Impact of Hexadecane and Water Droplets on Amphiphobic Surfaces

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ABSTRACT

Extremely water and oils/alkanes repellent surfaces - with *solid-liquid-air* and *liquid-liquid-air* working interfaces - have been realized on metals, alloys, glasses and ceramic by deposition of nanostructured hybrid layers or lubricated-infused ones. Contact angles (CA) with water as high as 178°, CA Hysteresis (CAH) lower than 5° and CA with hexadecane up to 130° were achieved. The evaluation of the drop impact on these surfaces was performed by a high-speed camera, simulating different fluid conditions as expressed by the Weber (*We*) number. The main objective of this study was to find out the relationship, if any, between the drop impact outcomes and the surface wettability taking into account both the liquid (impact velocity, surface tension) and the solid surface (morphology and chemistry) parameters.

***Keywords*:** amphiphobicity, drop impact, deposition, rebound, *We* number

1 INTRODUCTION

The control of surface wetting and the ability to actively modulate its response against different liquids, in different environments and fluid conditions can make a bulk material a new "*functional*" one. In the field of materials science, the impact of drops onto dry solid surfaces is a key phenomenon in many industrial applications, whose control - through a deep comprehension of the physico-chemical interactions at surface level - can lead to relevant innovation. In this work, amphiphobic (superhydrophobic plus oleophobic) metals, alloys, glasses and ceramic having CA with water as high as 178°, CAH lower than 4° and CA with hexadecane up to 130° have been obtained.
A full characterization of their surfaces was undertaken by XPS analyses and FESEM observations, while the impact and rebound behavior of both water and hexadecane drops was assessed at different impact speeds and *We* numbers using a high-speed camera. For a given liquid, looking at the correlation between the drop impact outcomes - rebound, splash, receding breakup or deposition of the liquid – and the wetting response of the material, the main evidence is that the relationship is not trivial and also depends on the parameters of the liquid drop (impact velocity, surface tension) and the solid surface (morphology and chemistry). To simplify, in the following test, results concerning wetting and impact phenomena only refer to aluminum as substrate.

2 MATERIALS AND METHODS

The wetting behavior of sandblasted aluminum foils before (TQ samples) and after the deposition of organic-inorganic hybrid coatings (S samples) or lubricant-infused hybrid coatings (SI samples) was determined. Results are presented in Table 1.

Surface	Water		Hexadecane	
	CA ± st.d	CAH ± st.d	CA ± st.d	CAH ± st.d
TQ	96 ± 23	24 ± 1	4 ± 1	Not detectable
S	176 ± 6	4 ± 3	130 ± 2	11 ± 2
SI	178 ± 5	4 ± 4	128 ± 2	12 ± 2

Table 1: Static Contact Angle (CA) and Contact Angle Hysteresis (CAH) values measured for water and hexadecane drops on sandblasted aluminum surface, either untreated (TQ), hybrid-coated (S) or coated and infused with lubricant (SI). For each data, standard deviation is also reported.

SEM images of S and SI surfaces showed a flower-like nanostructure made up of crossed, 200 nm long flakes and nanometric cavities (Figure 1). This peculiar nanostructure, combined with the micron-scale roughness induced by sandblasting, led to a hierarchical featured surface able to greatly enhance the repellency properties against liquids. Indeed, both S and SI samples displayed water CA > 170° and CAH < 5°, e.g. they behave as superhydrophobic from both the static and dynamic point of view. We can assume that water drops on S surfaces were in the Cassie-Baxter wetting state, meaning that the surface morphology was able to retain air within its features and did not allow the penetration of water. Even though SI surfaces were based on a different liquid repellency mechanism (according to the SLIPS approach[1]), the high water CA value suggests that the Cassie-Baxter wetting was achieved on these surfaces too. S and SI surfaces also presented remarkable oleophobicity, as their CA with hexadecane was as high as 130° and their CAH in the order of 12°. In summary, S and SI surfaces proved to be both amphiphobic. On the other hand, TQ surfaces, displaying only the microstructure originated by sandblasting, had much lower CAs and higher water CAH values. Liquid drops on TQ surfaces were in the Wenzel wetting state, so that the liquid could fill the micron-sized cavities on the surface.

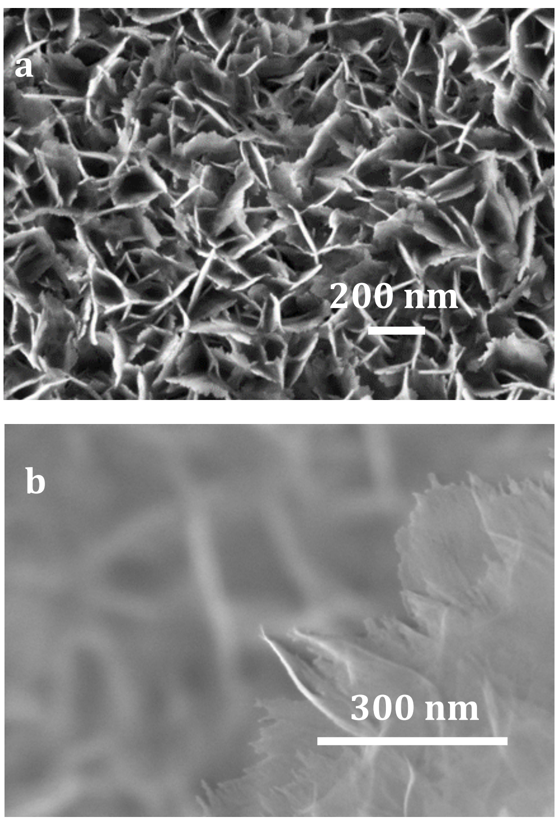

Figure 1: FE-SEM images of a) the flower-like structure on aluminum coated surface and b) detail of the nanometric flakes.

A typical experimental apparatus for drop impact studies was used[2], with the following experimental conditions: impact speed V = 0.05÷4.2 m/s, drop diameter D_0 = 1.5÷2.6 mm, Weber number We = 0.1÷635 and Ohnesorge number Oh = 0.0023÷0.0186. Briefly, drops were manually dispensed from a syringe hanging at various heights above the sample surface, leading to different impact speeds. Images of drop impacts were recorded using a high-speed camera (PCO 1200-HS) with typical frame rates of 1568 and 2477 fps and a pixel resolution of 31 μm/pixel.

3 RESULTS AND DISCUSSION

In Figure 2, image sequences of the four types of observed drop impact outcomes are shown, while in Figure 3, the summary scheme of all the outcomes coming from these tests is reported. Four main regimes stand out: receding breakup, rebound, prompt splash, deposition.

Both statically water-repellent surfaces S and SI showed rebound of water drops for both very low (< 1) and very high (> 550) We numbers. The nano-scale voids in the flower like structure could develop a high capillary pressure P_C against wetting[3], therefore Cassie-Baxter wetting was maintained, as impinging drops were not able to displace the air entrapped in the hierarchical surface structure. The existence of Cassie-Baxter state at such extreme We values has never been reported in the literature before. On the other hand, drops with We < 200 penetrated the micron-scale roughness of TQ surfaces, achieving a Wenzel wetting state. At higher We, the kinetic energy of the impinging drop was large enough to cause receding breakup. These outputs are in good agreement with the low CA and the high CAH values observed for water drops on TQ surfaces.

Hexadecane drops showed a completely different behavior, since they deposit on all surfaces at We ≤ 100 notwithstanding the quite different contact angles displayed by the surfaces. Such behavior could be attributed to the low surface tension γ of hexadecane (γ = 27.5 mN/m at T = 293 K) and to the correlation between P_C and γ as demonstrated by Kwon and Lee[3]. P_C, in fact, scales with the liquid surface tension. For hexadecane drops, P_C falls well below liquid hammer pressure P_{LH}, which causes impalement (e.g. deposition and Wenzel wetting) at low We. Increasing the impact velocity, the low γ of hexadecane led to drop fragmentation, e.g. prompt splash. Remarkably, the transition from deposition to splash regimes occurred at lower We for hierarchically structured materials with respect to the TQ one. It must be highlighted that the presence of a lubricant layer on SI samples surface determined no difference in terms of both wetting properties and drop impact outcome.

These results highlight the specific need of considering all the physical and morphological parameters related to the liquid drops and the solid surface when predicting the drop impact behavior. In contrast with the already developed theories, we observed that the analysis of the wetting behavior of a surface, in terms of evaluation of the provided CAs and CAH values, is not sufficient for the prediction of drop impact outcomes, especially in the case of low surface tension liquids. In order to obtain reliable outputs, numerical simulations will have to take into account additional and more complex aspects such as the correlation between the surface tension of liquids (γ and the capillary pressure (P_C) values, which in turn depend on the surface morphology at the nanoscale.

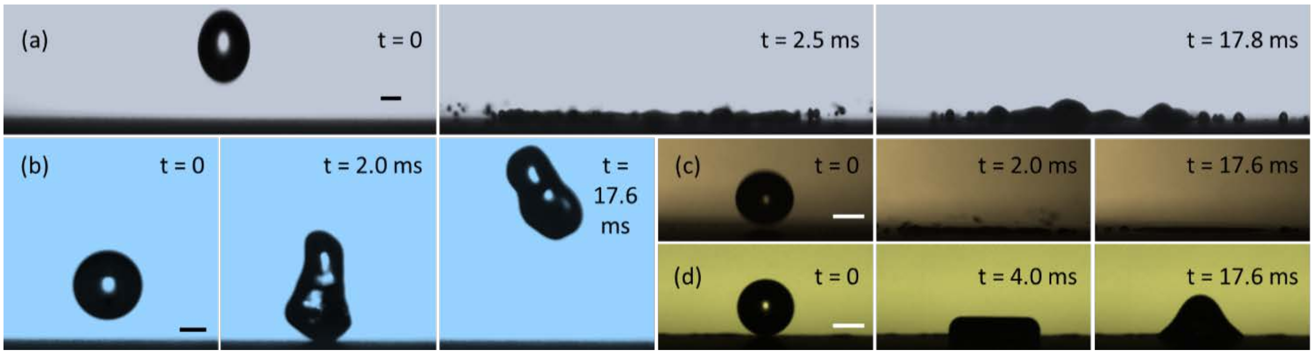

Figure 2: Image sequences for the four drop impact outcomes observed on the tested surfaces: (a) receding breakup of a water drop with We = 588 on a TQ surface; (b) rebound of a water drop with We = 54 on a SI surface; (c) splash of a hexadecane drop with We = 580 on a SI surface; (d) deposition of a hexadecane drop with We = 17 on a S surface. In each frame, a scale bar equivalent to 1 mm and the recording time after impact are reported.

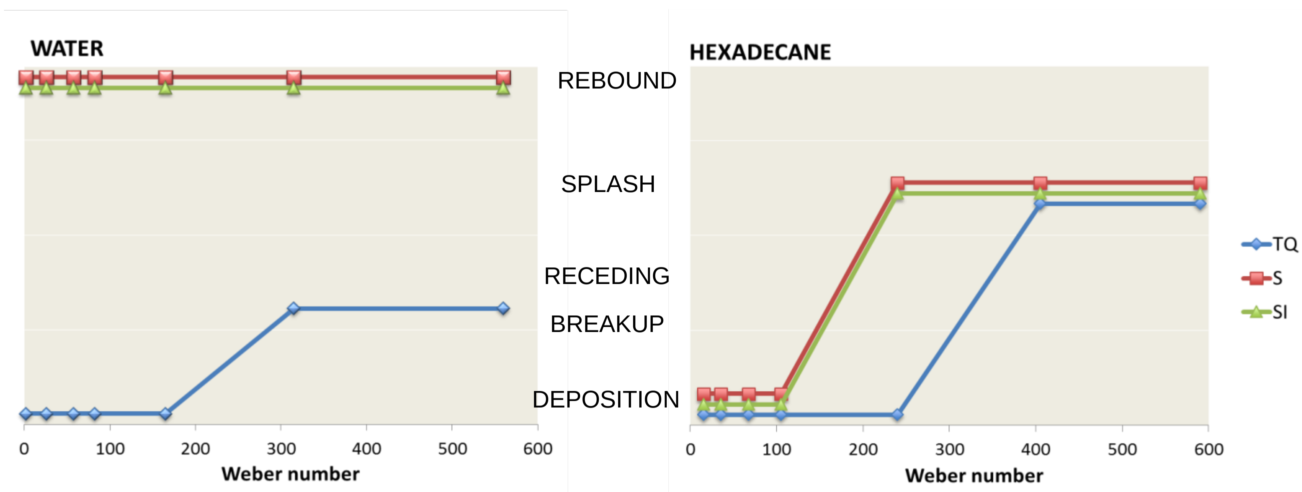

Figure 3: Scheme of the different impact outcomes observed for the TQ, S and SI surfaces as a function of the Weber number.

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