J. Cosmet. Sci., 61(1): 33-41 (Jan/Feb 2012)

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 of sensitive equipment. Motivated by these considerations, we developed a new methodology, termed as differential wetting characterization (DWC), which would allow simple and reliable characterization of the wetting property of hair fibers. This method is based on observation of a number of droplets suspending on a pair of parallel fibers tauted 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 sitting on the fibers assume a symmetric configuration. In contrast, the droplets will assume a skewed configuration when the wetting characteristics of hair fibers are dissimilar. This makes it possible to differentiate the hydrophobicities of the tested fibers. In this paper, it was demonstrated that the proposed DWC method is capable of differentiating the changes of 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

Surface of undamaged, so-called Virgin hair, is naturally hydrophobic due to existence of 18-methyl-eicosanoic acid in the outmost layer of epicuticle [1]. 18-methyl-eicosanoic 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-methyleicosanoic acid is accompanied with 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].

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 perfect elliptical cross-section of the hair fibers, the circumference of 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, however, with 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 when treated with a conditioner. Furthermore, 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 those described by Jones and Porter [6]. One 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 could 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 envelope 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 [7-9]. This method

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has been utilized to determine the contact angles of cholesterol-containing squalane on hair fibers, in which the measurement was conduced in water [7]. Furthermore, Carroll [10] reported a decrease in contact angle with increasing cholesterol concentration, an outcome attributed to the lowering water/squalane interfacial tension with increasing cholesterol concentration. So far, the above methods have provided practicable measurements of contact angels on hair fibers, however the measurements usually rely on single droplets and therefore are time-consuming and not reliable in some cases.

Therefore, 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 sitting between two tauted parallel fibers of dissimilar wetting characteristics will invariably assume a skewed configuration towards the fiber of larger hydrophilicity. This paper is to demonstrate that such an observation can be utilized to develop an efficient while reliable technique for fiber wetting characterization, referred herein as fiber differential wetting characterization (DWC), and to 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 wetting property variation of other microfibers.

EXPERIMENTAL

In this study, hair characterization was carried out using Caucasian Brown Virgin hair and Caucasian Brown Bleached hair that was bleached to two levels: 1 hour bleached and 2 hour bleached. All the hair samples were supplied by the International Hair Importers (Valhalla, NY, USA). One sample of Brown Virgin hair stripped off 18-methyl-eicosanoic acid was produced by soaking the hair tress in a 0.1 M KOH/methanol solution for 30 mins 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 1 Hour Bleached hair tress was treated with a commercial rinse-off conditioner (double application followed by an extensive rinse with 40°C tap water and DI water).

The advancing contact angles were measured using a Cahn DCA-315 tensiometer. The fibers were first submerged into iso-octane (assuming complete wetting), and 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. Wetting properties of the hair fibers were determined by mounting the hair fibers on an in-house built stage (see Fig. 2) 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 tauted fiber pair by using a micro syringe installed with a 33-gauge needle. Finally, 10~15 droplets were placed along the fiber pair with the length ~6 cm as shown in Fig. 2. The droplets were observed using an Olympus* BX 40 microscope under 20x magnification and the images were taken using a coupled Nikon* 4500 digital camera.

RESULTS AND DISCUSSIONS

CONTACT ANGLE BY WILHELMY’S METHOD

The contact angles on the Virgin, Stripped, Bleached 1 Hour, Bleached 1 Hour Treated and Bleached 2 Hours were measured using Wilhelmy’s method by assuming a rod-like probe instead of the traditional plate configuration. The determination was carried out at the middle of 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, as some of the initial experiments were believed being compromised due to such effect. The circumference of each fiber was determined by dipping the fiber into an iso-octane liquid. Following this determination, the fiber segments exposed to the iso-octane liquid were trimmed and then submerged into 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 [1]:

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

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

Figure 1 shows variation of the advancing contact angle (measured while the hair was submerged) of hair fibers with varying surface treatment. As expected, removal of 18-methyl-eicosanoic acid by methanolic KOH solution resulted in a decrease of the contact angle from 88°±2° of the Virgin hair down to 83°±2° (the Stripped hair). The 1 Hour Bleached hair fibers exhibit a lower contact angle of 78°±1°. Conditioner treatment of the 1 Hour Bleached hair fibers yielded an increase of the contact angle up to 83.5°±0.2°. In contrast, the 2 Hour Bleached hair fibers produced a contact angle of 77°±1°. Interestingly, the 2 Hour Bleached hair fibers had the contact angle close to that measured from the 1 Hour Bleached hair fibers within a negligible experimental deviation. Such a similarity is surprising when considering the larger extent of oxidative damage observed in the 2 Hour Bleached hair fibers, as evidenced by the higher concentration of sulfate groups as characterized by means of FT-IR.

DIFFERENTIAL WETTING CHARACTERIZATION

Differential wetting property was characterized by placing DI water droplets between two parallel hair fibers tauted in a horizontal plane on the test stage as shown in Fig. 2, 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 were to assume 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, e.g. in the case of the hair fibers with large contact angles, droplets were found to 'sit' on the top of fibers as shown in the cell A6 in Fig. 3.

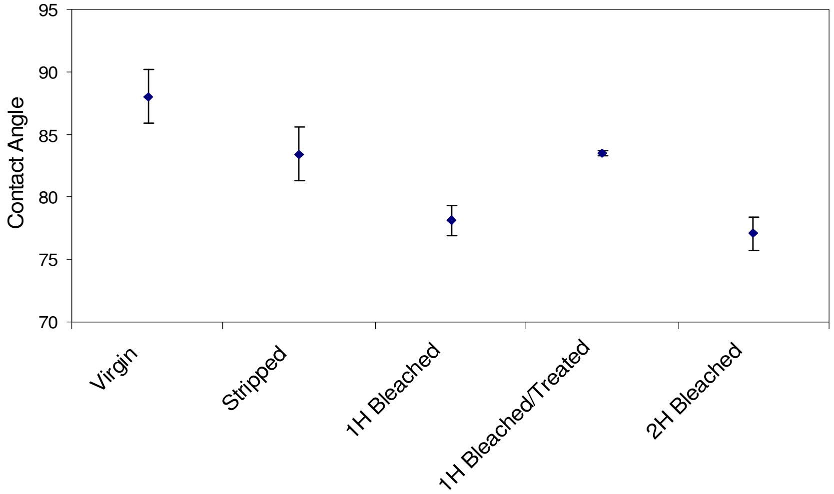


Figure 1. Variation of the DI water contact angle on hair fibers with varying surface treatment

The droplet configurations shown in Fig. 3 are four sets of parallel fibers made up of (A) Virgin vs. Virgin, (B) Virgin vs. Stripped, (C) Virgin vs. 1 Hour Bleached, and (D) Virgin vs. 2 Hour Bleached. Note that the 'reference' fiber was placed underneath in each case. In addition, each tested hair fiber was randomly extracted from the corresponding hair tress and therefore it is reasonably assumed that the tested fiber carried the average wetting property. Images shown in column (A) of Fig. 3 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 Fig. 3, as noted, is due to the droplet resting on the top of the parallel fibers–a phenomenon occasionally observed due to larger droplets wetting on fiber pairs at high contact angles. Furthermore, columns B, C and D of Fig. 3 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 removed), the 1 Hour Bleached and finally the 2 Hour Bleached hair fibers.

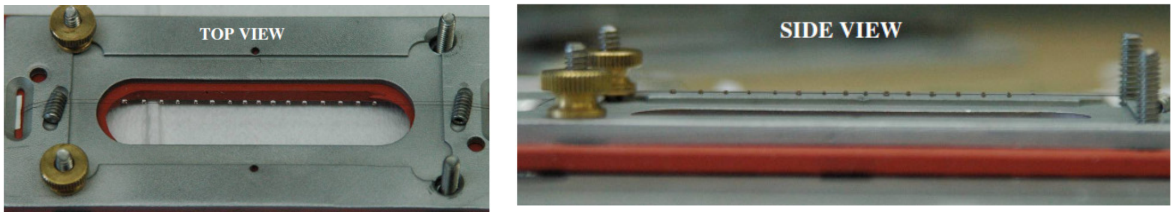


Figure 2. Experimental assembly used for differential wetting characterization (DWC). The upper image is the top view of the droplet placement between hair fibers. The lower image is the side view of the assembly to show the droplets suspended between tauted parallel hair fibers.

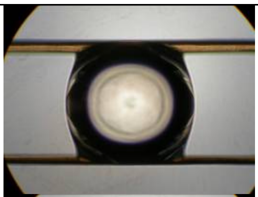
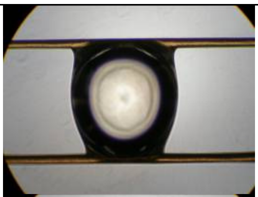
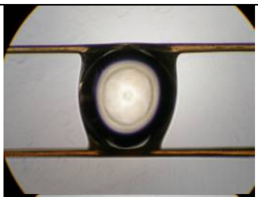
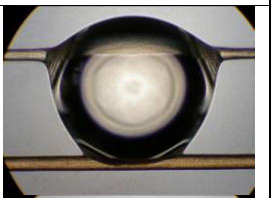
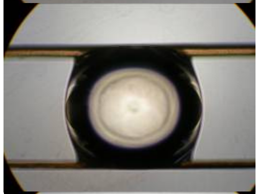
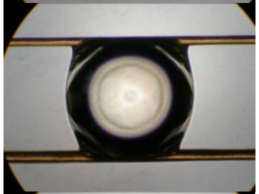
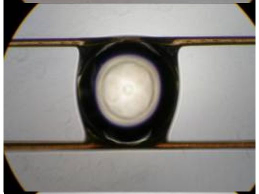
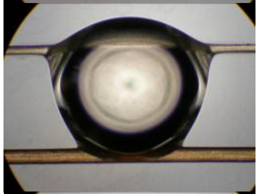
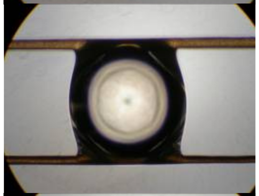
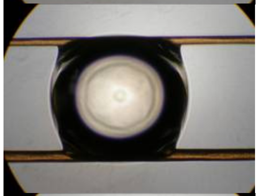
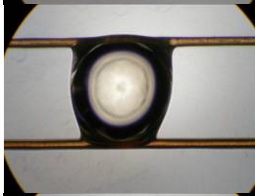
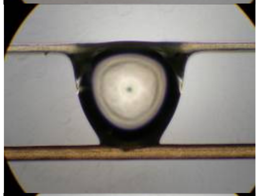
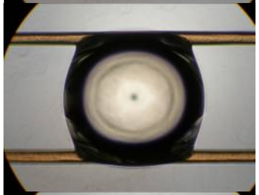
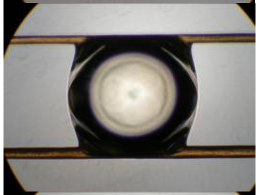
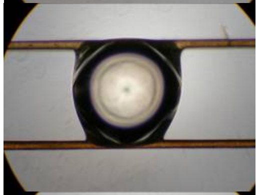
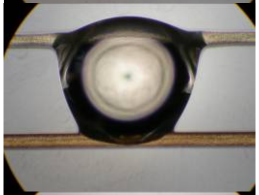
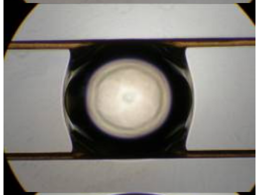
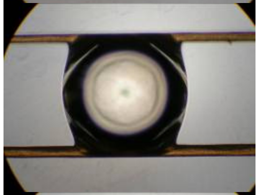
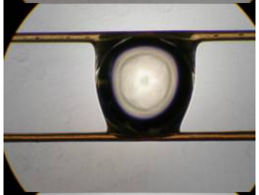
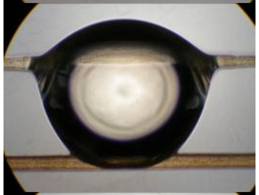
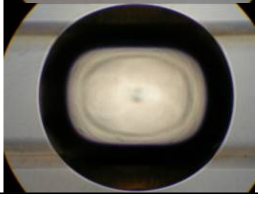
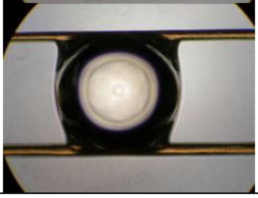
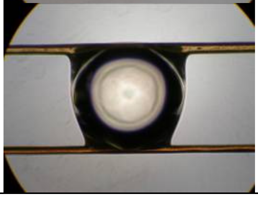
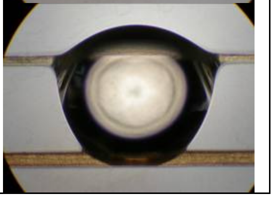
	Virgin vs. Virgin A	Virgin vs. Stripped B	Virgin vs. 1 Hour Bleached C	Virgin vs. 2 Hour Bleached D
1				
2				
3				
4				
5				
6				

Figure 3. Variation of the droplet configuration with the extent of hair damage (I). Column A: Virgin vs. Virgin, column B: Virgin vs. Stripped, column C: Virgin vs. 1 Hour Bleached, and column D: Virgin vs. 2 Hour Bleached. Note that the reference fiber (Virgin in this case) appears at the bottom of each image.

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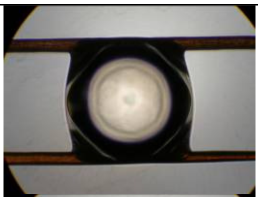
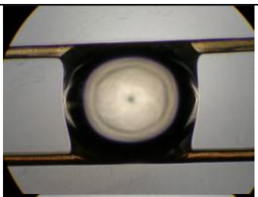
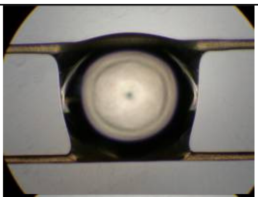
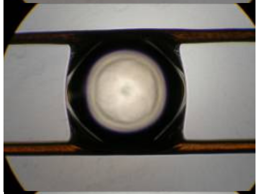
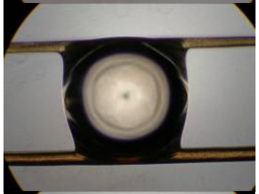
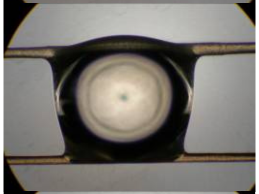
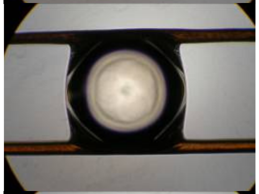
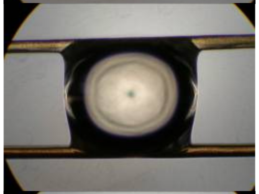
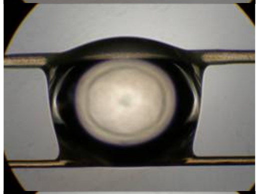
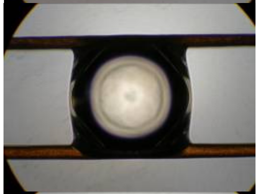
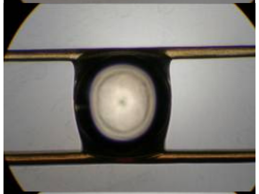
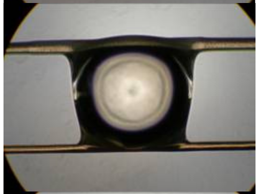
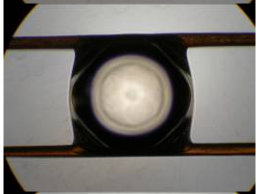
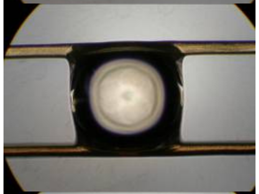
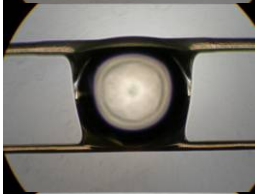
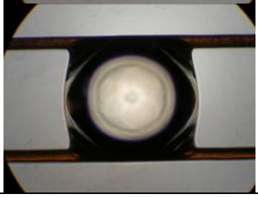
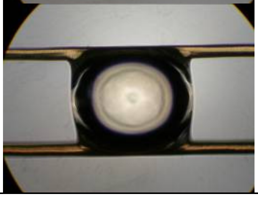
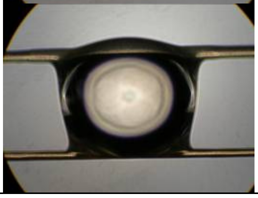
1			
2			
3			
4			
5			
6			

Figure 4. Variation of the droplet configuration with the extent of hair damage (II). Column A: Stripped vs. Stripped, column B: Stripped vs. 1 Hour Bleached, and column C: Stripped vs. 2 Hour Bleached.

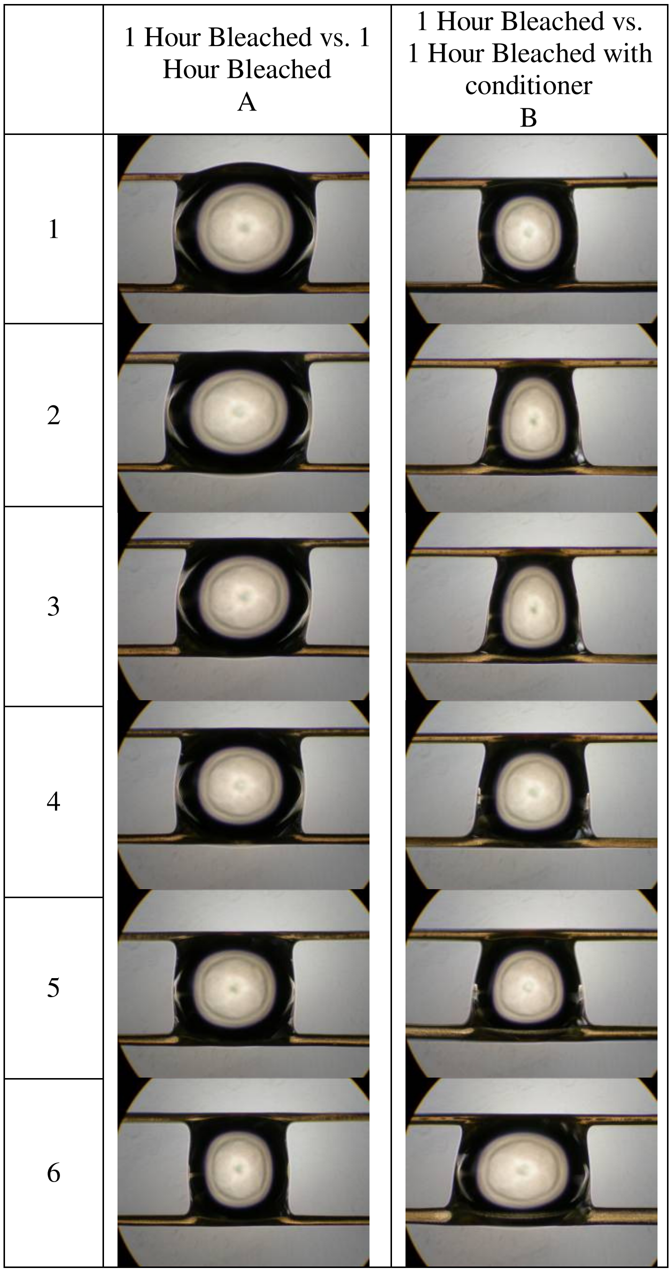
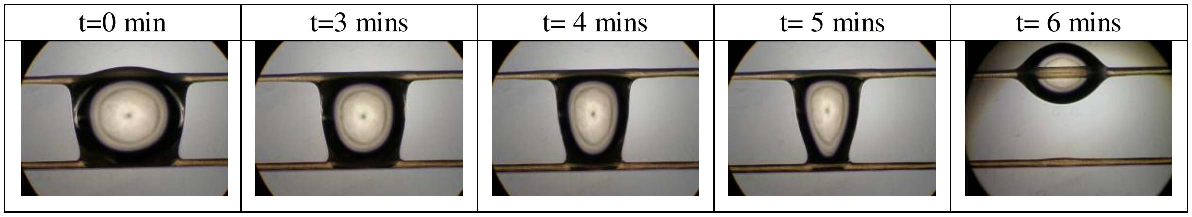


Figure 5. Variation of the droplet configuration with the hair treatment. Column A: 1 hour Bleached vs. 1 Hour Bleached, and column B: 1 Hour Bleached vs. 1 Hour Bleached/Treated with a conditioner.

To validate the observed trend as shown in Fig. 3, we further considered the wetting behavior of another combination of hair fibers, in which Stripped hair fibers were used as the control samples. Images of droplets wetting between Stripped vs. Stripped (set A), Stripped vs. 1 Hour Bleached (set B) and Stripped vs. 2 Hour Bleached (set C) were taken. Images in Fig. 4 confirm the conclusion drawn from the droplet configuration observed in Fig. 3 such that the Stripped hair fibers are most hydrophobic, followed by the 1 Hour Bleached and then the 2 Hour Bleached hair fibers. Images in Fig. 4 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 the fibers of different extents of damage. Besides, by comparing the images in columns C and D of Fig. 3 and those in columns B and C of Fig. 4, one can draw the conclusion that the 2 Hour Bleached hair fibers are more hydrophilic than the 1 Hour Bleached hair fibers. By comparison with the traditional Wilhelmy's method that fails to differentiate between fibers, the proposed DWC method is truly a more sensitive method applicable for wetting characterization of microfibers.

Next we demonstrate the use of DWC method in evaluating the impact of conditioning treatment. Once again, for the purpose of comparison and validation, column A in Fig. 5 shows the droplet configuration between two 1 Hour Bleached hair fibers; column B shows the droplet configuration between the 1 Hour Bleached hair fibers and the 1 Hour Bleached hair fibers treated with a conditioner. The droplets in Fig. 5 are nearly symmetric for the 1Hour Bleached vs. the 1 Hour Bleached. However, in the case of the 1 Hour Bleached vs. the 1 Hour Bleached/Treated, the droplets are systematically skewed toward the 1 Hour Bleached/Untreated. 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 6 shows the shape evolution of an evaporating droplet between the Stripped and the 2 Hour Bleached hair fibers. The extent of skew becomes stronger as the droplet shrinks, with the final image unequivocally illustrating which fiber has a stronger affinity to water.



t=0 min | t=3 mins | t= 4 mins | t= 5 mins | t= 6 mins

Figure 6. The morphology evolution of an evaporating droplet between the Stripped (top fiber) and the 2 Hour Bleached fibers (bottom fiber), illustrating the effect of evaporation on the droplet shape.

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

Surface FEM is further employed to simulate the 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 theoretically examine the sensitivity of the present DWC method on both the contact angle and the fiber diameter. The images based on the numerical simulations are shown in Figs. 7-8. In each set of images, the first illustrates a droplet as viewed from the top as that in Figs. 3-6, 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 7 shows the simulated shapes of droplets on fibers with the identical diameter of 75 µm, in which the fiber separation is fixed at 0.75 mm, and the droplets with a volume of 0.3µl are suspended between the fibers. Variation of the droplet shape is explored with respect to the contact angles such that 60^o vs. 100^o (set A), 80^o vs. 100^o (set B) and 60^o vs. 80^o (set C). As expected, the three sets of simulations yielded skewed droplet orientations with the largest extent of skew in the case of set A (60^o vs. 100^o) while the smallest in the case of set C (60^o vs. 80^o).

Besides, Fig. 8 explores the effect of fiber diameter on the droplet shape. The motivation behind this effort is to theoretically explore the possibility that a fiber with large diameter may lead to a large wetting length on the fiber as to yield a misleading droplet configuration, though this phenomenon has not been observed yet in experiments to date. As an example, the images in column C of Fig. 3 have shown the droplets between the Virgin and the most damaged 2 Hour Bleached hair fibers. All the droplets were clearly skewed towards the damaged hair fibers regardless of the fact that the diameter of the Virgin hair fibers appears to be substantially larger than that of the 2 Hour Bleached hair fibers. Images in Fig. 8 also demonstrate the variation of droplet configuration with respect to both the fiber diameter and the contact angle. It can be clearly observed from Figs. 7A and 8A that the larger fiber diameter increases the wetting length and however decreases the extent of skew. Furthermore, the skew becomes less pronounced at smaller difference in contact angles as illustrated in Figs. 8B and 8C. However, the variation of fiber diameter clearly does not overwhelm the impact of contact angle.

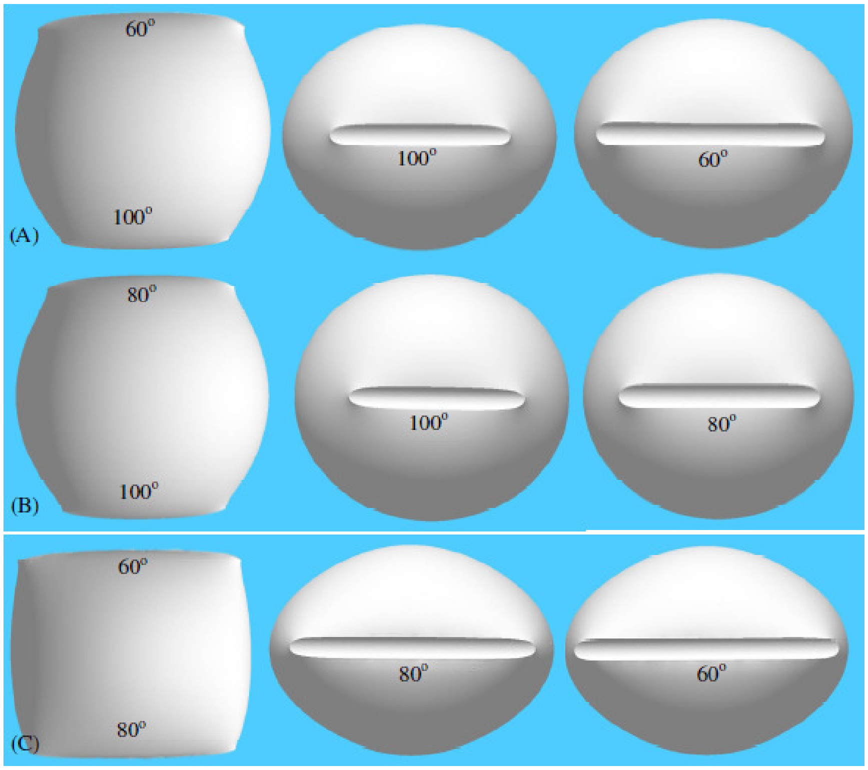


Figure 7. Simulated 0.3 μl droplet shapes between 75 μm fibers at 0.75 mm separation with contact angles of (A) 100° vs. 60°, (b) 100 vs. 80° and (C) 80° vs. 60°, respectively.

CONCLUDING REMARKS

Determination of the contact angle between liquid and hair fibers is a challenging task which is further complicated by the non-uniformity of both the fiber dimensions and surface properties not only from fiber to fiber but also along the fiber axis. The DWC method proposed in this study has provided an efficient while reliable technique for the characterization of the surface wetting property. This method is based simply on the direct observation of a number of droplets sitting on a tested fiber pair thus effectively suppressing the possible experimental errors resulted from single point determination. The current method has been validated by controlled tests in the present study where the hair fibers behaved as the same hydrophobicity trend as characterized by means of Wilhelmy's method. Moreover, in the case of highly damaged hair fibers, i.e. the 2 Hour Bleached hair fibers as considered, the proposed DWC method offers an improved differentiating capability against to Wilhelmy's method.

When carrying out DWC test of fibers, one should be aware of the potential impact of fiber diameter on the distortion of the droplet morphology. Nevertheless, both numerical simulations and experiments demonstrated in this study have concluded that fiber diameter does not significantly interfere with the droplet shape even when the fibers behave substantially different in wetting properties.

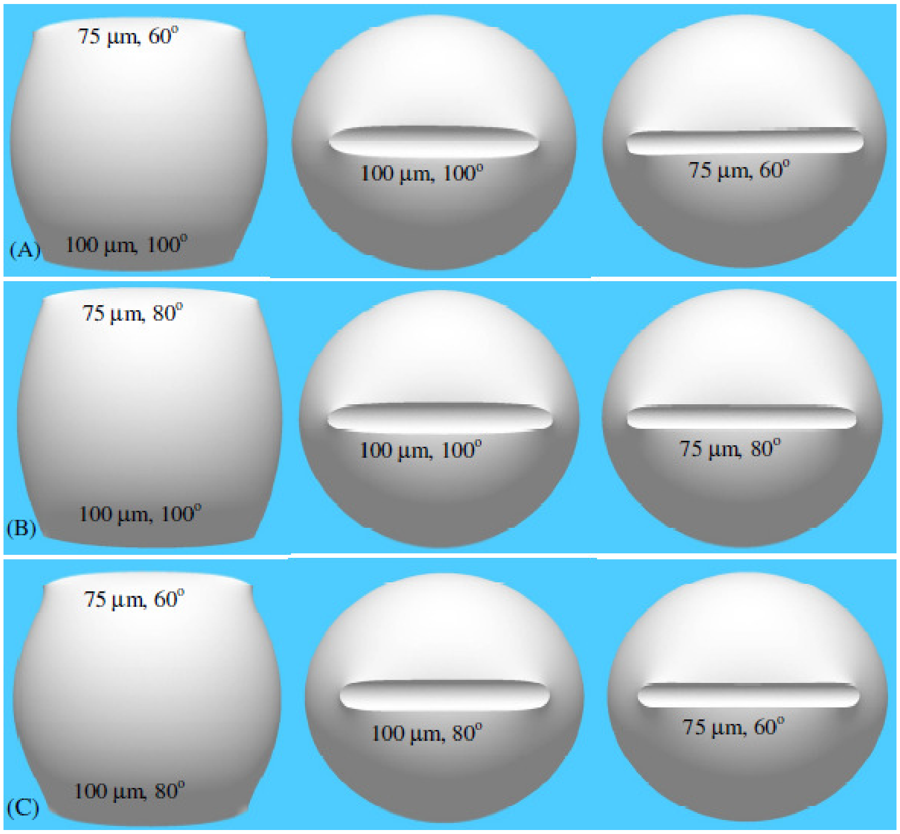


Figure 8. Simulated 0.3 µl droplet shapes between fibers of 0.75 mm separation with the following properties: (A) 100 µm and 100° vs. 75 µm and 60°, (B) 100 µm and 100° vs. 75 µm and 80° and (C) 100 µm and 80° vs. 75 µm and 60°, respectively.

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