Properties of Superhydrophobic Surfaces made by RESS Technique

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Abstract

The properties of superhydrophobic [1, 2] surfaces produced by Rapid Expansion of Supercritical Solvent (RESS) were studied. These surfaces were produced on paper surfaces by spraying alkyl ketene dimer (AKD, a wax commonly used in paper industry) dissolved in SC-CO_2 through a nozzle onto a moving paper substrate in ambient conditions [3, 4]. Pressure and temperature of the SC-CO_2 were optimized, giving a pressure of 200 bar and a temperature of 65 °C. The speed of the substrate and the distance between the nozzle and the substrate were varied. The surfaces were studied with Scanning Electron Microscopy (SEM) and contact angle measurements to water. In the whole production parameter range the procedure resulted in a coating consisting of merged evenly sized flaky particles. A combination of high surface roughness and a hydrophobic material, as AKD, is important when creating a superhydrophobic surface [1,2]. The spraying distance showed to be of importance, with distances below 60 mm giving complete surface coverage while distances above 100 mm giving an incomplete surface coverage. The developed method is robust and repeatable, giving surfaces with water contact angles above 160 °.

Introduction

Superhydrophobic surfaces, often exemplified by the leaf of the sacred lotus (*Nelumbo nucifera*)[5], which with their ability to stay dry and clean in wet and dirty environment quickly attained a lot of attention.

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A lot of theory on the subject exist, at least seven review articles have been published on the subject only during the year of 2008 including [6–8], but generally it can be said that superhydrophobicity depends on an interplay between the surface roughness and a hydrophobicity of the used material.

In recent works by the authors, [3, 9], methods to render paper superhydrophobic with the inexpensive and common chemical Alkyl Ketene Dimer (AKD), commonly used in the paper industry to make paper less prone to absorb water [10] which has earlier proven to be a useful substance to prepare superhydrophobic surfaces on glass [11, 12]. By the methods presented by the authors [3, 4] the most promising was the one based on the Rapid Expansion of Supercritical Solvents(RESS) process[13, 14]. In the RESS process a solute dissolved in supercritical solvent is typically sprayed through a nozzle. As the pressure is decreased the solvent strength decrease and the solute precipitate into a powder which is later collected. In the present method the spraying nozzle is instead directed towards a target surface mounted on a X-Y table so that the surface is coated by the particles which merge into a film. Unlike similar methods[15] the present method do not use any fluorinated compounds.

The here presented method works on a wide variety of materials including but not limited to stainless steel, wood and , a variety of polymers e.g. Poly(methyl methacrylate) a.k.a. acrylic glass and High-Density PolyEthylene. In this work, however paper is chosen as it is cheap, renewable and has good mechanical properties, especially high specific stiffness, and the main weakness of paper, especially compared to plastics, is the great sensitivity to water and moisture. It is not clear in which paper products superhydrophobicity could be best utilized but for different packaging products, where paper is exposed to water the technique should, be of interest. [16, 17].

Materials and methods

Materials

AKD granules (DR SF 300) containing a mixture of C18 AKD and C16 AKD were supplied by EKA Chemicals (Bohus, Sweden). The paper used was, uncoated whitetop craftliner, of the type Korsnäs Classic supplied by Korsnäs (Gävle, Sweden)

Sample preparation

The samples where prepared using a Bench scale RESS unit(SFE-MR 500) Thar Technologies(Pittsburgh,USA) The AKD was dissolved in supercritical CO_2 at 65°C and 200 bar. The AKD-CO_2 solution was sprayed through a sapphire nozzle with 0.004" inner diameter, onto paper substrates mounted on a computer controlled x-y table, Arrick robotics (Tyler,USA) moving in the pattern 5cm right, 3cm down, 5cm left 3cm down, etc, (Figure 1) at constant speed along the path. This

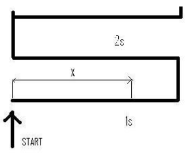

Figure 1: The sprayed path on the sample paper. For a table speed of X cm/s the sample point marked *1s* and *2s* will be at x cm and 2x cm from the starting point.

for the sprayed path to not overlap itself, if the vertical step is lowered, a continuous superhydrophobic surface will be produced. The x-y table was placed at various distances from the nozzle, spraying distance, and its speed speed was changed between the experiments.

Measurements

Contact angles were measured with a CAM200 contact angle metre (KSV-instruments Helsinki, Finland) with automatic dispenser. Static contact angle measurements with 5 µl droplets of MilliQ deionized water was conducted. The contact angle used in this work was a mean value for the left and right angle of five images of each droplet.

SEM images were taken with a Hitachi FE-SEM, Hitachi, Japan. The samples was unsputtered.

Results and discussion

The two varied variables in this study is the spraying distance and the speed of the x-y table. The distance were varied between 2cm and 10cm and the speed was varied between 5 cm/s and 14 cm/s. (Table 1In this interval a selection points made using MODDE software, Umetrics (Umeå, Sweden.), to facilitate future statistical treatment of the data. Contact angle measurements were made on the paper at positions where it hade passed the spraying nozzle after 1s and 2s respectively measured from the opening of the valve between the pressurized cell and the nozzle. This is of interest as the process is of batch type and the solute concentration will decrease with time when SC-CO_2 is pumped into the cell to maintain the pressure throughout the spraying process. One important factor is the deposited material per area unit. This will decrease with spraying distance, spraying time and speed of the x-y table. This is seen in the Table 1 but it may also be noted that for the samples with spraying distance of 2 cm the contact angle is lower for the samples with the slower table-speed. In the SEM images shown in Figure 2 it shows that the surface coverage is not complete for the samples C2 and C3.

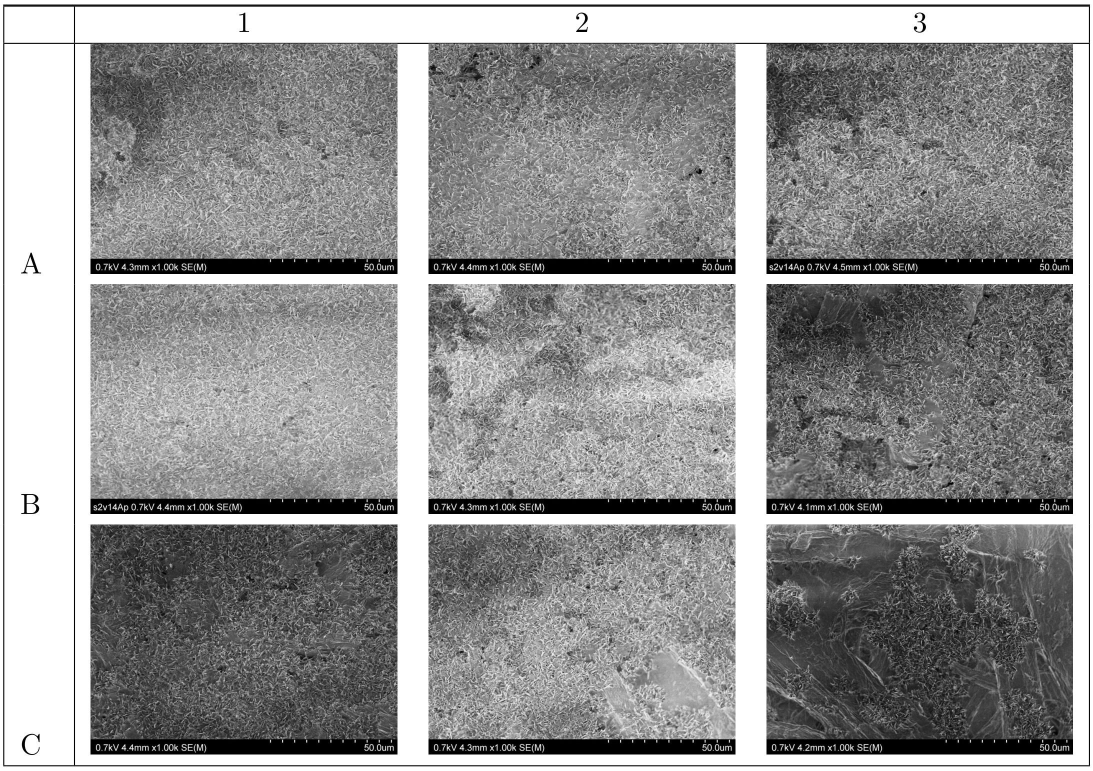

Figure 2: Representative SEM images in 1000X for the surfaces sprayed after one second. The sample label referring to 1 can be read from the rows and columns in the figure. Even if one should be careful not to draw to many conclusions from a individual pictures one may note the lesser surface coverage in C2 and C3 corresponding to the longest spraying distance seen in Table 1.

sample label	Distance, nozzle to target[cm]	Speed of x-y table[cm/s]	Contact angle for area sprayed after 1 s	Contact angle for area sprayed after 2 s
A1	2	5	160°	163°
A2	2	5	157°	165°
A3	2	14	170°	167°
B1	2	14	170°	172°
B2	6	9.5	161°	161°
B3	6	9.5	165°	160°
C1	6	9.5	150°	155°
C2	10	5	161°	130°
C2x	10	5	162°	no value measured
C3	10	14	142°	142°

Table 1: Contact angles for water measured on the samples taken on areas corresponding sprayed after 1 s and 2 s respectively. SEM images for some of the samples is seen in 2

Conclusions

It is possible to use the here presented method to produce superhydrophobic surfaces without any fluorinated compounds or organic solvents. The distance between the nozzle and the target is an important factor. The contact angle is correlated to the amount of deposited material per area unit but not for all cases. Clearly much optimization work remain.

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