# Superhydrophobic Surfaces Produced By Supercritical $CO_2$ Technology

Charlotta Turner[1,*], Irene Rodriguez-Meizoso[1], Louise Ovaskainen[2], Pontus Olin[2], Lars Wågberg[2], Samuel Chigome[3], Nelson Torto[3], Natasha Birkin[4], Steven M. Howdle[4]
[1]Department of Chemistry, Lund University, SE-221 00 Lund, Sweden
[2]Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden
[3]Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa
[4]School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK
Email: Charlotta.Turner@chem.lu.se
Fax: +46 46 222 8209

## ABSTRACT

In this lecture, the beauty of using supercritical carbon dioxide ($scCO_2$) as a solvent in particle formation processes is described. Superhydrophobic self-cleaning surfaces have been produced by dissolving a crystallizing wax in $scCO_2$, followed by spraying the solution through a nozzle by the rapid expansion of supercritical solution (RESS) technique. Our results show that by using alkyl ketene dimer (AKD) as a coating wax, water contact angles between 150-170° are obtained on basically any surface [1-4]. Recent results also demonstrate the feasibility of combining the RESS technique with electrostatic deposition (RESS-ED). Polymeric coatings were made by RESS-ED using a copolymer, poly(vinyl acetate)-poly(vinyl pivalate) [5], giving water contact angles of above 153° and hysteresis under 5°.

## INTRODUCTION

There are lots of fascinating materials in nature that are smart in terms of energy conservation and survival. For instance, the leaf of the sacred Lotus (*Nelumbo nucifera*) has a rough surface made of wax pilars, which makes water droplets roll-off rather than slide off, giving the surface self-cleaning properties. The geometric structure of the surface should be rough enough to maintain air pockets in-between micron-sized wax pillars, on top of which water droplets will rest and slide with low friction. Surfaces can be considered superhydrophobic when they exhibit this property [6-8]. Superhydrophobic, self-cleaning surfaces are of interest in many industry applications, such as packaging material, automobile and trucks, boat hulls, outdoor/sport textiles, building materials, windows, parabolic antennas and wind turbine blades.

In our research, superhydrophobic surfaces are produced by Rapid Expansion of Supercritical Solution (RESS). A crystallizing wax or other hydrophobic crystallizing compound is dissolved 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. 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.

## MATERIALS AND METHODS

See our already published papers for experimental set-ups as well as chemicals and methods used [*1-3;9;10*].

## RESULTS

We have explored the idea of using a seeding agent to influence crystallization of the wax as a way to make an impact on the wettability and wear resistance properties of the coating. Betulin is a natural compound with antibacterial properties. Therefore, the choice of betulin as seeding material also aimed to provide the coatings with added bacteriostatic properties. Mixtures of betulin/AKD were co-sprayed by RESS to obtain composite coatings. Results from powder X-ray indicate that AKD crystallized from warm acetone shows a long-range order crystalline phase that is not affected by the presence of betulin. However, results from the samples processed by RESS show that the crystallization process has an effect on the crystalline structure of the AKD. AKD sprayed by RESS crystallizes as a mixture of phases. In the presence of betulin, results show a mixture of phases that is structurally related to neat AKD. At the same time, the presence of betulin decreases the size of the AKD crystals obtained by RESS (see Figure 1). The decrease in size may correspond to an increase in supersaturation of the supercritical solution during the RESS process.

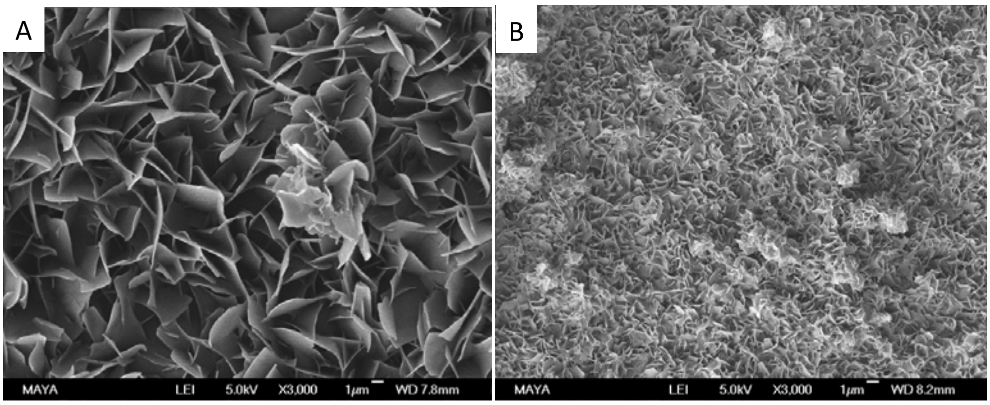


**Figure 1.** Scanning electron microscope pictures of a) neat AKD and b) betulin/AKD mixture sprayed by RESS.

Concerning the use of polymers to create a more wear-resistant superhydrophobic surface by RESS technology, solubility in $scCO_2$ is the main issue. We have previously shown that the addition of 10% of acetone to the $scCO_2$ enables solvation of a copolymer of vinyl acetate and vinyl pivalate (P(VAc-VPi)) [*5*]. Another challenge is the collection of the formed particles in the RESS process on a surface. Recent experiments show that by applying a high-voltage field between the spray nozzle in RESS and the surface to be coated (RESS-ED equipment in Figure 2), polymer particles could be successfully collected on the surfaces [*11*]. Obtained surfaces were thinner and of larger-area, compared to using only RESS. In addition, all the coatings made by RESS-ED had contact angles of a water droplet above 153°, hysteresis under 5° and a tilt angle below 11° at which a 5 µL water droplet rolled off the surface. Examples of SEM images of surfaces made by spraying 7.5 wt% solution of P(VAc-VPi) in the novel RESS-ED process is shown in Figure 3.

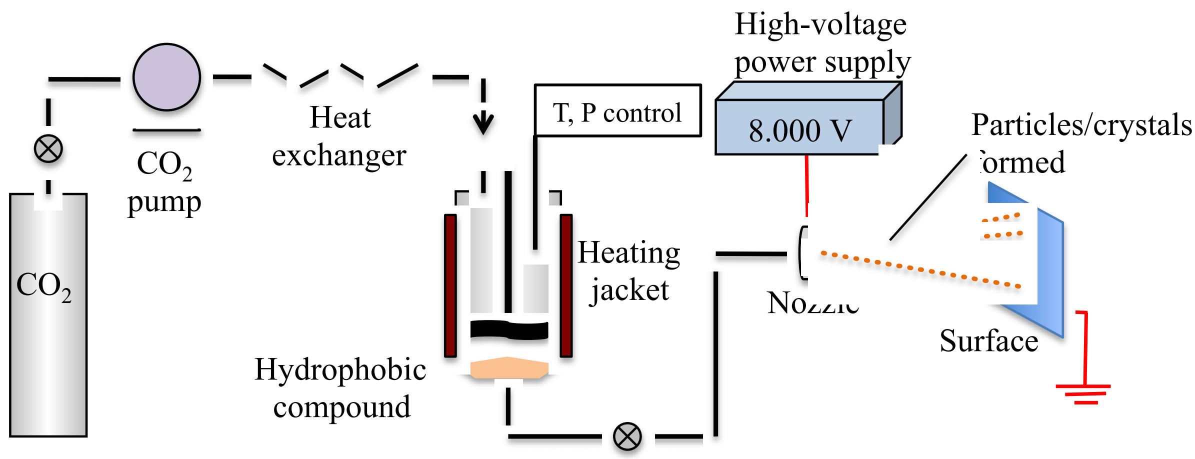


**Figure 2**: Schematic of RESS-ED equipment used in our research.

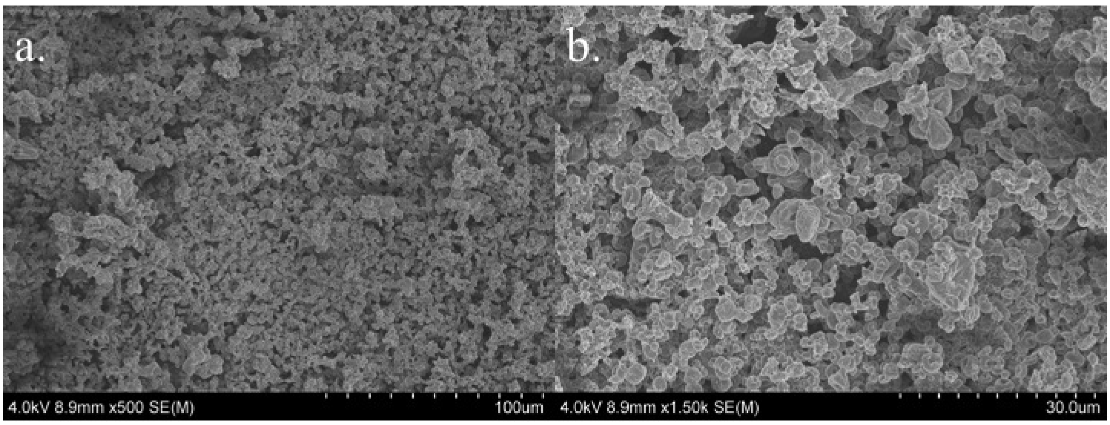


**Figure 3**: SEM images of 7.5 wt% solution of PVAc-PVPi sprayed at distance of 3 cm with the RESS-ED process at a magnification of 150 (a) and 1500 (b).

## CONCLUSION

Surfaces coated 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 betulin 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 improves the superhydrophobic properties of the surface. Superhydrophobic surfaces can also be prepared using a hydrophobic "$CO_2$-philic" polymer, PVAc-PVPi, using RESS coupled to electrostatic deposition, giving thinner, larger coating of excellent superhydrophobic water-repellent properties.

## AKNOWLEDGEMENTS

The Swedish Foundation for Strategic Research (SSF, RMA08-0044) and the Swedish Research Council (VR, 2010-333) are greatly acknowledged for financial support.

## REFERENCES


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

[2] 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). *Journal of Supercritical Fluids* **2012**, *67*, 53-59.

[3] 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. *Journal of Supercritical Fluids* **2012**, *61*, 25-33.

[4] Werner, O.; Quan, C.; Turner, C.; Wågberg, L.; Eriksson, J.-C., Method to prepare superhydrophobic surfaces on solid bodies by rapid expansion solutions, Patent: WO2009005465A1, **2009**.

[5] Ovaskainen, L.; Rodriguez-Meizoso, I.; Birkin, N. A.; Howdle, S. M.; Gedde, U.; Wagberg, L.; Turner, C. Towards superhydrophobic coatings made by non-fluorinated polymers sprayed from a supercritical solution. *Journal of Supercritical Fluids* **2013**, *77*, 134-141.

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

[7] 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.

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

[9] Werner, O.; Quan, C.; Turner, C.; Pettersson, B.; Wagberg, L. Properties of superhydrophobic paper treated with rapid expansion of supercritical $CO_2$ containing a crystallizing wax. *Cellulose* **2010**, *17*, 187-198.

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

[11] Ovaskainen, L.; Chigome, S.; Pettersson, T.; Torto, N.; Birkin, N. A.; Howdle, S. M.; Wagberg, L.; Turner, C. Superhydrophobic polymeric coatings produced by rapid expansion of a supercritical solution coupled with electrostatic deposition (RESS-ED). *manuscript in prep.* **2014**.