

# Influence of the plasma chemistry and the topography for the elaboration of superhydrophobic surfaces

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**Abstract:** Superhydrophobic surfaces development can be bio-inspired from the lotus effect where both chemistry and topography approaches are necessary. Several hydrophobic coatings obtained from plasma deposition on various rough steel substrates has been studied showing the effect of the surface roughness on the wettability: from flat to rough surfaces, the hydrophobicity increases. Then, applied to multi-scale structures developed by laser texturing, these metallic surfaces appear to evolve from hydrophobic to superhydrophobic.

**Keywords:** Lotus effect, plasma polymer, multi-scale structures, superhydrophobic

## 1. Introduction

Over almost two decades, efforts have been made to reproduce the water repellent property of the lotus effect [1], theorized by Barthlott and Neinhuis in 1997. Superhydrophobicity of any material consists in fulfilling two conditions: poor wettability and non-adhesion property. Firstly, lowering the surface free energy of a substrate means, here, to reduce the wettability of the surface quantified by the water contact angle (WCA) measure. In such an example, the water contact angle reaches value up to  $150^\circ$  or even more (Fig.1.) and also presents a low hysteresis (few  $^\circ$ ). In such conditions, the chemical or physical affinity of substrate towards water is negligible. Illustrations are given with Lotus leaves constituted by micrometric and sub-micrometric structures and also covered by an organic hydrophobic compound, both allowing water droplets to stay in suspension onto fakir-like superhydrophobic surface. Such a configuration is representative of the so-called Cassie-Baxter state (Fig. 2.). These two factors, chemical hydrophobicity and surface roughness are required, since the water contact angle on smooth surfaces is rarely higher than  $120^\circ$ .

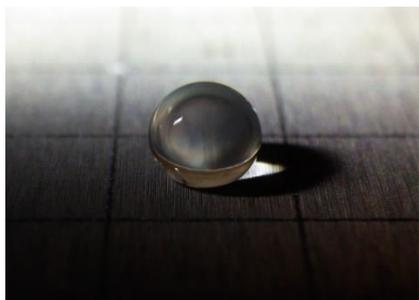


Fig. 1. Example of a water repellent surface, with water contact angle above  $150^\circ$

Nevertheless, hydrophobic depositions on relatively flat surfaces such as glasses are relevant in order to extract the influence of the chemistry on the wettability.

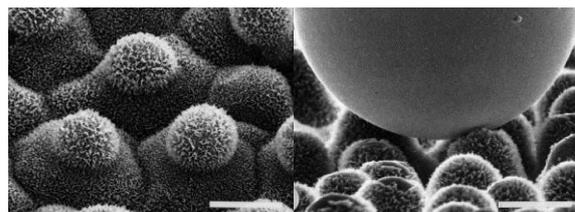


Fig. 2. (left) Zoom  $\times 1000$  of a MEB picture taken from a superhydrophobic leaf and (right) with a mercury droplet on it [1]

In this work, the hydrophobic chemistry of the lotus effect was supported by the plasma chemistry developed for several substrate roughnesses. Therefore, laser textured metallic surfaces were prepared for the obtention of two levels of roughness at micro and nano scales. Finally, our plasma and laser-modified substrates were characterized by wettability measures, microscopies and spectrometries.

## 2. Experimental setup

A 13.56 MHz (RF) plasma generation apparatus was used with a power range from 0 to 200W. Low pressure plasma processes were performed during 5 min using three types of organic precursors: hydrocarbons[2], fluorocarbons[3] and organosilicons[4]–[6]. Additionally, each one was combined with carrier gas like helium, argon and tetrafluoromethane ( $\text{CF}_4$ ) with purity above 99,995%. All metallic substrates with different roughnesses and each multi-scales texture is provided by IREPA LASER company. Roughnesses and profiles are measured with ALICONA infinite focus system.

### 3. Result and discussion

Hydrophobic films were initially built in smooth surfaces like glass with Ra close to hundreds of nanometers. This substrate is covered by a layer applied for 5 min under vacuum plasma deposition, to a thickness of at least 20 nm based on interferometer analysis. Several precursors had been tested in order to reach water contact angles above 100°. Consequently, it turns out that organosilicons provide interesting results with or without carrier gas and for many plasma parameters. Other chemical species tested were less functional giving angles between 50° and 70°. In Fig. 3. we present a plasma polymerized hexamethyldisiloxane (HMDSO) coated on a glass substrate with different argon flow rates during 5 min at 10<sup>-2</sup> mbar and for 100W.

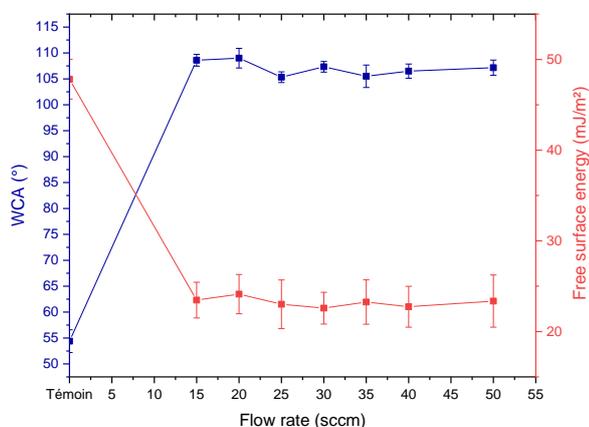


Fig. 3. Water contact angle and free surface energy of HMDSO/Ar mixture on glass substrate depending on Ar flow rate (at 100W during 5 min and at 10<sup>-2</sup> mbar)

The same process was performed onto substrates with higher roughnesses and then, into laser textured steel surface. All water contact angles were measured and compared to their own topography as shown in Table 1. All HMDSO/Ar mixture coated substrates with multi-scale laser textured surfaces became superhydrophobic, in such a way that water contact measurements were impossible.

Table 1. Roughness and Water Contact Angle for HMDSO/Ar deposition upon 3 substrates

Substrate	Roughness	WCA
Glass	Ra < 0.3 μm	max 108° (± 2°)
Steel	0.5μm < Ra < 1μm	max 119° (± 2°)
Laser textured steel	15μm < Ra < 20 μm	Superhydrophobic

### 4. Conclusion

Starting with the theoretical explanation of the superhydrophobicity of the lotus leaf, we were able to reproduce this effect on metallic surfaces with plasma polymerization processes. The two necessary conditions which were, poor wettability and non-adhesion property were successfully replicated using laser textured multi-scale structures coated by a thin hydrophobic layer. The water contact angle on a smooth substrate was shown to be 108° with the proper organosilicon and with the right plasma parameter. Then on rougher surface, it rises up to 119° for the same plasma process, until it gets impossible to measure the angle for laser textured surfaces.

### 5. Acknowledgements

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### 6. References

- [1] W. Barthlott and C. Neinhuis, "Purity of the sacred lotus, or escape from contamination in biological surfaces," *Planta*, vol. 202, no. 1, pp. 1–8, 1997.
- [2] G. Le Dû, N. Celini, F. Bergaya, and F. Poncin-Epaillard, "RF plasma-polymerization of acetylene: Correlation between plasma diagnostics and deposit characteristics," *Surf. Coat. Technol.*, vol. 201, no. 12, pp. 5815–5821, Mar. 2007.
- [3] J. Fresnais, J. P. Chapel, and F. Poncin-Epaillard, "Synthesis of transparent superhydrophobic polyethylene surfaces," *Surf. Coat. Technol.*, vol. 200, no. 18–19, pp. 5296–5305, May 2006.
- [4] F. Palumbo, R. Di Mundo, D. Cappelluti, and R. d'Agostino, "SuperHydrophobic and SuperHydrophilic Polycarbonate by Tailoring Chemistry and Nano-texture with Plasma Processing," *Plasma Process. Polym.*, p. n/a-n/a, Jan. 2011.
- [5] C.-R. Hsiao, C.-W. Lin, C.-M. Chou, C.-J. Chung, and J.-L. He, "Surface modification of blood-contacting biomaterials by plasma-polymerized superhydrophobic films using hexamethyldisiloxane and tetrafluoromethane as precursors," *Appl. Surf. Sci.*, vol. 346, pp. 50–56, Aug. 2015.
- [6] L. ForoughiMobarakeh, R. Jafari, and M. Farzaneh, "The ice repellency of plasma polymerized hexamethyldisiloxane coating," *Appl. Surf. Sci.*, vol. 284, pp. 459–463, Nov. 2013.