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Differential wetting characterization of hair fibers

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Synopsis

Surface wetting is one of the key properties of human hair used to indicate the extent of chemical/mechanical damage and the outcome of conditioning treatment. Characterization of hair wetting property is a challenging task due to the non-homogeneous nature of hair fibers and the requirement for sensitive equipment. Motivated by these considerations, we developed a new methodology, termed a differential wetting characterization (DWC), which would allow rapid and reliable characterization of the wetting property of hair fibers. This method is based on observation of a number of droplets suspended on a pair of parallel fibers stretched in a horizontal plane. The wetting behavior of the fibers can be deduced from the shape assumed by the droplets. When the wetting properties of the two hair fibers are identical, the droplets suspended between the fibers assume a symmetric configuration. In contrast, on the fibers with dissimilar wetting characteristics, the droplets will assume a skewed configuration towards a more hydrophilic fiber. This makes it possible to differentiate the hydrophobicities of the tested fibers. In this paper it is demonstrated that the proposed DWC method is capable of differentiating the changes in wetting property of hair surfaces in response to either chemical or physical treatment. Results of the paper indicate that the DWC method is applicable for broad wetting differentiation of various fibers.

INTRODUCTION

The surface of undamaged, so-called virgin, hair is naturally hydrophobic due to the existence of 18-methyl-eicosanoic acid in the outmost layer of epicuticle (1). This acid is covalently bound via a thioester linkage to the cell membrane complex (2) and can be removed as a result of weathering and chemical treatment. Typically, the loss of 18-methyl-eicosanoic acid is accompanied by noticeable coarsening of hair to the touch and an increase in combing forces in both wet and dry states. Cosmetic treatments aim to alleviate the negative effect of hair damage. For instance, treatment of damaged hair with silicones and quaternary surfactants can restore both the manageability and hydrophobicity of human hair. Improvement of the hair wetting property has been the concern of cosmetic chemists. Consequently, a number of techniques have been practiced in determining the wetting properties of human hair fibers (3–10).

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Historically, Kamath *et al.* (3) were the first to adopt Wilhelmy's balance principle to characterize the wetting property of single human hair fibers. By assuming the perfect elliptical cross section of the hair fibers, the circumference of the hair fibers was calculated from the lengths of the major and minor axes measured by means of optical microscopy. In the study, the contact angle of the hair fibers in water was determined using the wetting force and the estimated circumference. More recently, Molina *et al.* (4) and Lodge and Bhushan (5) reported the contact angle measurements on human hair fibers using Wilhelmy's balance approach as well, but with the notable exception of estimating the hair fiber circumference based on the fiber wetting force measured in low-energy hydrocarbon fluids where complete wetting was assumed. These studies indicated lower contact angles on damaged vs undamaged hair, as expected. In addition, Lodge and Bhushan (5) measured an increase in contact angle on damaged hair treated with a conditioner.

Contact angle can also be measured by a direct observation. Though it is a relatively simple process when a liquid droplet is sitting on flat surface, the high curvature assumed by fibers requires specialized equipment, such as that described by Jones and Porter (6). The technique mentioned therein was based on passing a fiber horizontally through a stationary eyelet containing a droplet of water. The fiber produces an advancing or receding contact angle that can be directly measured using a low-magnification optical microscope.

Another method of determining the contact angle on microfibers is based on observing the barrel-shaped droplets as they envelop the surface of fibers. In this case, the barrel dimensions, i.e., the diameter and length, accurately define the contact angle as a function of the wetting length and fiber diameter (7–10). This method has been utilized to determine the contact angles of cholesterol-containing squalane on hair fibers, in which the measurement was conducted in water (10). Furthermore, Carroll (10) reported a decrease in contact angle with increasing cholesterol concentration, an outcome attributed to the decreasing water/squalane interfacial tension with increasing cholesterol concentration. So far, the above methods have provided practicable measurements of contact angles on hair fibers; however, the measurements usually are time-consuming and rely on single-point measurements.

In this paper we provide a novel method to determine the wetting property of human hair fibers. This method is based on the observation that a droplet suspended between two stretched parallel fibers of dissimilar wetting characteristics will invariably assume a skewed configuration towards the fiber of larger hydrophilicity. This paper demonstrates that such an observation can be utilized to develop an efficient and reliable technique for fiber wetting characterization, referred herein as fiber differential wetting characterization (DWC). We provide detailed validation based on direct experimental observation of droplet configuration as a function of fiber wetting properties and numerical simulations. Although developed and validated for characterization of human hair fibers, the proposed DWC method can be considered as a universal technique equally applicable for rapid characterization of the wetting property variation of other microfibers.

EXPERIMENTAL

In this study, hair characterization was carried out using a 12-inch-long Caucasian brown virgin hair tress and a Caucasian brown hair tress bleached for one hour. All the hair samples were supplied by International Hair Importers (Valhalla, NY). One sample of brown virgin hair stripped of 18-methyl-eicosanoic acid was produced by soaking the hair tress in a 0.1 M KOH/methanol solution for 30 minutes as described by Swift and Smith (11). Hereafter, we designate the hair with 18-methyl-eicosanoic acid removed as "stripped." All the hair tresses were cleaned by rinsing with methylene chloride followed by methanol and deionized (DI) water, as described by Molina *et al.* (4). The one-hour-bleached hair tress was treated with a commercial rinse-off conditioner (double application of 0.5 gram of conditioner to three grams of hair, followed by 30 seconds of hair massaging and an extensive rinse with 40°C tap water for approximately two minutes and DI water for one minute). All hair characterization was carried out at approximately the middle of 12-inch-long hair fibers.

The advancing contact angles were measured using a Cahn DCA-315 tensiometer. The fibers were first submerged into iso-octane and, assuming complete wetting, the fiber circumference was determined based on the measured force. The contact angles in water were then calculated using the force and the estimated fiber circumference. During the measurement, the fibers were submerged to a depth of 2 mm with a rate of 20 μm/s.

The wetting properties of the hair fibers were determined by mounting the hair fibers on an in-house built stage (see Figure 1) that carried a pair of parallel hair fibers in a horizontal plane with a separation of ~0.75 mm. Water droplets of the volume of 0.2~0.4 μl were then applied onto the stretched fiber pair by using a microsyringe with a 33-gauge needle. Droplets (10~15) were placed along the fiber pair with a length ~6 cm as shown in Figure 1. The droplets were observed by an Olympus BX 40 microscope under 20× magnification, and the images were taken using a Nikon 4500 digital camera.

RESULTS AND DISCUSSION

CONTACT ANGLE BY WILHELMY'S METHOD

The contact angles on the virgin, stripped, bleached, and bleached/treated fibers were measured using Wilhelmy's method. The determination was carried out at the middle of

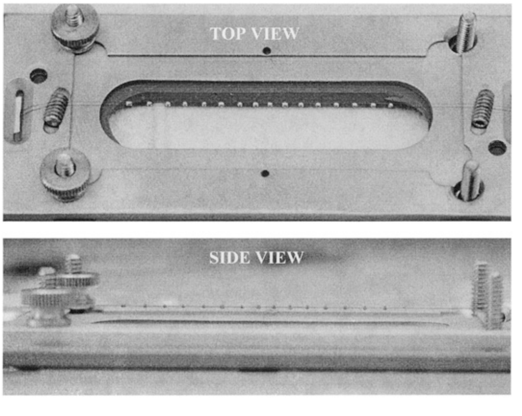

Figure 1. Experimental assembly used for differential wetting characterization (DWC). The upper image is the top view of the droplet placement between hair fibers. The lower image is the side view of the assembly to show the droplets suspended between parallel hair fibers.

three randomly selected hair fibers. The fibers were first prepared on an aluminum foil and neutralized with a Milty Zerostat* anti-static gun to eliminate the possible electrostatic effect that may be induced in the processes of packaging and handling. The circumference of each fiber was determined by dipping the fiber into iso-octane. Following this determination, the fiber segments exposed to the iso-octane were trimmed and then submerged in DI water. By assuming that the circumference of hair fibers does not vary appreciably over a short fiber length, the contact angle can be calculated such that (1):

$$\cos(\theta) = \frac{F}{\gamma L} \tag{1}$$

where F is the measured force, γ is the surface tension of water, and L is the fiber circumference.

As expected, removal of 18-methyl-eicosanoic acid by methanolic KOH solution resulted in a decrease in the contact angle from 88° ± 2° of the virgin hair down to 83° ± 2° (the stripped hair). The bleached hair fibers exhibited a lower contact angle of 78° ± 1°. Conditioner treatment of the bleached hair fibers yielded an increase in the contact angle to 83.5° ± 0.2°.

DIFFERENTIAL WETTING CHARACTERIZATION

The differential wetting property was characterized by placing DI water droplets between two parallel hair fibers stretched in a horizontal plane on the test stage as shown in Figure 1, where the fiber separation was ~0.75 mm and the volume of water droplets was 0.2 ~0.4 μl. It was found that the majority of the droplets assumed a symmetrical configuration against the horizontal plane, which transected the fibers. In contrast, the droplets with relatively large volume sagged below the hair fibers. Occasionally, for example, in the case of the hair fibers with large contact angles, droplets were found to "sit" on the top of fibers, as shown in cell A6 in Figure 2.

The droplet configurations shown in Figure 2 are three sets of parallel fibers made up of (A) virgin vs virgin, (B) virgin vs stripped, and (C) virgin vs bleached fibers. Note that the "reference" fibers, i.e., the fibers in reference to which the hydrophobicities are determined, appear as bottom fibers in all images. In addition, both the reference and the test fibers were randomly extracted from the corresponding hair tresses, and therefore it is reasonably assumed that the fibers carried the average wetting property. Images shown in column A of Figure 2 show the droplet configurations between two virgin hair fibers. In this case, the droplets assumed nearly symmetrical configurations. This indicates, as expected, nearly identical wetting properties of the two fibers. The "unusual" appearance of the droplet as shown in image A6 of Figure 2, as noted, is due to the droplet resting on the top of the parallel fibers—a phenomenon occasionally observed with larger droplets on fibers with higher contact angles. Columns B and C of Figure 2 show the droplet configurations being progressively skewed. This indicates the sequence of decreasing hydrophobicity, in which the virgin hair fibers exhibited the highest extent of hydrophobicity, followed by the stripped (i.e., 18-methyl-eicosanoic acid removed) and bleached hair fibers, in full agreement with contact angle measurements.

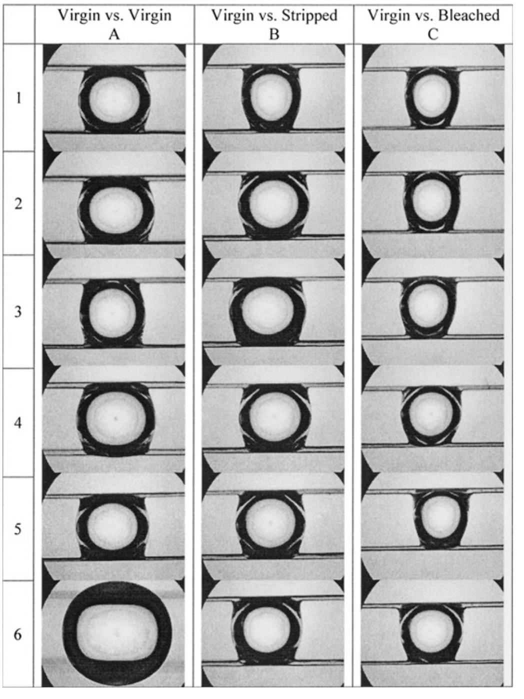

Figure 2. Variation of droplet configuration with extent of hair damage (I). Column A: virgin vs virgin fibers. Column B: virgin vs stripped fibers. Column C: virgin vs bleached fibers. Note that the reference fiber (virgin in this case) appears at the bottom of each image.

To validate the trend shown in Figure 2, we further considered the wetting behavior of another combination of hair fibers, in which stripped hair fibers were used as the reference fibers. Images of droplets wetting between stripped vs stripped fibers (set A) and stripped vs bleached fibers (set B) appear in Figure 3. Images in Figure 3 confirm the conclusion drawn from the droplet configuration observed in Figure 2 that stripped hair fibers are more hydrophobic than bleached hair fibers. Images in Figure 3 also examine the sensitivity of the proposed DWC method. Thus, it has been demonstrated that the present method is capable of distinguishing not only the virgin hair fibers from the damaged fibers but also fibers with different extents of damage.

Next we demonstrate the use of the DWC method in evaluating the impact of conditioning treatment. Once again, for the purpose of comparison and validation, column A in Figure 4 shows the droplet configuration between two bleached hair fibers; column B shows the droplet configuration between the bleached hair fibers and the bleached hair fibers treated with a conditioner. The droplets in Figure 4, as expected, are nearly symmetric for the bleached vs bleached fibers. However, in the case of the bleached vs the bleached/treated fibers, the droplets are systematically skewed toward the untreated bleached fiber. This implies the larger hydrophobicity of the hair fiber after conditioner treatment.

Finally, we demonstrate that in case of doubt as to the droplet orientation, one could simply allow the water droplets to evaporate while observing the shape evolution of the evaporating droplets. Figure 5 shows the shape evolution of an evaporating droplet

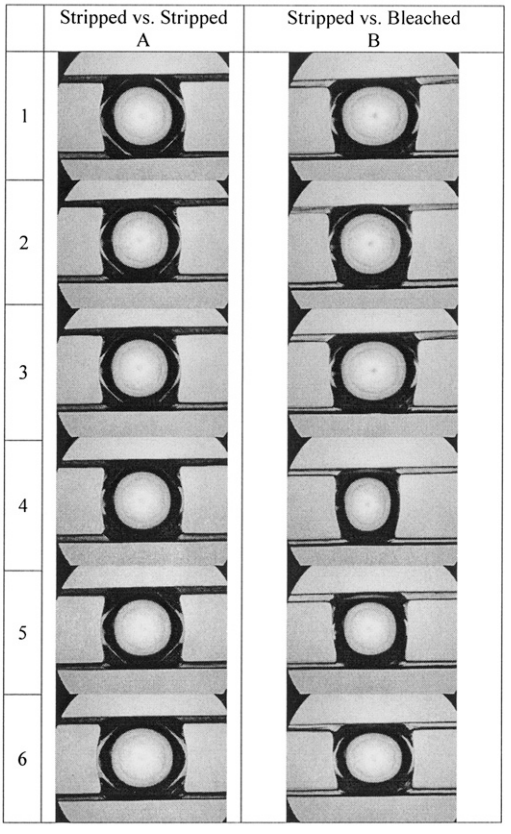

Figure 3. Variation of droplet configuration with extent of hair damage (II). Column A: stripped vs stripped fibers. Column B: stripped vs bleached fibers.

between fibers with different degrees of damage. The extent of skew becomes stronger as the droplet evaporates, with the final image unequivocally illustrating which fiber has a stronger affinity to water.

NUMERICAL VALIDATION OF THE DROPLET CONFIGURATION BY THE SURFACE FINITE ELEMENT METHOD (FEM)

Surface FEM is employed to simulate droplet appearance as a function of droplet volume, fiber separation, and diameter, as well as contact angles. The surface FEM method is based on minimization of the surface potential energy of a droplet-on-fiber system, as detailed elsewhere (8,12). The purpose of the numerical simulations is to confirm that water droplets suspended between fibers with dissimilar contact angles would produce skewed orientation, with the degree of skew proportional to the difference in contact angles. The images based on the numerical simulations are shown in Figure 6. In each set of images, the first illustrates a droplet as viewed from the top, like that in Figures 2–5, while the second and third show the droplets as viewed in the horizontal plane (side view), with the fibers (not shown) located in front of the image.

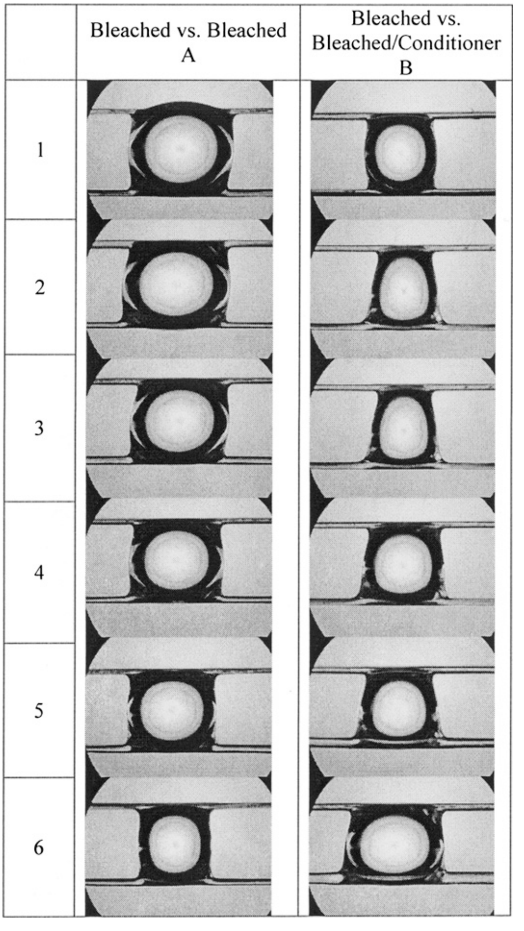

Figure 4. Variation of droplet configuration with hair treatment. Column A: one-hour bleached vs bleached fibers. Column B: bleached vs bleached/treated fibers with conditioner.

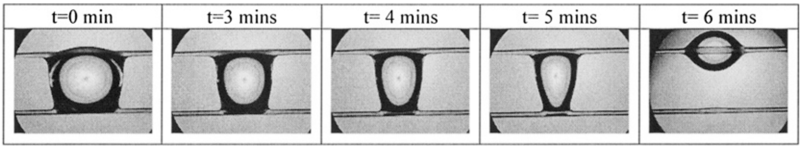

Figure 5. Morphology evolution of an evaporating droplet between two fibers with dissimilar hydrophobicities.

Figure 6 shows the simulated shapes of droplets on fibers with the identical diameter of 75 μm; the fiber separation is fixed at 0.75 mm, and the droplets, with a volume of 0.3 μl, are suspended between the fibers. Variation of the droplet shape is explored with respect to the contact angles: 60° vs 100° (set A) and 80° vs 100° (set B). As expected, the simulations yielded skewed droplet orientation, with the largest extent of skew observed in the case of set A (60° vs 100°).

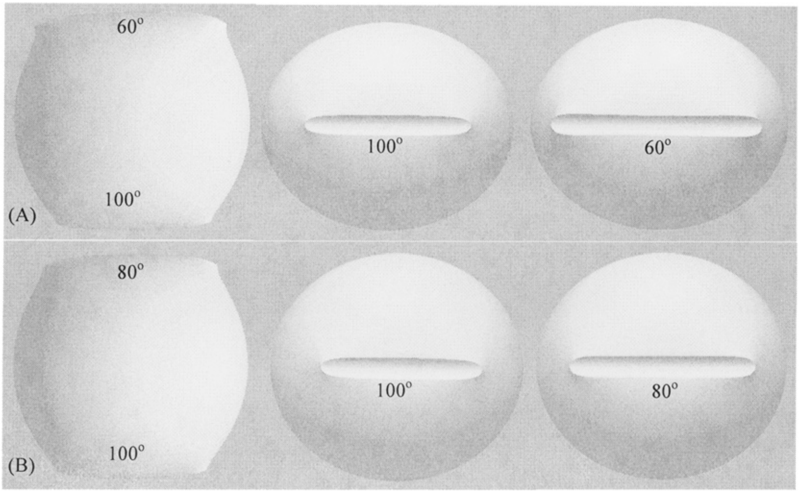

Figure 6. Simulated 0.3-µl droplet shapes between 75-µm fibers at 0.75-mm separation with contact angles of (A) 100° vs 60° and (B) 100° vs 80°.

CONCLUDING REMARKS

The DWC method proposed in this study has provided an efficient and reliable technique for the characterization of the surface wetting property. This method is based on the direct observation of a number of droplets sitting on a fiber pair, thus effectively suppressing the possible experimental errors resulting from single-point determination. The current method has been validated by controlled tests in the present study, in which the hair fibers followed the same hydrophobicity trend as characterized by means of Wilhelmy's method.

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