# Nanotribological characterization of human head hair by friction force microscopy in dry atmosphere and aqueous environment

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Friction force microscopy was employed for the tribological investigation of human head hair in two different environments: a dry atmosphere and de-ionized water. The fibers were immobilized by embedding them in indium. The effects of bleaching, conditioning, and immersion in methanolic KOH were quantified in terms of the relative coefficient of friction ( $\mu$ ). The virgin fibers were clearly distinguished in terms of friction coefficient from the chemically damaged ones in both environments, while all categories of hair exhibited higher friction coefficients in the aqueous environment. Secondary ion mass spectroscopy was used as a complementary technique to examine the presence of fatty acids on the cuticular surface of the different categories of hair as well as the conditioner distribution. Neither bleaching nor 30 min treatment in methanolic KOH was found adequate to completely remove the fatty acids from the fibers' surface. Conditioner species were detected along the whole cuticular surface. © 2010 American Vacuum Society. [DOI: 10.1116/1.3432462]

# I. INTRODUCTION

The introduction of atomic and friction force microscopies (AFM and FFM) has facilitated an increase in our capacity to study the morphological and tribological properties of various materials at the nanoscale.<sup>1–7</sup> Hair is an important biological material. It is both topographically and chemically a complicated fiber, down to the nanometer scale, creating significant challenges for its characterization. The application of AFM and FFM in its surface investigation is thus attractive. Since the first reported study of human hair with AFM by Goddard and Shmitt,<sup>8</sup> there has been an increasing use of AFM and its derivative techniques in hair characterization to examine, both qualitatively and quantitatively, various properties of hair, from topographical and adhesive to mechanical and tribological ones.<sup>9–15</sup>

The quantitative tribological examination of hair by FFM was first reported by McMullen and Kelty<sup>13</sup> who showed that the effects of various treatments on hair (e.g., bleaching, solvent extraction, and conditioning) can be distinguished and characterized in terms of the relative coefficient of friction ( $\mu$ ) measured using a silicon nitride tip. It was demonstrated that the macroscale frictional properties of hair after different treatments are not only related to the topographical alteration of the cuticular architecture, but also to the chemical modification of the cuticular surface.

In a subsequent study by Breakspear *et al.*<sup>16</sup> it was shown that the nanotribological properties of hair strongly depend on the presence of 18-methyleicosanoic acid (18-MEA) on their surface, which apart from rendering them hydrophobic acts also as a lubricant layer. The same conclusion was derived by Sadaie *et al.*<sup>17</sup> who used a hydrophobically modified tip to examine  $\mu$  for hair as a function of the distance from the root end of the fiber. As the distance from the root end increased and more physical damage was present because of the history of the fiber (that is, less 18-MEA),  $\mu$  increased.

The lubricant effect of 18-MEA was further supported by a series of studies by Bhushan and co-workers, <sup>14,18–22</sup> who examined the effects of factors such as humidity, ethnicity, temperature, etc., and at different scales, i.e., macro-, micro-, and nanoscale, on hair subjected to different treatments (e.g., chemically or chemomechanically damaged, water soaked, and conditioned). In every case, whenever the outer layer of 18-MEA was removed by either chemical or chemomechanical damage,  $\mu$  increased significantly, irrespectively of the subcuticular layer exposed after each kind of damage.

However, the exact mechanisms that underlie the changes in the frictional properties of hair are still not well understood. One contributing factor is that most studies have been performed under ambient conditions, where the presence of poorly defined capillary forces may add an unquantifiable effect to the pure frictional differences. Moreover, different kinds of treatments have been used by different researchers, while most of those treatments have an uncertain effect on the chemistry of the cuticular surface. Of course, the fact that

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hair is a complicated fiber in terms of structural components, of nonuniform surface chemistry, and quite unique for each individual depending on the gender, origin, dietary, and physical and mental health, surely contributes to the difficulty of characterizing and standardizing the effects of different treatments on hair, and especially at the nanoscale.<sup>23</sup>

In order to overcome the above issues hair fibers of the same individual where examined by FFM in both dry atmosphere and de-ionized water. The chemical effect of bleaching and immersion in methanolic KOH on the surface of hair was further examined by secondary ion mass spectroscopy (SIMS) to provide a better insight on the chemical modifications responsible for the changes in the value of  $\mu$  observed.

# **II. EXPERIMENT**

#### A. Hair samples

The human head hair used throughout this study was from the same Caucasian male individual,  $\sim 25$  years old. The samples were of  $\sim 1$  cm length and  $\sim 1$  cm distance from the scalp. The categories of hair examined and the corresponding treatments are listed below.

- (1) Virgin. Virgin hair was sonicated for 2 min in 1% aqueous solution of sodium dodecylsulphate, followed by copious rinsing with de-ionized water and cautious drying in a stream of nitrogen to remove surface detritus.<sup>16</sup>
- (2) KOH-damaged. Hair fibers were placed in methanolic KOH (0.1 mol dm<sup>-3</sup>) for 30 min at 25 °C, which has been reported to completely remove 18-MEA from the hair surface.<sup>24</sup> The samples were then rinsed with copious amounts of de-ionized water and carefully dried in a stream of nitrogen.
- (3) Bleached. The samples were placed in the bleaching solution for 30 min at 32 °C. They were then rinsed with copious amounts of de-ionized water and carefully dried in a stream of nitrogen. Solution A (bleach base) was prepared by dissolving 10 g urea, 7 g NaCl, and 12 ml NH<sub>4</sub>OH (28%) in 100 ml of de-ionized water. Solution B (6% hydrogen peroxide) was prepared by adding 17.1 ml H<sub>2</sub>O<sub>2</sub> (35%) to 82.9 ml of de-ionized water. The bleaching solution was then prepared by mixing equal proportions of solutions A and B just before use.
- (4) Virgin conditioned. Virgin hair, prepared as described above, was immersed in the conditioner for 1 min. The main components of the conditioner (Unilever, Port Sunlight, UK) were a quarternary ammonium compound (behetrimonium chloride) and silicone (dimethicone). It was rinsed with de-ionized water for 1 min and carefully dried in a stream of nitrogen.
- (5) KOH-damaged conditioned. KOH-damaged hair, prepared as described above, was placed in the conditioner for 1 min. It was then rinsed with de-ionized water for 1 min and carefully dried in a stream of nitrogen.

#### B. Secondary ion mass spectroscopy

Single hair fibers were carefully mounted on a heating/ cooling sample holder between a coarse molybdenum grid  $(5 \times 5 \text{ mm}^2 \text{ apertures})$  and a small piece of silicone-free double-sided tape (3M "scotch tape" grade 665) attached to the base plate of the sample holder. After mounting, the samples were placed into the instrument airlock, which was continuously flushed with dry nitrogen gas ("oxygen-free, BOC Gases, Manchester, UK") with the airlock door slightly open. The airlock door was closed after 5 min and the gas flush turned off. Liquid nitrogen was used to cool the sample holder via a cold finger and storage Dewar for approximately 2 h before the vacuum pumps were turned on. The sample holder temperature was  $\sim -100$  °C at this point. The airlock pressure reached  $\sim 2 \times 10^{-6}$  mbar after 2 min pumping time. The sample holder was cooled for a further hour to  $\sim$ -140 °C before transfer to the main analysis chamber. The sample holder was also cooled in the analysis chamber via a cold finger and storage Dewar and the temperature remained at  $-140 \pm 5$  °C for  $\sim 5$  h during the subsequent analysis.

Static SIMS analyses were carried out using an ION-TOF "TOF-SIMS IV–200" instrument (ION-TOF GmbH, Münster, Germany) of single-stage reflectron design.<sup>25</sup> Positive and negative ion spectra and images of the hair samples were obtained using a Bi<sub>3</sub><sup>2+</sup> focused liquid metal ion gun at 20 keV energy, incident at 45° to the surface normal and operated in "burst alignment" mode for high spatial resolution. This unbunched mode of operation uses 100 ns wide pulses with a repetition rate of 10 kHz. Charge compensation was effected by low-energy (~20 eV) electrons provided by a flood gun. The total ion dose density was less than  $1 \times 10^{16}$  ions m<sup>-2</sup> in all cases. The topography of the sample surface and the ion gun mode of operation limited the mass resolution in this work to  $\sim m/\Delta m = 200$ .

Positive and negative ion static SIMS spectra of the virgin, KOH-damaged, and bleached hair samples were recorded at ~-140 °C with a 128×128 pixel raster and a field of view of 100×100  $\mu$ m<sup>2</sup>. Positive and negative ion static SIMS spectra and images were recorded from the virgin, virgin conditioned, KOH-damaged, and KOH-damaged conditioned hair samples at ~-140 °C. Raw data containing the secondary ions recorded at each pixel were acquired with a 256×256 pixel raster and a field of view of 100 ×100  $\mu$ m<sup>2</sup>.

#### C. Atomic force microscopy

All AFM experiments were performed with a Digital Instruments Nanoscope IV Multimode instrument (Veeco Instruments Ltd, Cambridge, UK), using an E-scanner and rectangular silicon nitride tips with a nominal spring constant of 0.04 N m<sup>-1</sup> (Olympus Co. Ltd). The instrument was operated in contact mode and at 1 Hz scanning speeds for both imaging and friction measurements. Friction measurements were acquired while scanning square regions of area 4.0  $\mu$ m<sup>2</sup>. Care was taken to locate the scan area at the central region of the cuticles to avoid contributions from the cuticles' edges, and also from the "ghost" edges formed by the removal of the overlaying cuticle due to mechanical damage [Fig. 1(a)].<sup>26</sup>



FIG. 1. (Color online) Schematic illustration showing the orientation of the scan direction and the approximate dimensions of the hair fiber and cuticles.

The fast scanning direction was perpendicular to the fiber axis as well as to the long cantilever axis, as shown in Fig. 1(b), because it was found, in agreement with previous literature,<sup>17</sup> that differences in friction after treatment were significantly more pronounced in the direction perpendicular to the fiber axis. To reduce the possibility of contamination the fibers were immobilized by embedding them in indium.<sup>27</sup> The use of indium eliminates the possibility of a tape-adhesive material migrating onto the fibers during the measurements. The fibers were gently pressed onto the indium substrate using a clean aluminum foil. Experiments took place under two different environments.

Measurements in dry nitrogen (relative humidity  $4 \pm 2\%$ ) were made using an enclosure constructed from Perspex [poly(methyl methacrylate) sheeting], sealed to prevent ingress of air and fitted with an inlet for nitrogen. The humidity was reduced simply by replacing the air with dry nitrogen. Measurements were recorded 1 h after the desirable relative humidity had been reached. Measurements were also made in double de-ionized water using a liquid cell fitted with an elastomeric O-ring. The cell was filled with water and the fibers were left for 30 min before measurements were acquired to ensure swelling of the fibers had finished.<sup>9,11</sup> In both cases the temperature was  $24 \pm 2$  °C.

Friction forces were determined from trace-retrace loops acquired along single lines. To minimize the topographical contribution to the frictional signal the mean signals in opposing directions were subtracted and, subsequently, halved.<sup>28,29</sup> The load range examined was 0–11 nN, using load increments of 1.6 nN. To obtain statistically significant results, five fibers were typically used from each category and seven to ten cuticles were examined on each fiber.

Calibration of normal forces was carried out in a two-step procedure. First, the normal spring constant of the cantilever was obtained from the power spectral density of its thermal fluctuations in the resonant frequency domain, at room temperature, according to the method introduced by Hutter and Bechhoefer.<sup>30</sup> This was achieved with the use of a routine implemented contained within the Digital Instruments PICO-FORCE software. Second, the normal photodetector sensitivity (nm V<sup>-1</sup>) was acquired by displacing a mica sheet verti-



FIG. 2. Normalized negative ion spectra. Relative Intensity vs m/z: (a) virgin, (b) KOH-damaged, and (c) bleached hair. Peaks denoted (1)–(4) correspond to 18-MEA and stearic, palmitic, and myristic acids, respectively.

cally against the tip.<sup>5</sup> Because of the much greater stiffness of mica in comparison to that of the silicon nitride cantilever, the *z*-piezodisplacement is assumed equal to the normal cantilever deflection when operating in the repulsive regime. So, the inverse gradient of the linear part of the force curve in that regime was identified as the photodetector sensitivity.

Coefficients of friction ( $\mu$ ) were obtained from plots of the friction versus the load. The lateral spring constant of the cantilever was not known. In order to enable comparison between the results, the value of  $\mu$  for a virgin hair was used as a reference standard, and the data normalized to this reference. Every time the lateral photodetector sensitivity ( $S_L$ ) and/or the lateral spring constant ( $K_L$ ) changed; e.g., due to probe change, laser realignment, reseating, photodetector adjustment, etc., the friction coefficient of virgin hair was redetermined and used for normalization of the data obtained while  $K_L$  and  $S_L$  were still the same.

#### **III. RESULTS AND DISCUSSION**

#### A. Secondary ion mass spectroscopy

Figure 2 shows negative ion SIMS spectra of virgin, KOH-damaged, and bleached fibers. A strong peak was observed at -341 m/z in the spectra of virgin hair [denoted as peak (1) in Fig. 2], attributed to the C<sub>20</sub>H<sub>41</sub>COS<sup>-</sup> ion, coming from the 18-MEA layer, which is linked through a thioester bond to the protein matrix.<sup>31,32</sup> This ion was also observed in

the spectra of the damaged fibers. For the virgin fibers, the -341 m/z (MEA) ion intensity was two orders of magnitude stronger than was the case for KOH-damaged and bleached hair. Peaks 2 and 4 in Fig. 2, at -227 and -283 m/z, were attributed to the myristic (C13H27COO-) and stearic  $(C_{17}H_{35}COO^{-})$  ions, respectively, while peak 4 at -255 m/zwas attributed to the palmitic ion  $(C_{15}H_{31}COO^{-})$ .<sup>31,33</sup> Peaks corresponding to the unbound fatty acids, myristic, palmitic, and stearic, were also present in the spectra of samples exposed to methanolic KOH for 30 min, but with a relative intensity that was two orders of magnitude smaller. For bleached hair, however, it appeared that more of the unbound fatty acids were present, and especially, palmitic ( -255 m/z, the signal for which was only reduced by a factor of 10 after bleaching. These unbound acids were probably dislodged by the chemical treatment. For 18-MEA 30 min bleaching appeared to remove as much of the material as 30 min in methanolic KOH; however, none of the treatments removed 18-MEA completely from the fiber surface.

The distribution of conditioner molecules at the surface was also examined by SIMS. The conditioner was silicone based, although the exact formulation was not known. The secondary ion spectra of the virgin and KOH-damaged hair were recorded at -140 °C, before and after conditioning. The overlaid positive spectra are shown in Fig. 3. The peaks at +73 and +147 m/z are characteristic of silicone-based attributed materials and are to  $Si(CH_3)^+_3$ and  $(CH_3)_3SiOSi(CH_3)_2^+$ , respectively.<sup>31</sup> The magnitude of the normalized intensities of both of those peaks was greater for the KOH-damaged hair. This is in agreement with Chen and Bhushan,<sup>34</sup> who reported that damaged hair exhibits a greater affinity for conditioner. SIMS imaging of those two peaks can provide an indication of the conditioner distribution on the fibers. As shown in Figs. 4(c) and 4(d), SIMS images showed that the conditioner was present on the whole cuticular surface, for both virgin and KOH-damaged fibers. The dark features (~1-2  $\mu$ m in diameter) in Figs. 4(b) and 4(d) were only observed in the damaged-conditioned hair by SIMS, while with AFM (discussed below) no such features were observed in any category of hair. Because these features exhibit dark contrast, they must be composed of a material that does not contain silicone. The fact that they were not observed by AFM suggests that they have similar mechanical properties to the conditioner. They could thus be due to the spreading of oil droplets or similar material that is not composed of silicones.

#### B. AFM topographical imaging

Figure 5 shows AFM topographical images of hair fibers that have been subjected to a variety of treatments. The data were acquired at different magnifications in de-ionized water. Typical characteristics of the human hair surface such as cuticle edges, ghost edges, and striations were observed.

Figure 5(a) shows an AFM topographical image of the cuticular surface of a virgin hair fiber. The cuticles exhibited a step height of  $350 \pm 100$  nm, which was some 50% larger than the value measured under dry conditions.<sup>9,11</sup> Some sur-



FIG. 3. Normalized positive ion spectra. Relative intensity vs +m/z: (a) KOH-damaged conditioned, (b) KOH-damaged, (c) virgin conditioned, and (d) virgin hair. Peaks 1 (m/z 73) and 2 (m/z 147) are characteristic of silicone-based materials.

face detritus was present on some of the cuticles, which was thought to be due either to incomplete removal of the surface detritus by the sonication procedure in the solution of sodium dodecyl sulfate, or to the presence of residual sodium dodecyl sulfate. The features were too small to obtain a compositional analysis by SIMS. Longitudinal ridges (striations) on the cuticular surface that have been previously reported with lateral repeat spacings of  $\sim$ 350 nm were also observed on all the categories examined and also remained present in deionized water [Figs. 5(b)-5(g)].<sup>26,35</sup> These striations are a typical characteristic of the cuticular surface that has not undergone serious mechanical damage. The step discontinuities between the cuticle edges, referred to as "ghost edges" in Figs. 5(b) and 5(d), were identified by Swift and Smith<sup>26</sup> as marking the original locations of the overlying cuticles before they were partly removed. To avoid topographical contributions from the ghost and cuticles edges in the frictional measurements, 4  $\mu m^2$  areas such as that shown in Fig. 5(c) were located to perform the quantitative measurements.

In the case of KOH-damaged and bleached fibers, surface debris on the cuticular surface was observed more often than in the case of virgin hair. This may be due to remaining fatty acids after the chemical treatments. Although it has been



FIG. 4. (Color online) SIMS images of hair. [(a) and (b)] Total ion images. (a) Virgin conditioned hair; (b) KOH-damaged conditioned hair. [(c) and (d)] Selective ion images formed by adding images of the distribution of the peaks at +73 and +147 m/z. (c) Virgin conditioned hair; (d) KOH-damaged conditioned hair.

reported that the conditioner can be detected by FFM near the cuticular edges,<sup>36</sup> in de-ionized water, where the capillary forces are absent, the conditioner was not observed anywhere. As reported in previous studies, apart from the swelling of the fibers and the increase in the cuticle step height, no great topographical differences were observed on the central cuticular surfaces where the frictional measurements took place either after the treatments performed (30 min in methanolic KOH, bleaching, and conditioning), or after aqueous exposure, that could account for the differences in the friction coefficient.<sup>11,32,37,38</sup> For samples of both types, the rms roughness was determined to be  $7.8 \pm 3$  nm over a  $2 \times 2 \ \mu m^2$  scan region.

# C. Quantitative friction force microscopy of human hair

#### 1. Measurements in a dry atmosphere

Although the hair fibers exhibited a pronounced curvature, and the cantilever fast axis was oriented parallel to the fiber axis, friction loops exhibited no curvature (Fig. 6). Subtraction of forward and reverse-direction lateral force traces yields a trace-minus-retrace (TMR) signal that is equal to twice the friction force.<sup>28</sup> Figure 6 shows the values of TMR/2 obtained by subtracting the lateral deflection traces shown. Not only does the TMR/2 trace not exhibit curvature,



FIG. 5. (Color online) AFM topographical images in de-ionized water of (a and b) virgin, (c) KOH-damaged, and (d) bleached hair. High magnification images: (e) virgin, (f) KOH-damaged, and (g) bleached. The region highlighted with a square in image (c) is representative of the areas used for the frictional measurements.

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FIG. 6. (a) Friction loop data for a typical hair specimen. Top: trace signal. Center: retrace signal. Bottom: TMR/2=half the difference between the trace and retrace signals, proportional to the friction force. (b) Corresponding topographical trace.

but it may also been seen that perturbations in the two lateral force traces attributable to topographical features are also removed.

Figure 7 shows characteristic graphs of the frictional response as a function of the load increments applied for different hair specimens. It is clear from Fig. 7 that the relationship between the lateral photodetector response (proportional to the friction force) and the load was linear for all the categories of hair examined, and the relative friction coefficient could thus be derived for each specimen and used as a characterization tool. For three of the specimens, the gradient of the friction-load plot passes through the origin. For two of them, the bleached and KOH-damaged samples, the slope



FIG. 7. Lateral photodetector response TMR/2 ([trace-retrace)/2], proportional to the friction force) vs normal load applied graphs for the categories of hair examined in dry atmosphere (relative humidity  $4\pm 2$ ). Each data series is the average from ten cuticles of the same fiber.



FIG. 8. (Color online) Relative coefficients of friction for the different categories of hair examined in a dry atmosphere. The data are normalized with respect to the friction coefficient of virgin hair. The plot is the outcome of approximately 40 cuticles characterized out of 5 fibers of each category of hair.

fitted to the friction-load data crosses the vertical axis just above the origin. This suggests that there is a small adhesive interaction for these fibers that is absent for the others. The relative friction coefficients  $\mu$  of the different categories of hair as obtained in a dry atmosphere are shown in Fig. 8, normalized to the value obtained for virgin hair. The value of  $\mu$  obtained for virgin, conditioned hair was similar to that obtained for virgin hair (allowing for experimental uncertainty). A very large increase was observed in the value of  $\mu$ for the KOH-damaged hair—to almost three times the value obtained for the virgin fiber. This was reduced, by a factor of approximately  $\frac{1}{2}$ , for conditioned hair, although the coefficient of friction still remained higher than that measured for the virgin fiber. For bleached hair, the value of  $\mu$  was approximately twice that for the virgin fiber.

In previous studies it was suggested that the increase in friction coefficient of chemically damaged hair could be partly due to the higher capillary forces being measured for the more hydrophilic damaged fibers, which cause an increase in the effective load and a resultant increase in friction.<sup>16</sup> However, it appears that also at very low humidity (R.H.=4±2%), where the capillary forces are expected to be significantly weaker, there is a pronounced difference in the values of  $\mu$ . For KOH-damaged hair the value of  $\mu$  is nearly three times greater than that for virgin hair. Increased roughness has been also suggested as another factor responsible for an increase in  $\mu$  in previous studies.<sup>18</sup> However, in the present study, the cuticular surfaces examined were quite similar in terms of topography between all categories of hair

used. Any changes must thus be due to alteration of the chemical composition and/or the mechanical properties at the cuticle surface.

The simplest explanation for the increase in the coefficient of friction during hair damage by both KOH and bleach is the partial removal of the outer layer of 18-MEA, which acts as a boundary lubricant at the hair surface. A substantial reduction in the amount of lubricant would be expected to increase the coefficient of friction, in agreement with the data in Fig. 8. Complete removal is likely after extreme treatments,<sup>24,39</sup> but under the conditions used here, both the FFM and the SIMS data suggest that some 18-MEA, at least, remains at the surface. First, the SIMS data in Fig. 2 show that signals diagnostic of 18-MEA are still detected for the KOH-damaged fibers albeit at much reduced intensity, suggesting it was not removed completely.<sup>38,40</sup> Second, the standard deviation in  $\mu$  was markedly greater for KOH-damaged and bleached hair. The surface properties of damaged hair were quite inhomogeneous in comparison to virgin hair, probably due to the uneven effect of the treatments on the different fibers used and maybe due to damage present prior to the deliberate chemical treatment. The best explanation for this is that while extensive removal of 18-MEA occurs, small amounts are left behind, yielding a patchy, submonolayer surface coverage and causing spatial inhomogeneities in the friction measurements.<sup>32</sup>

The presence at the surface of patches of 18-MEA, separated by bare regions, could account for the instabilities observed in the subtracted frictional signal (e.g.,  $100 \pm 40$  mV for a load of  $\sim 5$  nN) both in a dry atmosphere and water, as the cantilever twisting would considerably decrease during the passage of the tip above the areas of remaining 18-MEA. Such nonuniformity in the friction of the cuticles has been also reported by Sadaie et al.<sup>17</sup> and Dupres et al.<sup>32</sup> In the latter study it was attributed to selective elimination of the outer fatty acid layer by KOH and the subsequent presence of areas with increased density of dimensionally molecular holes of exposed protein matrix. In the light of the SIMS data in combination with those from FFM, it is concluded that removal of 18-MEA from the cuticular surface is not complete after 30 min of methanolic KOH treatment and that the cuticular surface is chemically nonuniform, possessing areas with different coverages of 18-MEA.

For the bleached hair the variance in  $\mu$  was also large. This greater standard deviation is probably due to a nonuniform distribution of the unbound fatty acids at the fiber surface. SIMS spectra showed that bleached hair had the same amount of, or less, 18-MEA at its surface, but much more unbound fatty acids, especially palmitic acid. It thus seems that the lubricating effect of the unbound fatty acids may also explain the observations. This could also explain the lower value of  $\mu$  for bleached hair in comparison to hair that was solvent extracted, i.e., had the unbound fatty acids removed, as reported by McMullen and Kelty.<sup>13</sup> Additionally, similar instabilities as in the case of KOH-damaged hair were observed in the subtracted frictional signal leading to the assumption that generally after both kinds of chemical damage



FIG. 9. Lateral photodetector response TMR/2 ([trace-retrace)/2], proportional to the friction force) vs normal load for hair in de-ionized water. Each data series is the average from ten cuticles of the same fiber. (1) Linear fit on the KOH-damaged conditioned data from 0 to 4 nN load, (2) linear fit on the KOH-damaged conditioned data from 5.4 to 10.8 nN load, and (3) linear fit on the KOH-damaged hair data from 0 to 10.8 nN load.

applied in this study the chemical composition of the central cuticular surface is not uniform, and consists of unevenly distributed regions of enhanced frictional interaction adjacent to others with smaller coefficients of friction. It is suggested that those treatments did not affect all fibers equally, nor all the cuticles of each fiber, leaving areas with different densities of 18-MEA and other unbound fatty acids covering the underlying proteinaceous layer.

#### 2. Measurements in de-ionized water

Figure 9 shows characteristic friction-load graphs of hair in de-ionized water. The relative friction coefficients obtained from these graphs are shown in Fig. 10. The frictionload relationships are linear for all of the samples, except the KOH damaged-conditioned one, where the data were fitted with two straight lines (slopes 1 and 2, Fig. 9). Below a load of about 5 nN the frictional response is quite similar to the virgin conditioned hair with the relative friction coefficient derived from slope 1 being  $1.3 \pm 0.1$ , compared to  $1.1 \pm 0.1$ for the virgin conditioned hair. Above 5 nN, the relative friction coefficient of the KOH-damaged conditioned hair (slope 2) is  $3.8 \pm 0.2$ , that is, equal to that of the KOH-damaged hair (slope 3). This suggests that at a load of  $\sim 5$  nN most, if not all, of the conditioner is removed from the hair surface, and the frictional coefficient of the surface is subsequently equal to that of the KOH-damaged hair from there on because the tip-sample interaction is influenced predominantly by the properties of the underlying damaged fiber surface.

For the rest of the samples the friction-load dependence remains linear for the whole range of loads examined. The trend in the coefficients of friction was essentially the same as that observed in air, but in both cases of damaged hair, KOH-damaged and bleached, the difference in the value of  $\mu$ from that measured for the virgin fibers was greater in water (Fig. 10). Again, for both of the damaged hair samples, there was significant heterogeneity in the samples, yielding large





FIG. 10. (Color online) Relative coefficients of friction for the different categories of hair examined in de-ionized water. The data are normalized with respect to the friction coefficient of virgin hair. The plot is the outcome of approximately 40 cuticles characterized out of 5 fibers of each category of hair.

FIG. 11. (Color online) Relative coefficients of friction for virgin and KOHdamaged hair examined in dry atmosphere and subsequently in de-ionized water. The data are normalized with respect to the friction coefficient of virgin hair in dry atmosphere.

errors. These data clearly show the importance of the cuticular surface chemistry and of the presence of a layer of fatty acids in the nanotribological properties of hair, since there are no capillary forces present under such conditions.

To better aid comparison of the behavior in air and in water, Fig. 11 shows coefficients of friction for virgin and KOH-damaged hair normalized to the virgin fiber in dry air. For both specimens, the coefficient of friction measured in water is substantially ( $\sim$ 50%) larger.

Hair fibers swell on exposure to water. The fibers were immersed in water for 30 min before the measurements were made so that swelling had ceased.<sup>9,11</sup> The consequent penetration of water molecules inside the fibers weakens the network of cross-links and the existing salt (ionic) bonds.<sup>37,38</sup> Consequently, when the tip contacts the surface under loading, the amount of plowing is increased, because the tip is able to penetrate further into the bulk of the fiber, leading to an increase in the rate of energy dissipation and hence an increase in the coefficient of friction. The chemically damaged fibers (KOH-damaged and bleached), being hydrophilic, absorb still more water<sup>21</sup> and, consequently, the tendency toward plowing in the sliding tip-sample contact is increased still further. Damaged fibers will likely exhibit smaller shear strengths under any circumstances, due to the penetration of the chemically damaging agents and the resulting weakening of the network of cross-links, through oxidation of the disulfide bonds and cleavage of the peptide ones.<sup>34,41,42</sup> Given that greater surface deformation under a certain load results in greater real area of contact with the tip, thus, in greater friction and, eventually, higher  $\mu$ , it is likely that a combination of these effects causes the higher frictional coefficients of chemically damaged fibers,<sup>21</sup> with water serving only to exacerbate the situation.

There is some evidence in literature indicating that the chemistry of the hair surface may also be altered in aqueous environments, providing an additional explanation for the increase in the coefficient of friction in water. A decrease in their adhesive properties has been reported after aqueous exposure for both virgin and chemically damaged hair.<sup>21,37,38</sup> This has been attributed to reorientation of the surface polar groups.<sup>38,40,43</sup> Apart from the mediation of water and the absence of capillary forces, the expected overall surface charge of both the silicon nitride tip and the hair surface is negative in de-ionized water and this might be expected to cause electrostatic repulsions that would further decrease the strength of adhesion between the tip and the surface.<sup>41,44</sup> However, all of these factors would, if anything, be expected to cause a decrease in the coefficient of friction, and thus cannot explain the changes observed here.

Maxwell and Huson<sup>40</sup> reported a different kind of modification to the surface composition. They found the mean adhesive force in water between a silicon nitride tip and a wool fiber similar to that with a polyamide (nylon) substrate and very different from that between the silicon nitride tip and a polyethylene substrate, while at low relative humidity the adhesion of the wool fiber was nearly the same as that of polyethylene. It was suggested that as more and more proteolipids reorient themselves in the aqueous environment, more and more polar protein groups are exposed and the interaction with the lubricant lipid layer is reduced. Considering also that all categories examined in this study were found to still possess lipids on their surface such reorientation of the surface groups should increase the friction coefficient of all categories, as indeed, is the case. The difference in the friction coefficient between KOH-damaged and virgin hair was found in the present work to be even greater in water, which implies that for the virgin hair the tip is still mainly interacting with the lubricant lipid layer. This could suggest that such reorientation, if indeed it takes place, is limited in the case of virgin fibers, possibly due to the molecular packing of 18-MEA and its covalent bond with the protein matrix, which do not offer the available space and mobility for total transition of the mainly hydrocarbon surface into proteinaceous, at least in the timescale examined (up to 60 min). A total transition should result in very similar friction coefficient between virgin and chemically damaged hair. However, the large difference observed here would suggest that if surface reorientation occurs, then it is substantial in the case of the damaged hair but much reduced in the case of the virgin hair.

Based on the data presented here it is likely that water penetration occurs for all hair categories, because all yield increased coefficients of friction in water, but that reorientation of surface lipids possibly makes an additional contribution in the case of the damaged fibers.

### **IV. CONCLUSION**

The tribological properties of virgin, KOH-damaged, bleached, virgin conditioned, and KOH-damaged conditioned hair were examined in dry atmosphere and de-ionized water using FFM. No topographical differences were observed on the central cuticular surface either due to the treatments imposed or due to aqueous exposure up to 60 min. The virgin fibers could be clearly distinguished in terms of friction coefficient from the chemically damaged and KOHdamaged conditioned ones in both environments. This was ascribed to the presence of a lubricant layer of 18-MEA. All categories exhibited higher friction coefficients in the aqueous environment, while the difference in  $\mu$  between the virgin and both categories of chemically damaged hair was enhanced in water. Those differences were partially attributed to the likely effect of water exposure on the mechanical properties of the various categories of hair (through water absorption leading to an increased extent of sample deformation during scanning) and also to the possible reorientation of the lipid layer at the surface of damaged samples under water, causing a reduction in the lubricating effect associated with the intact lipid film (18-MEA).

SIMS was also employed in order to examine the presence of fatty acids on the surface of hair. Bleaching and immersion in methanolic KOH were found to cause similar amounts of 18-MEA removal. However, neither bleaching nor methanolic KOH sufficed to totally remove 18-MEA from the cuticular surface. Bleached fibers were found to possess much more unbound fatty acids, especially palmitic, on their surface than KOH-damaged hair. In addition, detection and imaging of conditioner species by SIMS led to the assumption of the conditioner presence on the whole cuticular surface. The combination of SIMS with FFM data suggests that the main reason for the different tribological properties of the categories of hair examined is the altered chemistry of the surface, leaving a secondary role to factors such as roughness and capillary forces.

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