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The overall performance of optical equipment and devices is ultimately dependent on their transparency. This is especially evident when such devices are constantly exposed to varying environmental conditions. Thus the development of a robust, transparent and self-cleaning coating is highly desirable. This work discusses the inherent difficulties in the design of transparent self-cleaning coatings. Describing hydrophobicity and the potential challenges the achievement of transparency can introduce. Before detailing the various established methods of characterisation of super hydrophobic surfaces and outlining some of the group's preliminary results.

Hydrophobicity

Generally, a surface's wettability is defined by its water contact angle (WCA) [1].

- WCA < 90° hydrophilic
- WCA ≥ 90° hydrophobic
- WCA ≥ 150° classified as superhydrophobic

For a smooth surface the hydrophobicity is limited by the surface's chemistry (equ. 1), however the wetting behaviour of a surface is also dependent on the surfaces topography [2, 3]. Wenzel's equation states that as a solid surfaces roughness increases so too does it's hydrophobic/hydrophilic nature (equ. 2).

$$\cos\theta_o = \left(\frac{\gamma_{sv}-\gamma_{sl}}{\gamma_{lv}}\right) \qquad (1)$$

$$\cos\theta_r^w = r\cos\theta_o \qquad (2)$$

Cassie and Baxter [2] determined that a hydrophobic rough surface's liquid repellence prevents liquid from fully penetrating into the depressions of the morphology [4, 5]. As the surface is considered as a composite of solid and air, with a contact angle of θ_r^c:

$$\cos\theta_r^c = f(\cos\theta_o + 1) - 1 \qquad (3)$$

Where f the fraction of liquid – solid contact, the composite contact is established when $\theta_o > \theta_c$ and the threshold contact angle being: $\cos\theta_c = (f-1)/(r-f)$ [4, 5].

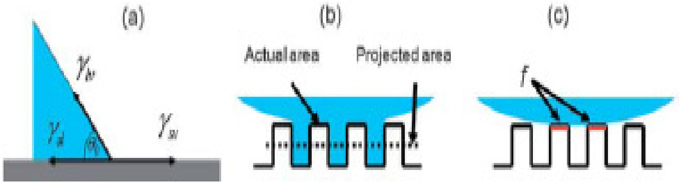

Figure 1: Illustration of different 'wetting states' (a) flat surface, were Young's model dominates (b & c) rough surfaces, were the substrate's topography influences it's wettability profile.

Self - Cleaning

For self-cleaning surfaces, a low level of water drop adhesion to the surface is important. This is the product of the WCA and the contact angle hysteresis (CAH), ($\Delta\theta = \theta_{adv} - \theta_{rec}$). A combination of high WCA and low CAH results in a decreased force being required to set a droplet in motion [6].

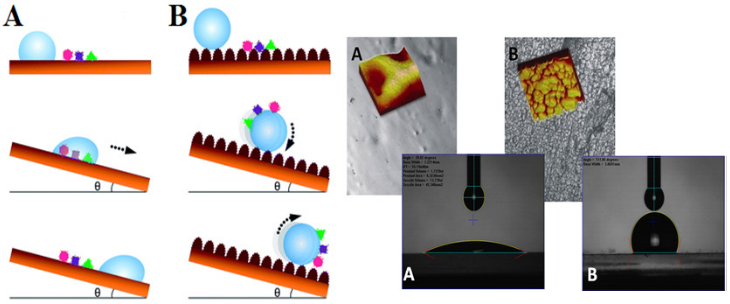

Figure 2: The effect of surface 'roughness' on it's wettability. and self-cleaning mechanism. (a) smooth surface, and (b) a superhydrophobic surface. When both surfaces are tilted to a certain degree, denoted as θ, the droplet passes over the dust of the normal surface, whereas the round droplet on the superhydrophobic surface removes the dust [7]

Light Scattering

As a hydrophobic surface's roughness increases

- WCA increases
- Optical Transparency decreases

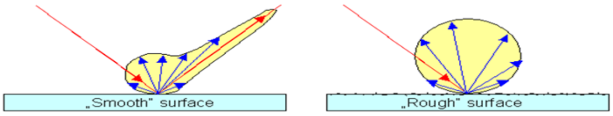

Figure 3:Schematic of the effect of a surface's roughness on it's transparency.

High transparency, superhydrophobicity and high water mobility require

- a rough surface with feature size ≤ 100 nm
- a surface topography with the ability to trap air
- a low surface energy passivation layer coated on the rough texture.

Coating Preparation

A hexamethyldisilazane (HMDS) capped tetraethoxysilane (TEOS) based sol was prepared and spin cast on to a glass substrate for characterisation.

Coating Characterisation

Practical applications require long term durability in a variety of harsh environments. Prompting a series of tests to determine the viability of a coating including: monitoring of WCA and sample morphology, tribology wear tests, water fall/jet and sand abrasion and bio-fouling tests [5,7].

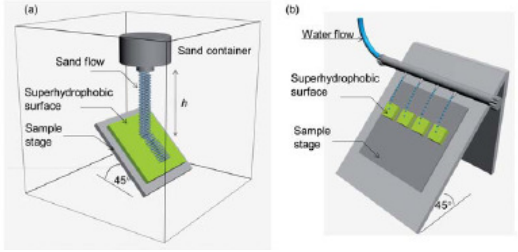

Figure 4: Illustrated representation of durability test setups:(a) sand abrasion (b) waterfall/jet test [5].

Summary of Preliminary Results

Table 1: Summary of test coating's initial characterisation

Properties	Test Method	Result
Hydrophobic	Contact Angle Instrument (CAI)	147.78° ± 1.179° (n=5)
Transparent	Spectrophotometer (S)	93.2 %
Durability (Aging)	CAI	1% reduction in CA Vs pristine sample
Durability (fouling)	S	7% decrease 11% for glass blank 4% protection
	CAI	2% reduction in CA - after 6 soil washes
Durability (constant water exposure – 6 weeks)	CAI	3% reduction in CA Vs pristine sample

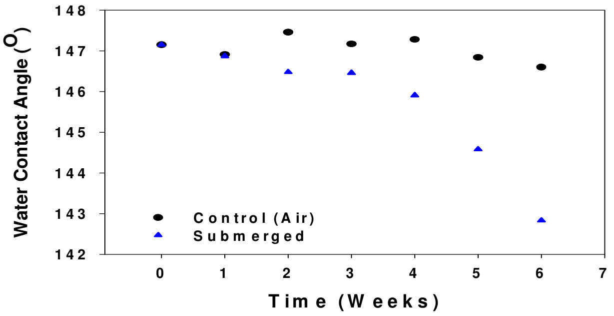

Figure 5: Determination of effect of constant submersion on the sol gel coatings WCA.

References

1. Young, T., Philosophical Transactions of the Royal Society of London, 1805. 95, 65-87.
2. Cassie, A. and S. Baxter, Transactions of the Faraday Society, 1944. 40, 546-551.
3. Wenzel, R.N., The Journal of Physical Chemistry, 1949. 53, 1466-1467.
4. Dodiuk, H., et al., Polymers for Advanced Technologies, 2007. 18, 746-750.
5. Rahmawan, et al., Journal of Materials Chemistry A, 2013. 1, 2955-2969.
6. McHale, G., et al., Langmuir, 2004. 20, 10146-10149.
7. Zhang, Y.L., et al., Soft Matter, 2012. 8, 11217-11231
8. Chapman, J., et al., International Biodeterioration & Biodegradation, 2013. http://dx.doi.org/10.1016/j.ibiod.2013.03.036

Conclusion

Initial work to produce an optically clear superhydrophobic coating has garnered;

- A coating of WCA 147.78° ± 1.179°
- 93.2% transparency
- Prolonged submersion had little impact on the coatings WCA
- However the coatings durability to harsher environmental testing suggests further development of the coating is necessary.

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