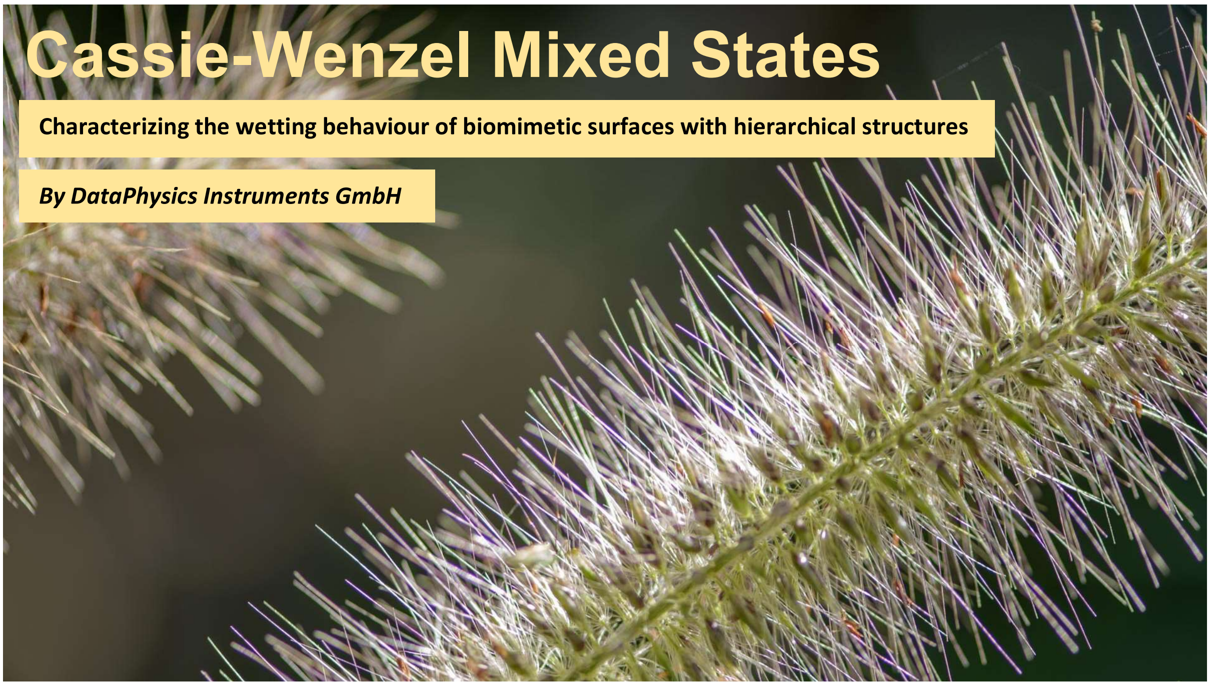
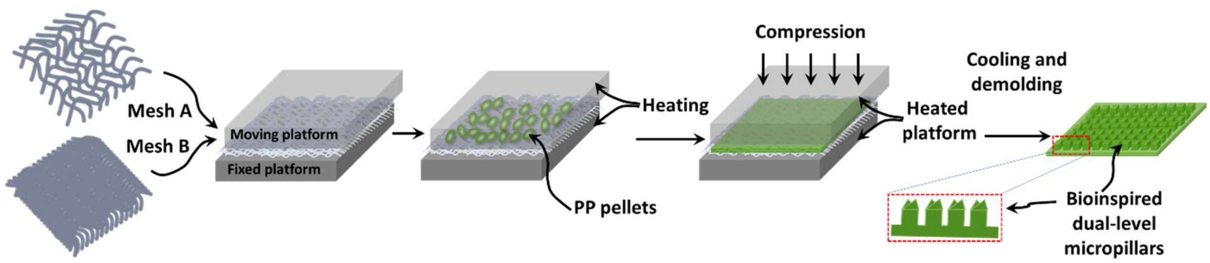
How contact angle measurements help to characterize replicas of natural surfaces



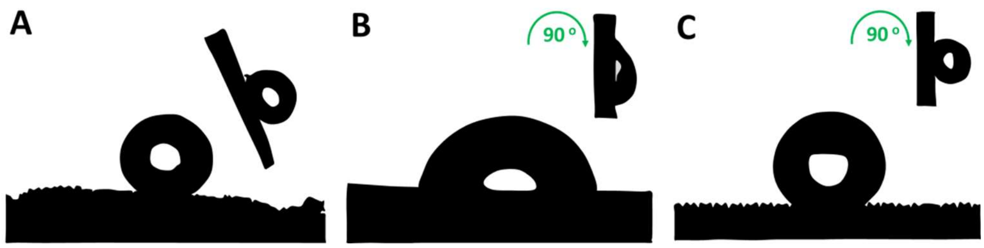
Inspired by natural occurring structures on rose petals, cicada wings, mosquito eyes and water striders, scientists developed a variety of smart biomimetic hierarchical micro/nanostructures. When these surfaces come into contact with liquids the wetting states can be classically divided into the Cassie-Baxter state where the surfaces structures show non wetted air pockets or in the Wenzel state where the surface is completely wetted. However, nature's ingenuity has brought forth also a mixture between these two states the so called Cassie-Wenzel states which will be discussed in this article. But before we go into details, we need to talk about how such structured materials from nature can be replicated in the lab in order to study them more deeply.

To form biomimetic hierarchical micro/nanostructures, synthetic polymers are an ideal platform due to their flexibility, good processing ability and low cost. Template method, as a basic approach to replicate structures based on living organisms were already often applied for building hierarchical micro/nanostructures with the desired wettability. In particular, two types of templates including the actual natural surfaces and an artificial bionic surface are often used to fabricate biomimetic micro/nanostructures. However, natural templates can typically not be reused due to their lack of durability, strength and toughness. Because of this, many researchers try to develop artificial templates for inheriting the prototype properties efficiently. Wu and colleagues recently have fabricated an artificial surface template with hierarchical microstructures to mimic green bristlegrass leaves. They first developed a bioinspired polypropylene replica with micropillars derived from steel sieves (**Picture 1**). By using Mesh A sieves with square holes and Mesh B sieves with tapered holes, micropillar with sufficient height and the tapered structure on top of the micropillar were molded. Scanning electron microscopy data showed dual-level micropillars on the polypropylene replica surface including the primary micropillars and tapered secondary microstructures with dense wrinkles, which inherited the morphology of microstructure on the leaf.



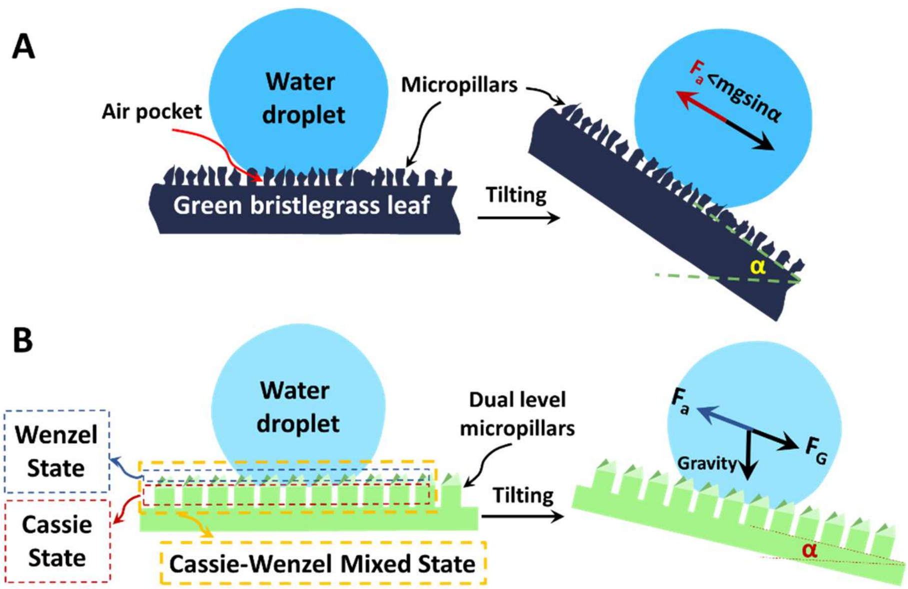
Picture 1: *Scheme of preparation process of bioinspired micropillars on polypropylene (PP) surface*

They then compared the wetting properties of a natural green bristlegrass leaf with contact angle (CA) of 155°±2° and a rolling angle (RA) of 79°±2° with the wettability of a smooth polypropylene surface that exhibited a CA of 85°±2° and RA>90° with the micro-structured polypropylene replica surface that exhibited a CA of 147°±2° and RA>90° —which was very similar to that of natural green bristlegrass leaf.



Picture 2*: Contact angle and rolling angle of 4 µL water droplet on (A) leaf surface, (B) bare polypropylene and (C) bioinspired polypropylene replica surface*

Why is this kind of wettability behavior beneficial in nature? Well, a rolling water droplet on the surface of green bristlegrass leafs can easily wash away pollen and dust to keep the leaf in an efficient photosynthesis state. This superhydrophobicity can be attributed to the microstructure with a tapered shape (length 1 µm). To further investigate the mechanism of dynamic wetting, they recorded the bouncing behavior of a water droplet impacting on a green bristlegrass leaf surface by using the contact angle analyzer from the OCA series of DataPhysics Instruments with a high-speed camera. The recorded footage could show that the initial spherical droplet with an 0.63 m/second impacting velocity deformed first, then spread on the surface rapidly over 2 milliseconds, and rebounded at 12 milliseconds. Under increased impacting velocity (0.99 and 1.4 m/second), the droplets presented a similar behavior but instead of a rebounder they adhered to the surface. Both the wettability and moderate surface adhesion force to water droplets can be correlated with the microstructures on the leaf surface. As shown in **Picture 3A**, air pockets are formed in the inter-microstructure areas, thus prevent the droplets from wetting the surface, and resulting in a superhydrophobic state with a moderate surface adhesion force. Only if the droplet gravity (m·g·sinα) component overcomes the surface adhesion force, the droplet will roll off the surface.



***Picture 3**: Mechanisms for superhydrophobicity and moderate surface adhesion force on (A) leaf surface and (B) bioinspired polypropylene replica surface*

As shown in **Picture 3B**, the tapered upper portion (blue dash) of the dual-level micropillars can be easily penetrated, which results in a Wenzel state with high adhesion; the bottom portion (red dash) can form a stable air pocket to prevent water penetration, which results in Cassie state with high hydrophobicity. This so-called Cassie-Wenzel mixed state makes the artificial surface superhydrophobic with moderate adhesion. In this case, once the gravity component (F_G) fails to overcome the surface adhesion force F_a, a water droplet can effortlessly be fixed on the surface.

Overall, by learning form green bristlegrass leafs, a promising template generated with steel sieves (Mesh A and B) was found to mimic the dense and tapered microstructures on the leaf surface. This template exhibits a Cassie-Wenzel wetting state. The hydrophilic polypropylene can be transformed to a hydrophobic polypropylene replica without additional surface coating or chemical modification. Due to this composite water wetting interface, the artificial polypropylene replica well inherited both the hydrophobicity and adhesion of the natural leaf.

An optical contour analysis system OCA (DataPhysics Instruments GmbH, Germany) was used in this research.

For more information, please refer to the following article:

Bioinspired preparation of regular dual-level micropillars on polypropylene surfaces with robust hydrophobicity inspired by green bristlegrass leaves; Heng Xie, Wen-hua Xu, Ting Wu; *Polym. Adv. Technol.* **2019***,* 1-9; DOI: 10.1002/pat.4786