SUPERHYDROPHOBIC SURFACES PRODUCED BY SUPERCRITICAL FLUID TECHNOLOGY

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INTRODUCTION

Superhydrophobic surfaces are commonly described as surfaces that mimic the Lotus flower and its self-cleaning properties (*1;2*). A search in Web-of-Science Aug-11 on the topic "superhydrophobic surface" gives 2.340 hits of which 2.018 were published 2007 and later. An explanation to this trend could be that novel techniques combined with new theoretical understanding have made it possible to synthetically produce superhydrophobic surfaces.

More strictly speaking, the term superhydrophobicity (*3*) 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 slide with extremely 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.

There are many obvious applications of superhydrophobic and self-cleaning surfaces such as windows and environmentally exposed glass or lacquered surfaces (*4*) but if the technique could be applied to for example paper surfaces it is easy to envisage how new products can be prepared from this commodity product, for example, rain repellency coatings for boxes or breathable cover materials that will allow moisture penetration but prevent condensed water transport. Today most printing papers must be sized to an appropriate level so that the interactions between the paper and printing ink can be controlled (*5*), but this treatment only produces a lower degree of hydrophobicity with contact angles around 110 degrees for fully sized papers where the fibers have been saturated with sizing agent (*6*). These papers are non-absorbent but far from superhydrophobic and they will be wet through with water if the water drops are placed on the surface for a prolonged period of time.

There are several examples in the literature where superhydrophobic surfaces have been produced with wood fibers as a base substrate. In one of the existing examples (*7*), a highly fluorinated, tailor-made polymer has been grafted onto filter paper using organic solvents.

However, fluorinated compounds are harmful to the environment, and hence more sustainable alternatives would be an important development. Furthermore, grafting to fibers is a relatively tedious procedure involving several chemical treatment steps often involving organic solvents. Another recently investigated technique is to deposit titanium dioxide nanoparticles onto the paper (8;9).

The methodology investigated in the presented research utilizes a common sizing agent used in the paper industry, alkyl ketene dimer (AKD). Since the described process does not require organic solvents but only supercritical carbon dioxide (scCO2) as solvent, it is also an environmentally more sustainable method. The particle formation and deposition technology used is the Rapid Expansion of Supercritical Solution (RESS) process. This technique could potentially enable a much more convenient way of making paper and basically any other solid substrate, superhydrophobic.

In our previous research, we have produced superhydrophobic self-cleaning surfaces by dissolving hydrophobic compounds in scCO2, followed by spraying the solution through a pressure nozzle employing the RESS technique (10;11). To the best of our knowledge, this combination of RESS and waxes has not been tested before and it was therefore considered interesting and important to investigate if this way of crystallizing AKD could be used to induce superhydrophobicity to solid substrates. The only processes developed so far based on scCO2 technology for making superhydrophobic coatings are relatively slow and they utilize fluorinated polymers (12-14). What we have developed is a rapid process (only a few seconds) using environmentally friendly coating chemicals. In the presented research, we have studied the effect of different pre-expansion pressure and temperature as well as distance between the nozzle and the treated surface, with regard to particle morphology and size distribution. Laser diffraction measurements have been conducted directly perpendicularly to the spraying cone from the RESS system, providing information about the particle size distribution as a function of spraying distance. Thermography was also used to obtain information about the phase transfer of CO2 from liquid to gas in the spray.

MATERIALS AND METHODS

AKD granules (DR SF 300) with a mean particle diameter of approximately 4.5 mm containing a mixture of C_{18} AKD and C_{16} AKD were supplied by EKA Chemicals (Bohus, Sweden). Liquid carbon dioxide purchased from Air Liquide Gas AB (Eskilstuna, Sweden) was used in the RESS process. The surfaces used were 15mm×15mm pieces cut outs from polished silicon wafers (150 mm, CZ/1-0-0/BORON/P, MEMC Electronic Materials, Novara, Italy), which were cleaned with water/ethanol/water before use.

The RESS system used in this study was a simple in-house made 50 ml horizontal cylindrical pressure vessel connected to a sapphire nozzle of diameter 0.004" (Thar Technologies, USA) via a valve. The nozzle and the tubing were at all time heated to a temperature slightly above that of the vessel. The laser diffraction system used was a Malvern 1000 E with a 100 mm Fourier lens (Malvern Instruments, Ltd.). The RESS spray was directed through the laser beam. With the Fourier lens of 100 mm, optical diameter sizes between 0.2 and 120 μm can be detected. The evaluation software was Mastersizer X v2.19. See **Figure 1** for a schematic of the system.
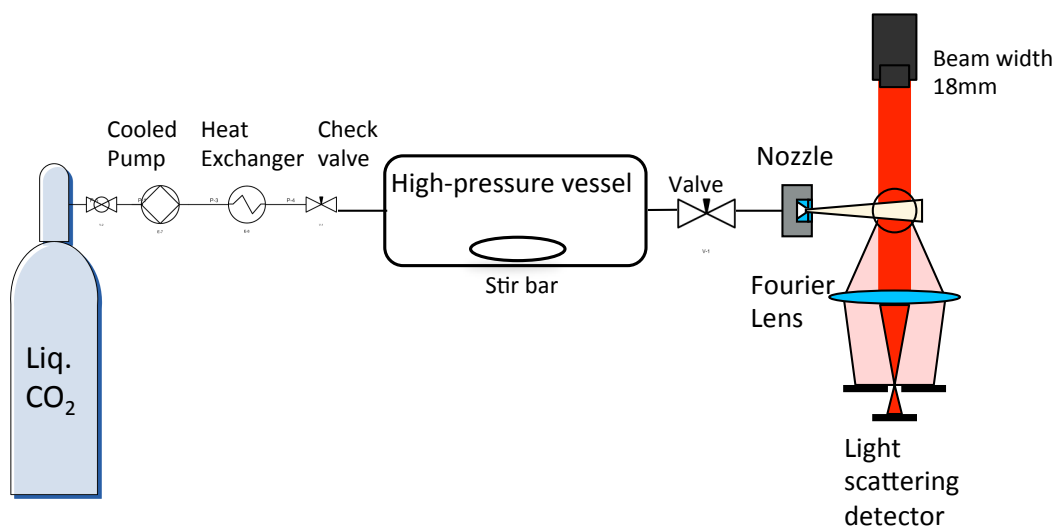
Figure 1. *Schematic of the RESS-laser diffraction system. SEM images were taken from surfaces produced at corresponding spraying distances, without the laser beam connected.*

Temperature has been measured in the spray cone. This has been done by spraying along a piece of thin sheet metal from which snapshots were taken with a Thermal Imager Ti30 by Fluke (Everett, Washington, USA) with the possibility to read temperatures from -15°C to 200°C. The metal sheet has been coated with ordinary scotch tape, which according to the manual of the instrument has an emissivity of 0.93 rendering it fairly close to a black body.

The SEM system used in this system was a LEO 1530 and the surfaces were sputtered with a 5 nm thick layer of gold/palladium before measurement. Contact angles were measured to study the hydrophobic properties of the AKD surface with the aid of a semi-automatic CAM200 contact angle system (KSV Instruments Ltd, Helsinki, Finland).

RESULTS AND DISCUSSIONS

A series sprayed at PET of 57°C and PET of 180 bar were measured at different distances from the nozzle using light scattering, as those conditions showed good repeatability and gave interesting results in initial tries. In order to separate the effect of the expanding CO2 from formation of the particles, measurements were also made on CO2 without dissolved AKD. **Figure 2** shows some of the obtained laser diffraction data as well as SEM micrographs.

For the blank (CO2 only) there is mainly a bell shaped peak at 10 μm. For the AKD samples a very sharp peak can be seen at around 2.5 μm for all the spray distances, but at longer distances a broader peak at around 6 μm is more pronounced. Thermography images revealed that the low temperature zone, for the selected pre-expansion state (57°C, 180bar) is approximately 60 mm long (data not shown). Since heavy cool down is depending on the phase transition of CO2 from liquid to gas, it is likely that 60 mm from the nozzle the phase transition is already complete. Hence, particles hitting the surface after traveling more than 60 mm will do so in a dry state while below 60 mm quite likely particles are still in liquid droplets of CO2.
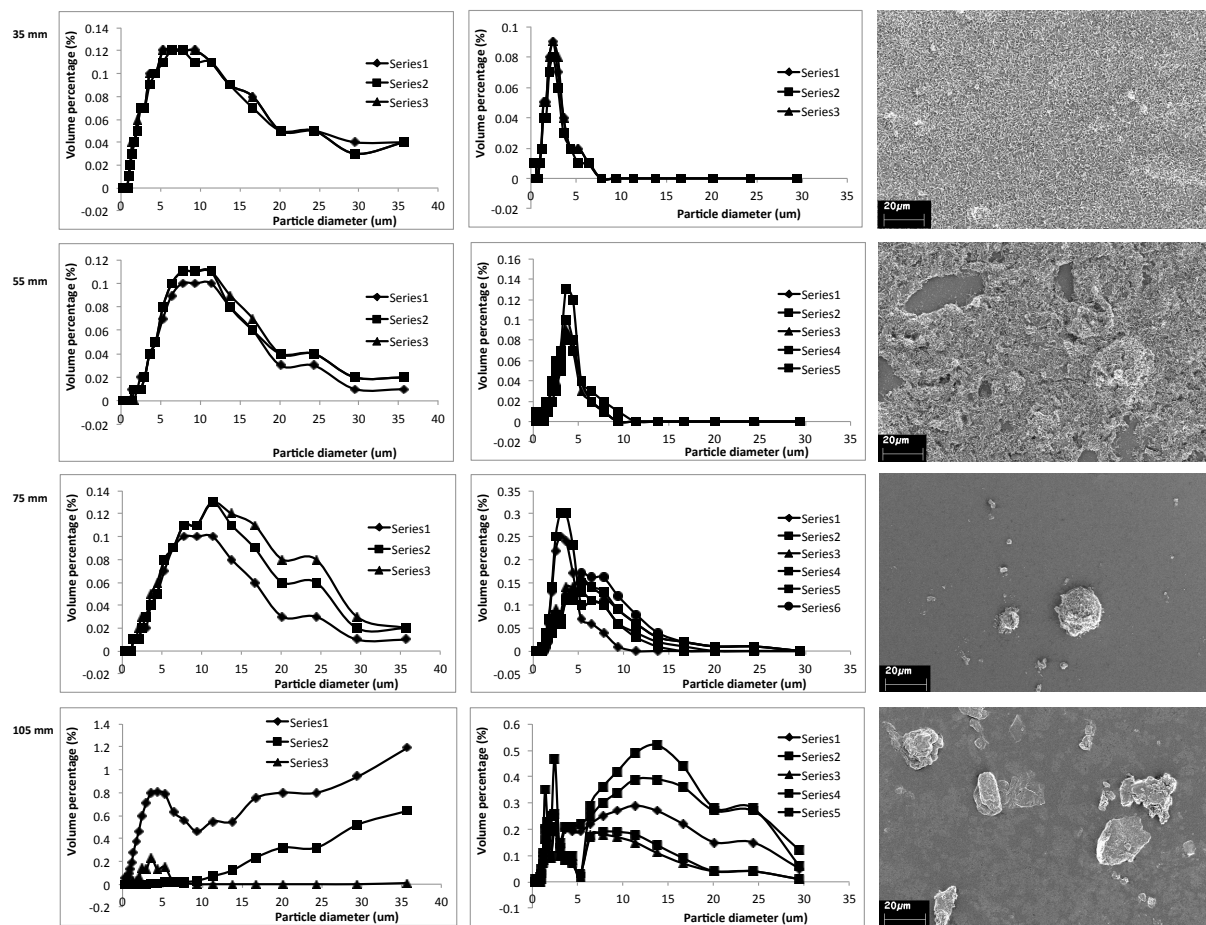
Figure 2. *Effect of spray distance on particle size distribution, as determined by laser diffraction. From top to bottom, the following spray distances were used: 35 mm; 55 mm; 75 mm; and 105 mm. To the right are SEM images showing representative parts of the respective sprayed surfaces.*

Comparing the SEM micrographs and diffraction data, the continuous surface seen for 35 mm and 55 mm correlates with the dominant peak at 2.5 μm. At longer spray distances, on the other hand, there was no continuous surface being produced, but rather unevenly distributed particles and particle agglomerates. This could be due to that dry particles are more difficult to capture on a surface, and that the small particles will not even reach this far, and if they do, they are spread out. The later assumption is supported by the diffraction data, showing that the 2.5 μm peak is not as distinct or repeatable at those longer distances.

In **Figure 3**, peak position (particle size) has been plotted against different pre-expansion temperature and density (pressure was varied between 90 and 200 bar). It is obvious that even though none of these parameters, within the experiments settings, can alone be set to hinder the formation of small particles, low temperature and high density is a prerequisite for the formation of mainly large ones.
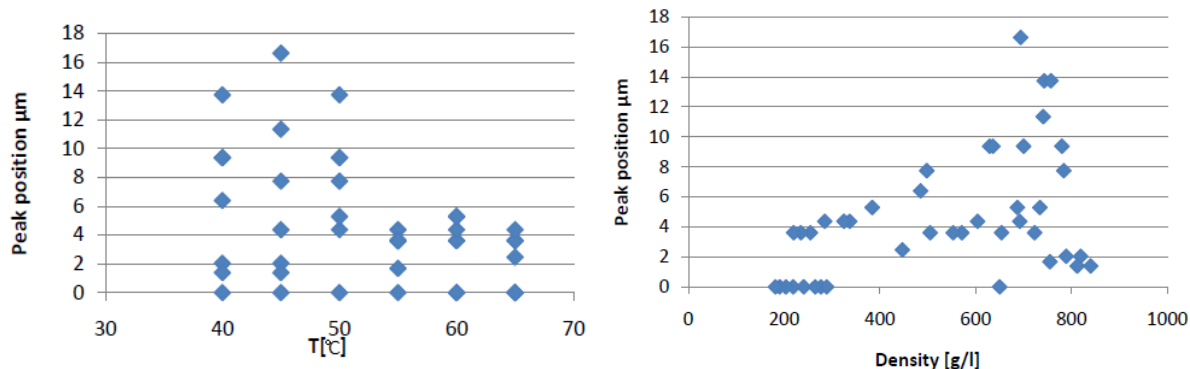
Figure 3. Peak size by laser diffraction as a function of pre-expansion temperature (left) and density (right).

Surfaces produced with high coverage of AKD crystals as discussed above are superhydrophobic, with static water contact angles of around 150-170°, see for example **Figure 4** below as well as our previous results in (*10*).
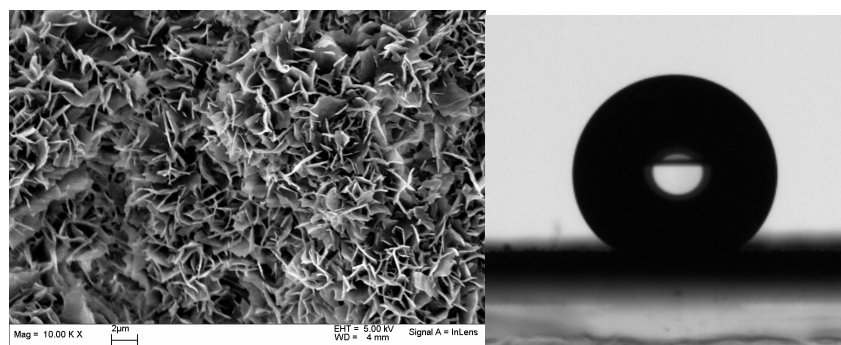

Figure 4. AKD-covered cellulose surface produced by RESS at 300 bar and 40 ℃, 100 mm spray distance. Obtained static water contact angle is 153°.

CONCLUSIONS

Light scattering data turned out to correlate well with SEM images when comparing the data obtained at different spray distances from the nozzle. A correlation could be seen for pre-expansion conditions producing smaller particles (as measured by diffraction) and a resulting evenly covered surface of small flakes (1-5 μm in diam.). By coupling data from SEM images, light scattering and thermography of the spray, conclusions could be drawn that at shorter distances CO_2 is still in liquid phase and enables efficient transportation and attachment of AKD crystals to the surface, while at longer spray distances, CO_2 is in gas phase and the formed particles are carried away aerodynamically without adsorbing to the surface.

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References

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

2. 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.

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

4. Yoshimitsu, Z.; Nakajima, A.; Watanabe, T. *et al.* Effects of surface structure on the hydrophobicity and sliding behavior of water droplets. *Langmuir* **2002**, *18*, 5818-5822.

5. Shen, W.; Zhang, H. L.; Ettl, R. Chemical composition of 'akd vapor' and its implication to akd vapor sizing. *Cellulose* **2005**, *12*, 641-652.

6. Wågberg, L. Polyelectrolyte adsorption onto cellulose fibres – a review. *Nord. Pulp Paper Res. J.* **2000**, *15*, 586-597.

7. Nyström, D.; Lindqvist, J.; Östmark, E. *et al.* Superhydrophobic bio-fibre surfaces via tailored grafting architecture. *Chem. Commun.* **2006**, *34*, 3594-3596.

8. Huang, L. H.; Chen, K. F.; Lin, C. X. *et al.* Fabrication and characterization of superhydrophobic high opacity paper with titanium dioxide nanoparticles. *J. Mater. Sci.* **2011**, *46*, 2600-2605.

9. Teisala, H.; Tuominen, M.; Aromaa, M. *et al.* Development of superhydrophobic coating on paperboard surface using the liquid flame spray. *Surf. Coat. Technol.* **2010**, *205*, 436-445.

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

11. Werner, O.; Quan, C.; Turner, C. *et al.* Properties of superhydrophobic paper treated with rapid expansion of supercritical co2 containing a crystallizing wax. *Cellulose* **2010**, *17*, 187-198.

12. Desbief, S.; Grignard, B.; Detrembleur, C. *et al.* Superhydrophobic aluminum surfaces by deposition of micelles of fluorinated block copolymers. *Langmuir* **2010**, *26*, 2057-2067.

13. Nikitin, L. N.; Gallyamov, M. O.; Said-Galiev, E. E. *et al.* Supercritical carbon dioxide: A reactive medium for chemical processes involving fluoropolymers. *Russ. J. Gen. Chem.* **2009**, *79*, 578-588.

14. Gallyamov, M. O.; Nikitin, L. N.; Nikolaev, A. Y. *et al.* Formation of superhydrophobic surfaces by the deposition of coatings from supercritical carbon dioxide. *Colloid J.* **2007**, *69*, 411-424.