the interaction with haircare formulations and, in particular, with complex natural polymers which should ultimately lead to more sustainable cosmetic products.

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**Session Classification:** Thin films and interfaces in soft matter and materials science III