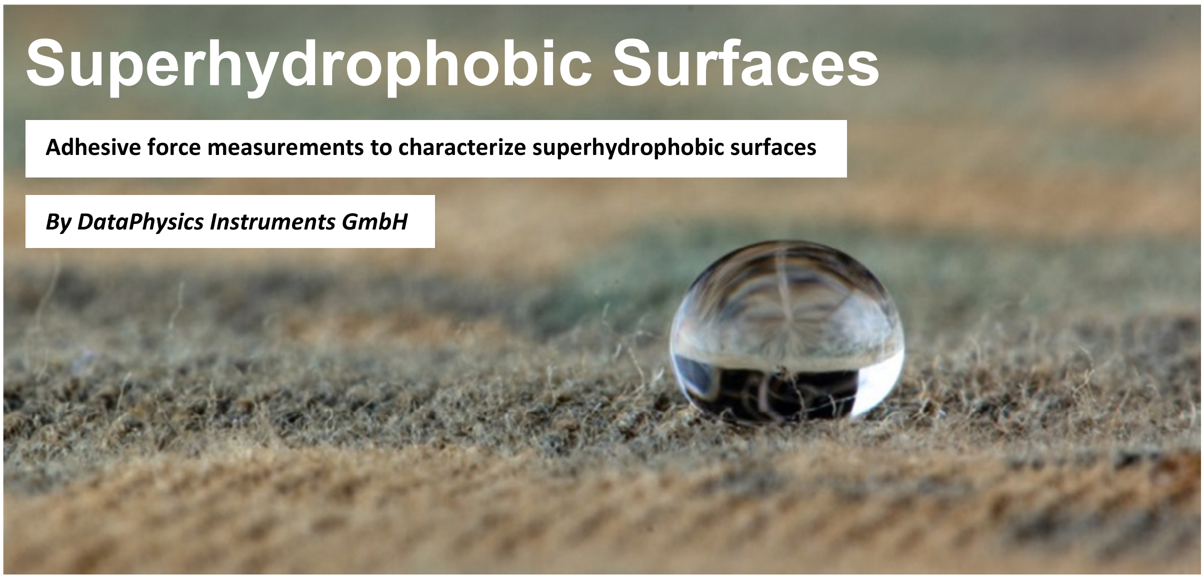
New tools for surface-wetting characterisation of super hydrophobic surfaces



Superhydrophobic surfaces (contact angle of 150° to 180°) are very important materials, due to their ability to shed water, self-clean and their inhibited tendency to be fogged. [1] This makes them invaluable when applied, for example, as a coating on glass surfaces or solar cells, to minimise contamination from air-borne particles. It is very important to have an accurate measurement technique, to characterise hydrophobic surfaces, during their development process. Often these surfaces are characterized by contact angle (CA) measurement, with water, to quantify the hydrophobicity of the surface. However, recent studies, from Ras et al., at Aalto University showed that even though contact angle measurement is an accurate method for contact angles below 120°, with errors in CA of around 1° for CAs ≤ 120°, these error increase with the increase of measured contact angle: 2° for CAs of 150°, 5° for CAs of 162° and 10° for CAs of 170° (Figure 1a). The CA uncertainty range in the measurements suggests that measuring big contact angles (CAs) between 150° and 180°, by an optical method, is prone to errors, which mainly originate from misplacing baselines, for super hydrophobic surfaces due, to optical resolution limitations. Uncertainty in the baseline position cause large CA errors, as shown in Figure 1b, a baseline positioned too low will lead to an increase in measured CA (light blue lines) and a baseline placed too low leads to a decreased CA (orange lines). Due to the limited accuracy of water contact angles on super hydrophobic surfaces other methods should be considered, in order to accurately quantify the surface properties.

a) b)

Figure 1: *a) The errors increase substantially as CAs become larger, especially for the super hydrophobic surface (CA > 150°). b) Errors in CA measurement are caused by accuracy limitations in baseline positioning.*

In the following we will introduce the method of adhesive force measurement as a much more accurate way to quantitatively evaluate the interaction between water and highly hydrophobic surfaces (Figure 2). In an adhesive force measurement a water droplet is placed on a sample holder which is connected to a tensiometer. The substrate is placed on a sample table which is slowly raised towards the water droplet on the sample holder (1). When the droplet touches the sample, the collection of balance signal data is automatically initiated (2) and the force between the droplet and the substrate is calculated and recorded. In order to increase the contact area the drop can then be further compressed (3a) or directly be pulled off by lowering the sample table (3b). Finally the drop will be pulled from the surface (4) and the maximum balance signal, during this sequence (and the force that this represents) is highlighted as a characteristic property for the surface. This calculated value can more precisely characterise the interaction at the solid-liquid interface, between the super hydrophobic surface and the liquid coming into contact with it; compared to CA measurement as will be described in Figure 3.

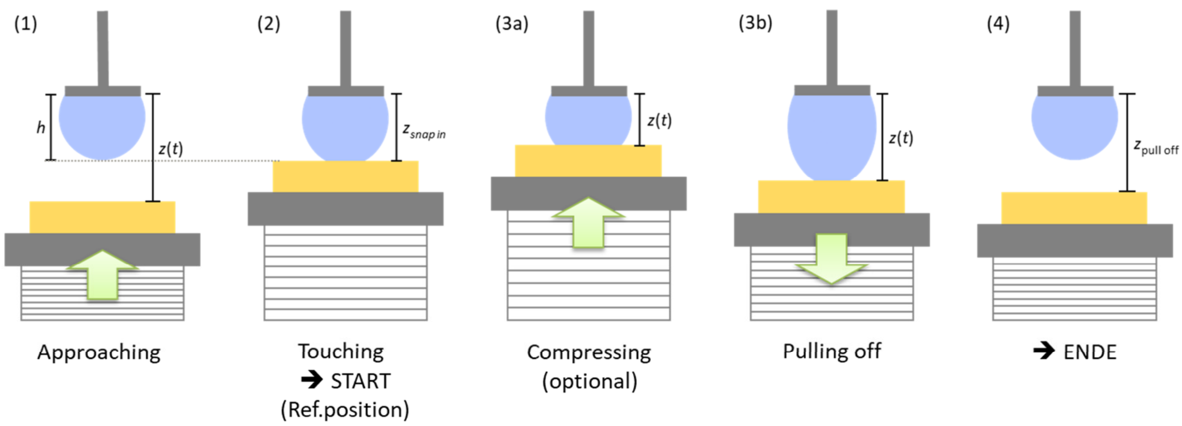


Figure 2: *The adhesive force measurement process.*

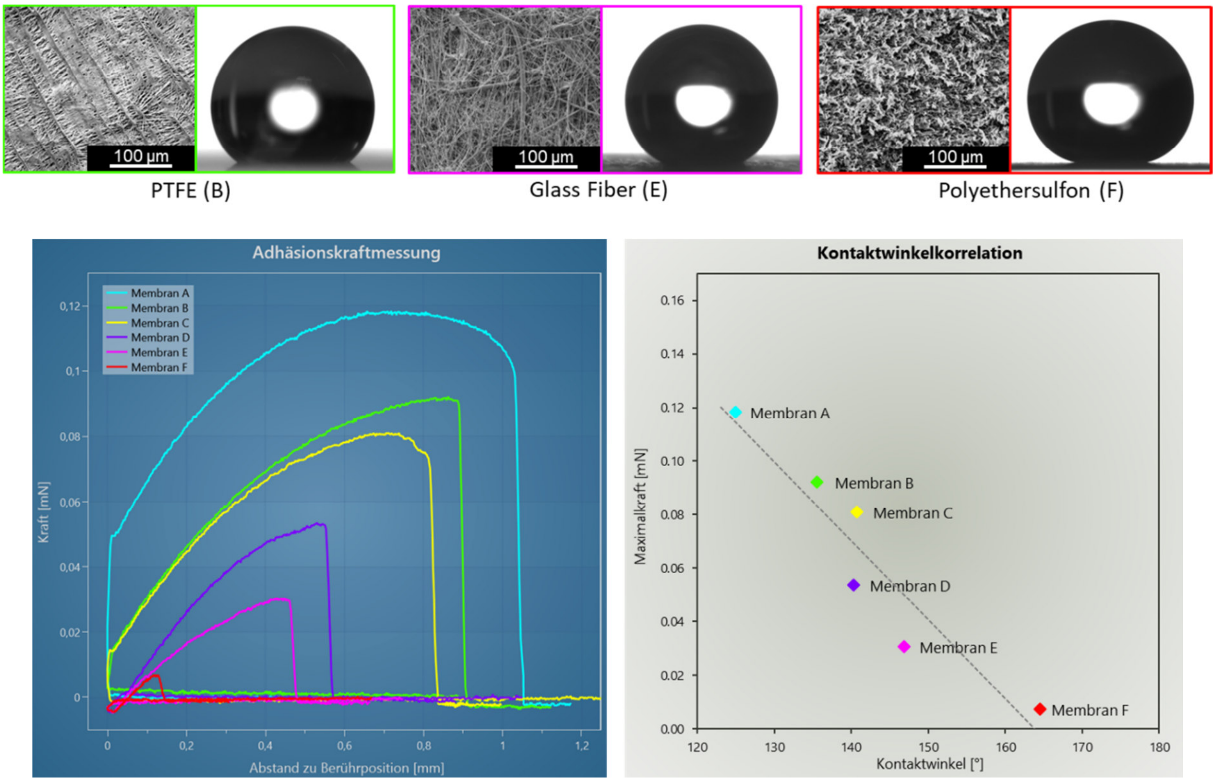


Figure 3: *Applied adhesive force measurement to characterize different kinds of materials, such as Polyethersulfone (Membrane A), PTFE (Membrane B), Polyethersulfone I (Membrane C), Polyethersulfone II (Membrane D), Glassfibre (Membrane E), Polyethersulfone (Membrane F)*

To illustrate the capabilities of adhesive force measurements we characterised different kinds of membranes from hydrophobic and super hydrophobic materials, namely Polyethersulfone (Membrane A), PTFE (Membrane B), Polyethersulfone I (Membrane C), Polyethersulfone II (Membrane D), Glassfibre (Membrane E), Polyethersulfone III (Membrane F). This method provides both, highly accurate, data and great reproducibility. During these studies we found that different macroscopically rough surfaces, with similar CAs, yielded very different adhesive forces (Figure 3; membrane C and D). We see from these measurements that materials, with quite similar water contact angles, can (still removed) exhibit (a removed) significantly different adhesive force; thus making measured adhesive force a much more reliable parameter to characterize these kinds of surfaces, compared with the measurement of contact angles, above 150°. If we compare, for example, membranes C, D, E for which the contact angle only differs by around 8°, with an error in this region of around ±2°, the adhesive forces differ by a factor of around 3 giving a much higher differentiation between these surfaces and making adhesive force measurements a much more accurate and precise tool to quantitatively characterize the interaction between water and highly hydrophobic surfaces.

Comment by DPI:

The Adhesive force method is an accurate and reliable way to quantitatively evaluate the interaction between water and highly hydrophobic surfaces and can thus boost liquid-repellent coatings' development.

If you want to know more about the content of the article, you can directly view the literature information below.

[1] **Improving Surface-Wetting Characterization**; Kai Liu, Maja Vuckovac, Mika Latikka, Tommi Huhtamäki, Robin H. A. Ras; *Science* **2019** *363* (6432), 1147-1148**;** DOI: 10.1126/science.aav5388

A comparison of contact angle measurement and adhesive fore measurement can also be found in the following article.

Study of Wetting and Adhesion Interactions between Water and Various Polymer and Superhydrophobic Surfaces; Benedict Samuel, Hong Zhao, Kock-Yee Law; *J. Phys. Chem. C* **2011**, 115, 14852–14861; DOI: 10.1021/jp2032466

Contact DPI for more information on adhesive force measurement that help you better understand how to quantitatively evaluate the interaction between water and highly hydrophobic surfaces.