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From conditioning shampoo to nanomechanics and haptics of human hair

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Synopsis

Shampoo treatment and hair conditioning have a direct impact on our wellbeing via properties like combability and haptic perception of hair. Therefore, systematic investigations leading to quality improvement of hair care products are of major interest. The aim of our work is a better understanding of complex testing and the correlation with quantitative parameters. The motivation for the development of physical testing methods for hair feel relates to the fact that an ingredient supplier like BASF can only find new, so far not yet toxicologically approved chemistries for hair cosmetics, if an in-vitro method exists.

In this work, the effects of different shampoo treatments with conditioning polymers are investigated. The employed physical test method, dry friction measurements and AFM observe friction phenomena on a macroscopic as well as on a nanoscale directly on hair. They are an approach to complement sensoric evaluation with an objective in-vitro method.

INTRODUCTION

Haptics refer to the tactile sense: External objects or forces are noticed at contact with the body, esp. with hands and fingertips. In the skin, there are cutaneous sensual organs with tactile receptors. Their density is highest at the tip of the tounge and of the fingers, which enables to differentiate fine structures. The skin on the back has the lowest density of tactile receptors. Tactile quality is noticed and evaluated in sensory assessments, where it can be distinguished with expressions like "luxury of touching soft, flowing hair".

Many hair cosmetic products such as shampoos, conditioning rinses and even hair sprays claim haptic attributes on their packaging like the suppleness of silk, cashmere, and velvet or claim attributes like smooth, sleek, silky, and soft.

METHODS AND RESULTS

In BASF's application lab, the sensoric or subjective evaluation of hair after various treatments is according to a ranking system: "hand mark" of 1=very good to 3=weak, bad. Different attributes of wet and dry hair are ranked as follows:

- detangling after shampoo application (complemented by physical test method),
- combability (complemented by physical test method),
- feel of wet and dry hair
  - positive: well conditioned, silky, soft, smooth ...
  - negative: coated (build-up), oily / greasy, rough / damaged, frizzy ...

Additionally, internal und external panel testing as well as external salon testing are accessable for sensoric evaluation.

The motivation to develop physical test methods for hair feel is for a raw material supplier like BASF to find new, toxicologically not yet approved chemistries for hair cosmetics without touching, so an in-vitro method is mandatory. The physics behind hair feel are an interplay of different forces:

- Mechanical forces of friction and lubrication during the movement along the hair surface with a finger or a comb, which reflects smoothness (Figure 1)
- Mechanical forces during hair bending which reflects softness and suppleness
- Capillary forces only for wet hair, esp. at combing

Mechanical forces of friction and lubrication can be addressed with the Universal Surface Tester (UST), the atomic force microscope (AFM), and dry friction measurements, and they correlate with surface morphology on a certain scale. This paper's focus is on these phenomena.

The phenomena, which lead to quality differences of hair cosmetic treatments, become visible to the observer on different scales: Macroscopically, hair feel and combability can be distinguished on hair bundles, whereas these properties on a micro- or even nanoscale are based on interactions between single fibers or hair–finger or hair–comb.

Important for friction is the hair surface morphology, e.g. roughness on a certain scale, as it is known from microscopic images of the cuticula: Virgin hair has flat cuticula scales, whereas damaged hair shows lifted scales and broken scale edges. Conditioning polymers (Figure 2) have different options to influence the hair surface and also haptics of hair.

Surface friction coefficients of hair with various cosmetic treatments were investigated with a Universal Surface Tester (UST, innowep). The system can be used for wet and dry hair. Caucasian, bleached hair was treated with concept shampoos based on SLES / CAPB, which contained different conditioning systems that are well known on the market:

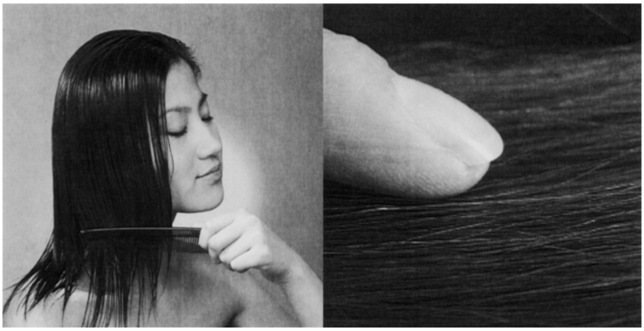

Figure 1. Friction and lubrication during the movement along the hair surface with a finger or a comb, which reflects smoothness.

Polyquaternium-7, Polyquaternium-10, Polyquaternium-44, Polyquaternium-87, and Guar Hydroxypropyl Trimonium Chloride combined with silicone emulsion.

The physical UST measurements wer complemented by sensoric evaluations of hair dressers: Their results correlated well with the UST results. The same trend also showed in the measurements of the combing force reductions.

The graph in Figure 3 shows the force reduction F_R in % of different samples as well as the combing force data in %. It is visible that silicone containing conditioning systems have higher values meaning less friction and less resistance to combing; it is remarkable that one conditioning polymer, the Polyquaternium-87 (1), reveals the same effect without any silicone.

The typical "silicone feel" on hair in terms of smoothness, which is currently the favored attribute, can also be observed taking a closer look to the wet combing curve profiles as well as the dry friction. The correlation between sensoric ranking and co-depositioning of silicone and polymer is shown in Figure 4.

A new method for the investigation of single fiber-fiber interactions was set-up on the AFM (2). In order to prepare a modified cantilever as a hair probe, standard single bleached Caucasian hair tresses were used. Hair fragments were cut with a P.A.L.M. Microbeam

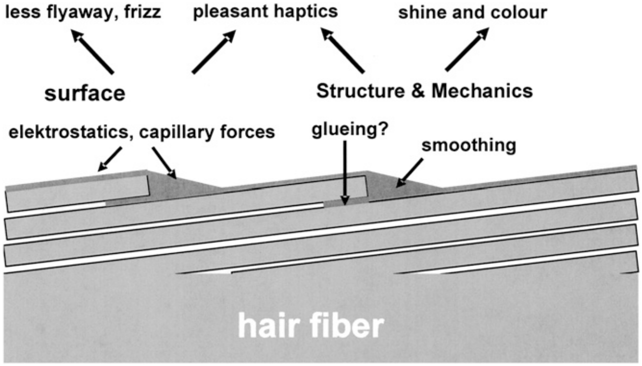

Figure 2. Options for conditioning polymers.

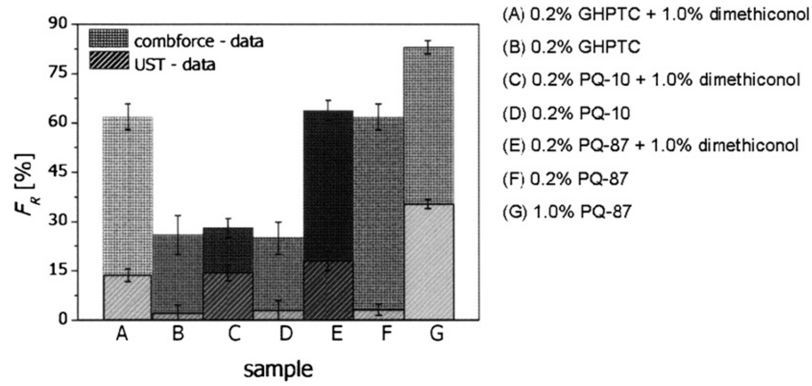

Figure 3. Correlation of wet comb force data and wet UST data.

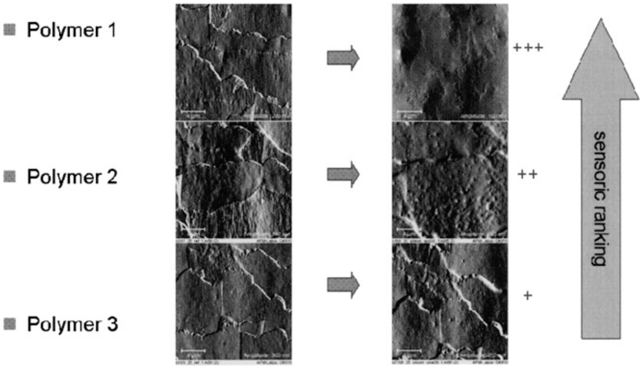

Figure 4. The correlation between sensoric ranking and co-depositioning of silicone and polymer is shown; +++ means well conditioned, "silicone feel."

laser (3). Then, these fragments of 50 µm diameter were glued to tipless cantilevers. We used a two component adhesive on an epoxy resin. Additionally, we prepared a hair as substrates and fixed them with an industrial double tape on microscope slides. The measurements were done with this set-up on a MFP-3D AFM (4). For measurements in water, we used a closed fluid cell.

Conventionally, colloidal particles used in colloidal probe AFM have a diameter dimension of up to 50 microns. Consequently, the hair is cut into units whose length is smaller than the hair diameter for avoiding difficulties due to inertia, hydrodynamic friction or weight of the attached object.

Figure 5 shows a representative force distance curve of a vertical single hair-hair measurement experiment in air with a relative humidity of 30 ± 5%. There are 100 curves plotted to emphasize the reproducibility at a single spot. The standard deviation of one position was around 2.3% ± 0.4%.

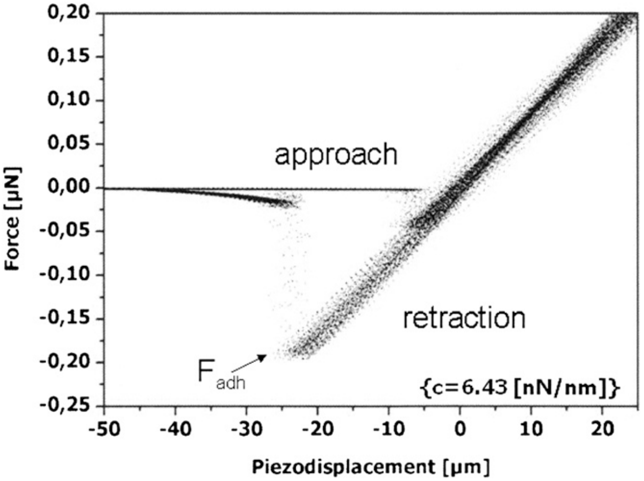

Figure 5. One hundred vertical force distance curves of a single hair-hair experiment by AFM to show the reproducibility of one spot of a hair in dry state.

The same hair probe setup was also used for a more detailed investigation of the friction properties between single hair fibers. In this case, we focused on the lateral signal which is detected by the photodiode. The directional friction effect of human hair is well known. As with most animal fibers, it is less effective to move over the hair in a root to tip direction than in the tip to root direction, because of anisotropic orientation of hair cuticles. A typical friction loop of the approach (upper curve part) and the retraction (lower curve part) is observed (Figure 6). The distance is < 1 μm. On average, the spacing between hair cuticle edges is around 5 μm. Consequently, this measurement is done on the cuticle surface between the edges.

Increasing the lateral range of measurement from 5 μm to 25 μm, the cuticle edges become apparent in the friction loops. This ratchet mechanism at the cuticle edges is also shown by LaTorre and Bhushan (5) during friction loops between a cantilever and a hair surface. A complete in-situ experiment is shown in Figure 7: The black line shows a friction loop after the system was rinsed with 40 ml water with a velocity of 0.20 ml/s. Comparable to the latter friction loop, the cuticle edges cause a higher signal. The application of 40 ml Polyquaternium-87, a new conditioning polymer for hair care (1), took also 200 s and confirms the assumption that the cationic polymer smoothes the cuticle edges. After rinse-off with water, the signal of the cuticles appears smoother compared to the untreated hair without PQ-87 treatment.

The peaks in the curves are the cuticle edges, in the opposite direction this significant feature is less pronounced.

SUMMARY

In this work, the effects of different conditioning systems applied in shampoos were investigated. We used physical methods like combing and friction measurements, UST, and AFM to observe friction phenomena on different scales directly on hair. This is an approach to complement sensoric evaluations with an objective in-vitro method to screen new chemistries and to do a structure property mapping.

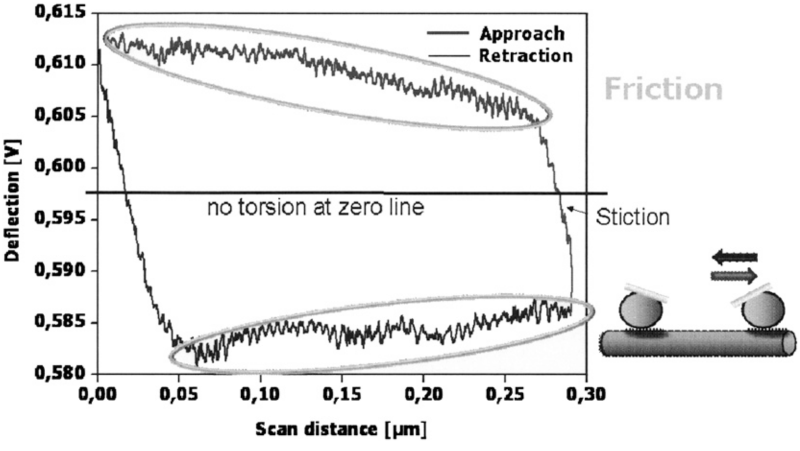

Figure 6. Friction loop on one cuticula scale; crossed cylinders scan distance < 1 μm.

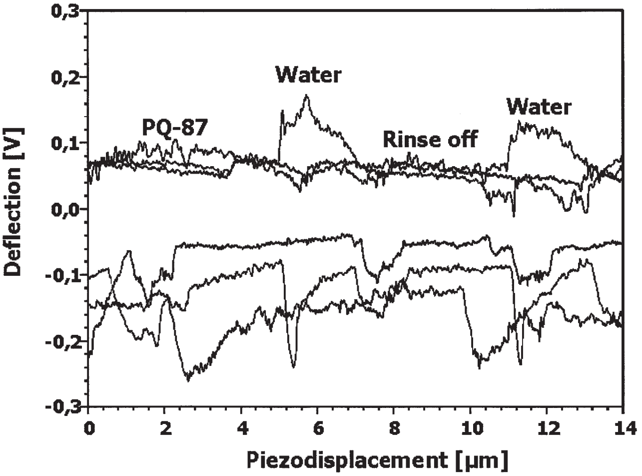

Figure 7. Friction loops after subsequent treatments in a fluid cell: *In situ* friction loop in water, followed by application of Luviquat® Sensation (INCI PQ-87) at a concentration of 200 ppm, followed by rinse-off with water.

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