SUPERHYDROPHOBIC SURFACES BY RAPID EXPANSION OF SUPERCRITICAL CO_2 CONTAINING CRYSTALLIZING COMPOUNDS

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Abstract. Superhydrophobic self-cleaning surfaces have been produced by dissolving hydrophobic crystallizing compounds in supercritical carbon dioxide (scCO2), followed by spraying the solution through a nozzle by the rapid expansion of supercritical solution (RESS) technique. Research has been focused on:

(i) Solubility of compounds of interest in scCO2 using the cloud-point pressure method as well as a novel method based on Raman spectroscopy (1;2).
(ii) Investigation of particle size distribution of formed crystals in RESS using laser diffraction (3).
(iii) Characterization of the produced surfaces by e.g. dynamic contact angle and sliding angle of water droplets, as well as filming of rolling water droplets using a high-speed camera (3;4).
(iv) Novel hydrophobic compounds and compound mixtures have been investigated with the aim to obtain smaller crystals on the surface as well as improved wetting behaviour and wearability. Some of the investigated materials are naturally occuring crystalline compounds and two polymers, polycaprolactone (PCL) and a statistical copolymer of vinyl acetate and vinyl pivalate (P(VAc-VPi)).

In this lecture, the most recent results will be presented from the project "SuperSurface" (www.kilu.lu.se/cas/research/collaborations/supersurface). Important applications including outdoor textiles, automobiles/trucks, metal constructions, windows and mirrors, and paper products will be discussed with respect to the different requirements that need to be fulfilled by the different surfaces.

Keywords: Rapid expansion of supercritical solution, superhydrophobic surfaces, crystallization, wetting, solubility

1. Introduction

Superhydrophobic surfaces are commonly described as surfaces that mimic the Lotus flower and its self-cleaning properties (*5;6*). More strictly speaking, the term superhydrophobicity (*7*) is used to describe the effect when a water droplet is rolling off a surface instead of sliding. This process is dependent on both the geometric structure and the intrinsic contact angle of the used material. In general, the geometric structure of the surface should be rough, containing micron-sized pillars with air pockets in-between, upon which water droplets will rest and slide with low friction. Surfaces can be considered superhydrophobic when they exhibit this property. As a rule of thumb contact angles towards pure water above 150 degrees indicate, but do not guarantee, superhydrophobic (strongly water-repellent), self-cleaning behavior.

Superhydrophobicity, resulting in water repellent, self-cleaning surface properties, perhaps in combination with minimal ice formation or algae growth on the surface, is of large interest in many applications. Examples of applications are boat hulls, outdoor textiles, building materials, packaging materials, windows, parabolic antennas and wind turbine blades.

In our research, superhydrophobic surfaces are produced using the Rapid Expansion of Supercritical Solution (RESS) technique. Shortly, a superhydrophobic surface is produced by dissolving a crystallizing hydrophobic compound in scCO_2, followed by spraying the supercritical solution through a nozzle where the CO_2 is expanded to gas, and the dissolved compound crystallizes, resulting in rapidly moving particles hitting the target-surface (see Figure 1). Using this methodology, we have shown that surfaces evenly covered by a thin, anisotropic flakes with their largest dimensión in the µm range,of for example the alkyl ketene dimer (AKD) wax can be formed. Water contact angle measurements showed that the produced surfaces have contact angles between 150-170° and with very low roll-off angles indicating that a real superhydrophobic surface had been created with this treatment.

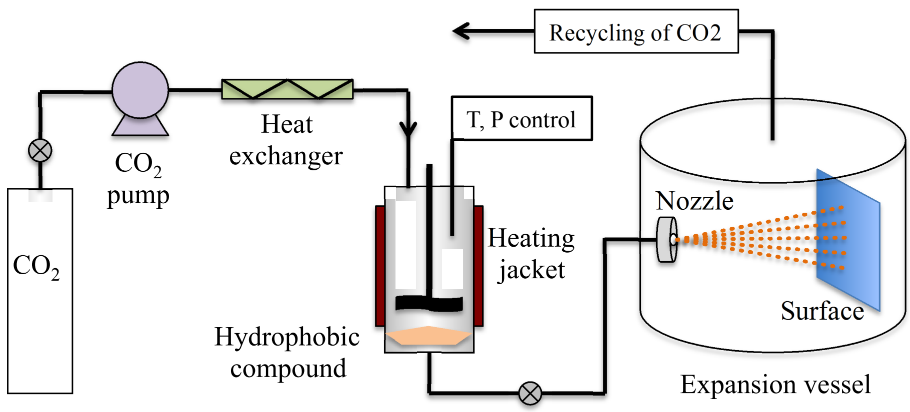

Figure 1. Schematic of the RESS system.

2. Materials and methods

See our already published papers for experimental set-ups as well as chemicals and methods used (*1-4;8;9*).

3. Results

3.1 Solubility in scCO_2

We have previously shown that the solubility of AKD in scCO_2 ranges from 1 to 14 mg AKD/g CO_2 at temperatures between 40 and 80 °C and pressures between 10 and 30 MPa. A significant increase in solubility was observed in the region above 50 °C and 20 MPa. The determined solubility in addition depends on which methods is used for the determination, if it is the cloud-point pressure method, a dynamic “extraction-type” of method, or a batch “equilibrium-type” of method (*2*).

More recent research shows the potential of using Raman spectroscopy to determine solubility of a solute in scCO_2 (*1*). Figure 2 shows typical Raman signals of scCO_2. Pressure can be calculated from delta (Figure 2a) using the Yamamoto´s equation (*10*). The presence of AKD affects the pressure obtained from the calculation, indicating solubility of AKD in scCO_2 respectively solubility of CO2 in AKD, see Figure 2b. As shown in Figure 2b a cross-over behavior is observed, which mainly depends on the density of the scCO_2.

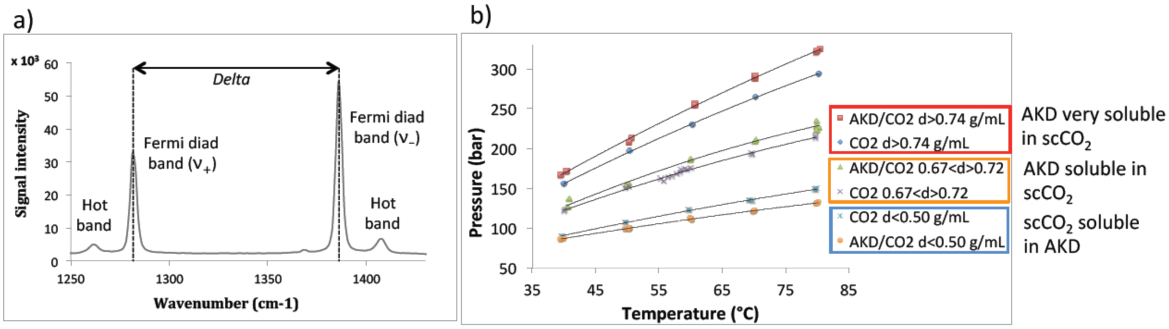

Figure 2 a) Raman signal of $scCO_2$, where delta is affected by pressure, temperature and the presence of electron donor-acceptor interactions. (b) Change in pressure with temperature in the AKD/$scCO_2$ and $scCO_2$ systems obtained from the Raman signals of CO_2. Regression functions compared by marginal change percentage using a t-test show significant difference.

3.2 Coating of surfaces using the RESS technique

Results previously reported demonstrated the ability to produce surfaces evenly covered by AKD crystalline flakes of diameters between 3-10 µm by using the RESS technique (*3;4;8*). An important aspect is to be able to produce smaller-sized crystals, in order to create thinner, preferably transparent, surfaces. Ongoing research shows that by mixing AKD with a crystallizing small natural compound, significantly smaller AKD crystals were formed, around 1 µm in diameter, see Figure 3.

As shown in Figure 3, the natural compound induces precipitation of AKD in smaller particles creating a first degree of roughness of 10-20 µm (Fig. 3A). At the same time, it provides a second degree of roughness with particles of diameters around 1-2 µm (Fig. 3B). In between the particles, air pockets of sizes less than 1 µm are formed. This morphology has shown improved contact angle hysteresis (in average Θ_a=157° and Θ_r=150°), which is translated into better superhydrophobic behaviour. For comparison, Figure 3C shows a SEM image of flakes obtained when AKD is sprayed without the natural compund. It is obvious that the AKD flakes are bigger in this case (the scale in Figures 3B and C is the same).

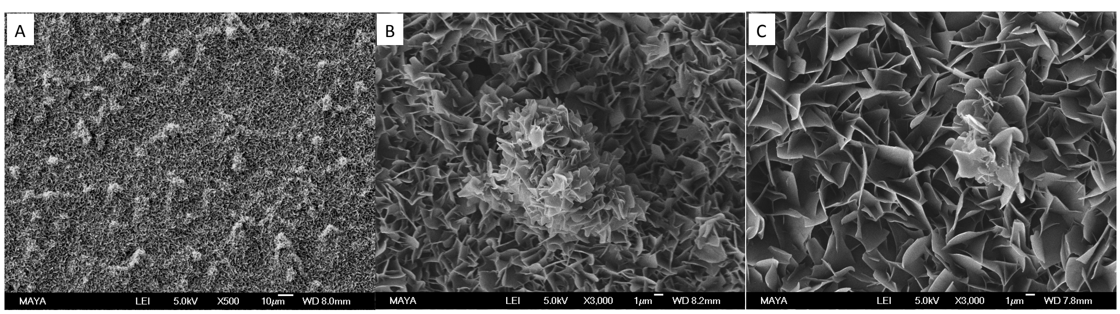

Figure 3. SEM images of produced surfaces. a-b: a mixture of 5% natural compound in AKD, and c: 100% AKD. b is a zoomed in image of a. T=70 °C, P=25 MPa.

3.3 Coating with polymers

Concerning the use of polymers to create a more wear-resistant superhydrophobic surface by RESS technology, solubility in $scCO_2$ is the main issue. It turns out though that the addition of a co-solvent of around 10 % significantly improves the situation, and acetone seems to be the most promising one (*9*). Acetone increases the solubility of both polycaprolactone (PCL) as well as the copolymers investigated. Figure 4 shows a silica wafer coated with one of the copolymers using $scCO_2$ mixed with acetone as a rapidly expanding solvent. Water contact angle measurements indicated superhydrophobicity (θ_a = 155 °). Solution casting of this polymer from acetone gave surface coatings with water contact angles of around 90 °. Spraying from RESS significantly increases the roughness of the coatings causing the superhydrophobic properties.

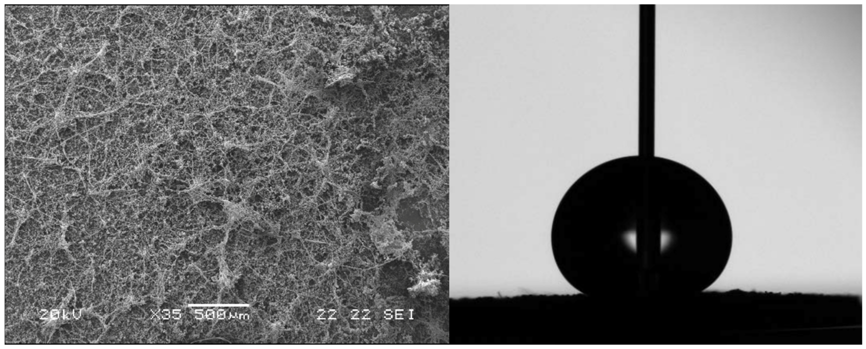

Figure 4. Biodegradable copolymer (M_W 20.6 kDa) sprayed from $scCO_2$ and acetone at 30 MPa and 40°C, showing a SEM image (left), and contact angle image of water on that surface, giving θ_a 155 ° (right).

4. Conclusions

Coating of surfaces with particles formed by the RESS process using a crystallizing hydrophobic compounds gives the surface superhydrophobic, self-cleaning properties. In many cases, water contact angles between 150-170 ° are obtained. In addition, mixing the wax AKD with a natural smaller crystallizing compound gives a surface of two structural levels of roughness, one of around 1-2 µm and the second one of around 10-20 µm which will improve the superhydrophobic properties of the surface. Superhydrophobic surfaces can also be prepared using a hydrophobic "CO_2-philic" polymer, which is promising when striving towards more robust, wear-resistant surfaces. Finally, Raman spectgroscopy is a novel tool to determine solubility of solutes in $scCO_2$.

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References

[1] Rodriguez-Meizoso, I.; Lazor, P.; Turner, C. In situ Raman spectroscopy for the evaluation of solubility in supercritical carbon dioxide mixtures. *J. Supercrit. Fluids* 2012, *65*, 87-92.

[2] Rodriguez-Meizoso, I.; Werner, O.; Quan, C.; Knez, Z.; Turner, C. Phase-behavior of alkyl ketene dimmer (AKD) in supercritical carbon dioxide. The implications of using different solubility measurement methods. *J. Supercrit. Fluids* 2012, *61*, 25-33.

[3] Werner, O.; Turner, C. Investigation of different particle sizes on superhydrophobic surfaces made by rapid expansion of supercritical solution with in situ laser diffraction (RESS-LD). *J. Supercrit. Fluids* 2012, *67*, 53-59.

[4] Quan, C.; Werner, O.; Wagberg, L.; Turner, C. Generation of superhydrophobic paper surfaces by a rapidly expanding supercritical carbon dioxide-alkyl ketene dimer solution. *J. Supercrit. Fluids* 2009, *49*, 117-124.

[5] Barthlott, W.; Neinhuis, C. Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* 1997, *202*, 1-8.

[6] Li, X.-M.; Reinhoudt, D.; Crego-Calama, M. What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces. . *Chem. Soc. Rev.* 2007, 1350-1368.

[7] Lafuma, A.; Quere, D. Superhydrophobic states. *Nat. Mater.* 2003, *2*, 457-460.

[8] Werner, O.; Quan, C.; Turner, C.; Pettersson, B.; Wagberg, L. Properties of superhydrophobic paper treated with rapid expansion of supercritical CO2 containing a crystallizing wax. *Cellulose* 2010, *17*, 187-198.

[9] Ovaskainen, L.; Rodriguez-Meizoso, I.; Birkin, N. A.; Howdle, S. M.; Gedde, U.; Wågberg, L.; Turner, C. Towards superhydrophobic coatings made by non-fluorinated polymers sprayed from a supercritical solution. *J. Supercrit. Fluids* 2013, *in press*.

[10] Yamamoto, Y. H.; Kagi, H. Extended micro-Raman densimeter for CO2 applicable to mantle-originated fluid inclusions. *Chem. Lett.* 2006, *35*, 610-611.