Superhydrophobic Surfaces Produced by Rapid Expansion of a Supercritical Solution Containing Wax

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In the presented study, superhydrophobic alkyl ketene dimer (AKD) surfaces were successfully produced on untreated paper surfaces by a Rapid Expansion of Supercritical CO_2 Solution (RESS) process [1-2]. The new method resulted in a degree of hydrophobicity, as measured by contact angles of water droplets on AKD surfaces, dramatically higher, up to 173°, compared to a conventional method consisting in melting AKD granules directly on the paper substrate, giving contact angles of around 109°. Experiments were conducted to investigate the effects of varying pre-expansion pressure (100-300 bar), pre-expansion temperature (40 and 60°C) and spraying distance (10 and 50 mm) on the properties of the treated surfaces. The surfaces were analyzed regarding AKD particle size, surface morphology and hydrophobicity with the aid of scanning electron microscopy (SEM) and contact angle measurements. The average particle diameter of the original AKD granules was approximately 4.5 mm, while the mean particle size after micronization via the RESS process was between 1 and 2 µm, depending upon the experimental conditions used. The average particle sizes of collected AKD particles were slightly smaller when using higher pre-expansion pressure and temperature as well as smaller spraying distance.

INTRODUCTION

During the last few years there has been a large interest in superhydrophobic surfaces and superhydrophobicity since new techniques and new theoretical understanding have made it possible to synthetically produce superhydrophobic surfaces that can mimic for example the Lotus flower and its self-cleaning properties [3, 4].

The term superhydrophobicity [5] 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 [6] 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 [7, 8], but this treatment only produces a lower degree of hydrophobicity with contact angles around 110 degrees for fully sized papers where the fibres have been saturated with sizing agent [9]. 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 few examples in the literature where superhydrophobic surfaces have been produced with wood fibres as a base substrate. In one of the existing examples [10], 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 fibres is a relatively tedious procedure involving several chemical treatment steps often involving organic solvents. The technique investigated in the presented research utilizes a common sizing agent used in the paper industry, alkyl ketene dimer (AKD) and also other waxy substances, e.g. stearic acid and stearine. Since the described process does not require organic solvents, it is also an environmentally more sustainable method.

One way of producing micro or nano-particles from nonpolar compounds such as waxy materials is the Rapid Expansion of Supercritical Solutions (RESS) process. This technique could potentially enable a much more convenient way of making paper and basically any other solid substrate, superhydrophobic. 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 process so far using SC-CO_2 as a solvent for making superhydrophobic coatings has been described by Gallyamov [11], but in this work fluorinated polymers have been used in a relatively tedious procedure taking several hours per coating. What we have developed is a rapid process (only a few seconds) using environmentally friendly coating chemicals.

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). Acetone (Tamro Medlab AB, Göteborg, Sweden) was used as organic solvent for solvent crystallization. Cryogenic grinding was performed manually in a mortar with liquid nitrogen (AGA, Stockholm, Sweden). Liquid carbon dioxide purchased from Air Liquide Gas AB (Eskilstuna, Sweden) was used in the RESS process.

A bench-scale RESS unit (SFE-MR 500) from Thar Technologies (Pittsburgh, USA) was used for making the surfaces. A certain amount of AKD granules (typically 300 mg) was firstly loaded into the 100-mL stainless steel pre-expansion vessel which temperature (T_{pe}) was controlled by a heating jacket. Liquid carbon dioxide cooled to around 4°C was delivered into the 100-mL vessel at about 60 bar and compressed to the predetermined pre-expansion pressure (PE, 100-300 bar) by a high pressure pump. The AKD granules were then dissolved in SC-CO_2 during agitation, and the AKD-CO_2 solution was sprayed through a sapphire nozzle into an expansion chamber at atmospheric pressure. Particles were collected directly on a SEM target substrate inside this chamber, which was then taken for further characterization.

Particle size and morphology of the sample specimen was analyzed by scanning electron microscopy (LEO 1550 EDS/OPAL/EBSD/STEM, Zeiss, Thornwood, USA, and Hitachi S-4300 FE-SEM, Hitachi, Japan) after coating with a thin Gold/Palladium film with the aid of a sputter coater SC7640 (Quorum Technologies, UK). 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

The effect of the pre-expansion pressure on the size of the AKD particles was tested at four different pressures (100, 150, 200 and 300 bar). Throughout the experiments, both the pre-expansion temperature (T_{pe}) and the temperature of the expansion chamber (T) were held constant at 60°C. The AKD particles were then sprayed onto a non-sized, i.e. a hydrophilic paper, through a sapphire nozzle for 10 seconds using a spaying distance of 10 mm. The SEM micrographs of the AKD particles and their particle size histograms with estimations of the mean particle size, a (µm), and standard deviation, d (µm), in normal distribution mode N(a, d), as calculated by Matlab are shown in Figure 1. As shown, the AKD mean particle size decreases from 2.2 µm to 1.3 µm when increasing the pressure from 100 bar to 300 bar.

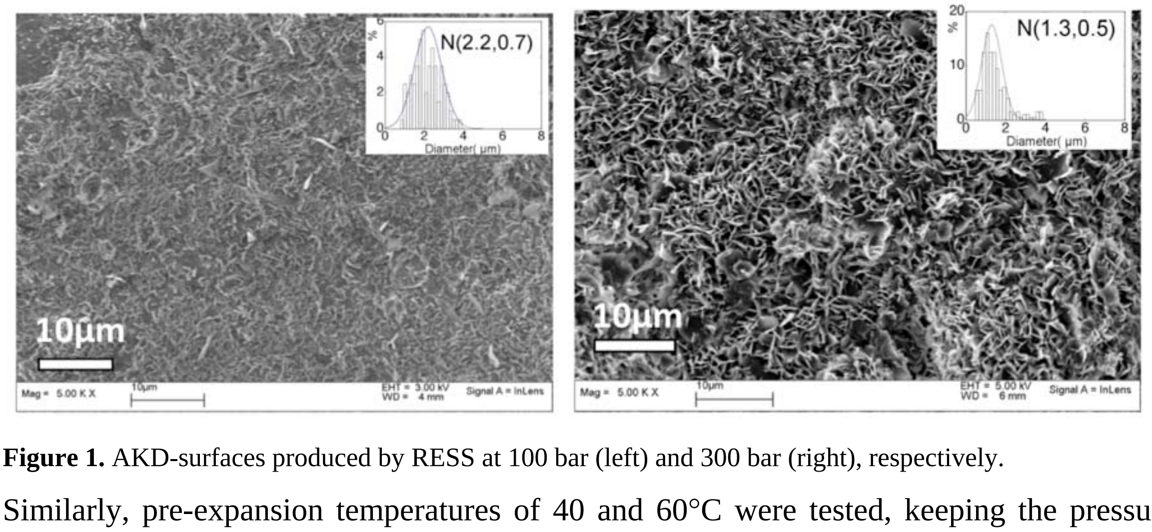

Figure 1. AKD-surfaces produced by RESS at 100 bar (left) and 300 bar (right), respectively.

Similarly, pre-expansion temperatures of 40 and 60°C were tested, keeping the pressure at either 200 or 300 bar. The results show that somewhat larger particles were produced at lower pre-expansion temperature (data not shown). Furthermore, results showed that the surface coverage decreased with shorter spraying distance, which also resulted in smaller contact angles to water.

A typical AKD surface made with the RESS technique is shown in Figure 2 at different SEM magnifications. It can be seen that the porous AKD surface consists of randomly aligned flakes and that there are also a few relatively large particles consisting of aggregated flakes which are distributed as separate entities on the surface forming valleys along their sides thus creating a rough film. Figure 2c shows the image of a typical large agglomeration of particles and in Figure 2d a magnified image of typically obtained flakes is shown, clearly demonstrating how the flakes are partially collapsed to form pores, thereby giving a relatively uneven surface. From the images it can be suggested that the formed AKD particles consist of crystalline AKD flakes that are aggregated to larger entities. Another suggestion is that they have grown in a fractal pattern. Such a scenario can be supported by the results from Onda et al. [12], who report AKD-crystals grown from a melt to have fractal morphology. Whatever is the case, different levels of hierarchy are known to enhance superhydrophobicity [13].

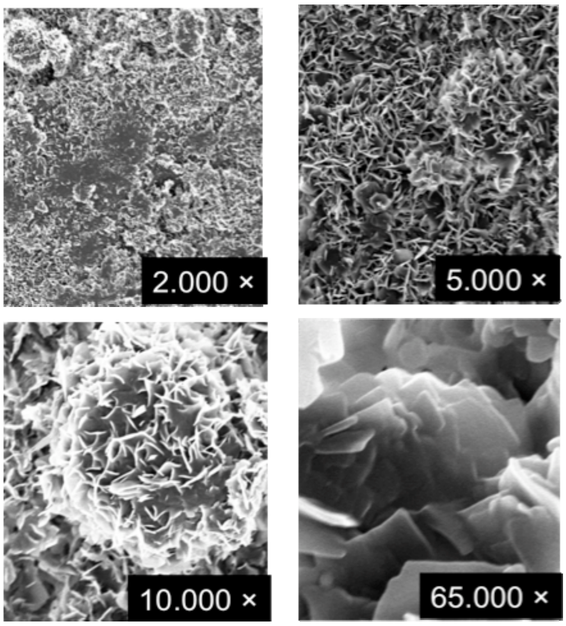

Figure 2. AKD surface produced by RESS at 300 bar, 60°C and 10 mm spraying distance at magnifications of 2.000x (a) ; 5.000x (b) ; 10.000x (c) ; and 65.000x (d).

Hydrophobicity of the surfaces was measured by determining static water contact angles of a 5-μL water droplet towards the surface (see Figure 3a). Figure 3b shows the water contact angle on a surface produced by melting AKD on an untreated paper surface, i.e. 109.0 ± 1.0°, which is not surprising since AKD is an inherently hydrophobic material. However, the results in Figure 3c and d reveal that the AKD surfaces generated by RESS spraying on untreated paper and paper roughened with an emery cloth have contact angles to water of 153.0 ± 1.0° and 172.0 ± 1.0°, respectively. Both these values are higher than 150°, and when a drop of water was placed on these surfaces, it was rolling rather than sliding off when the surface was tilted. In conclusion, this means that superhydrophobic surfaces can be successfully formed by a RESS process. This is most probably due to the fact that the AKD structure formed by the RESS process is a combination of a flaky structure and larger-scale unevenness as described in Figure 2. The structures formed by RESS were more uneven than the AKD melted surfaces (data not shown).

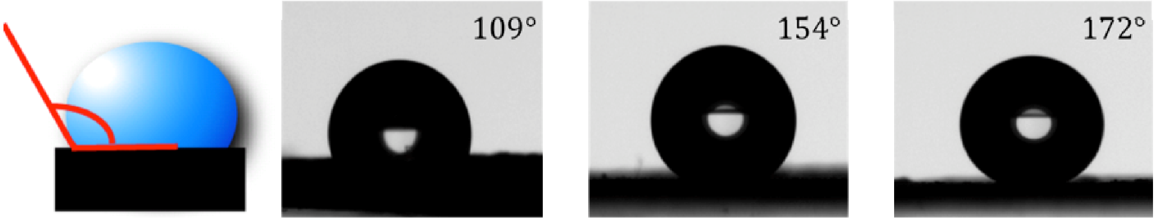

Figure 3. The principle for water contact angle measurements (a); and water contact angles obtained for 5-µL water droplets on surfaces produced by melting AKD on a paper surface (b) and by spraying AKD using the new RESS process on untreated paper (c) as well as roughed paper (d). RESS conditions: 300 bar, 40°C, 10 mm spraying distance.

CONCLUSIONS

AKD flake-like particles with sizes ranging from about 1 to 2 µm have been successfully produced by a RESS process. The effects of RESS operating parameters on the AKD particle size has been studied extensively: higher pre-expansion pressure and pre-expansion temperature, as well as a shorter spraying distance, resulted in smaller average particle size of the collected AKD. AKD flakes and aggregates of AKD flakes formed in the process resulted in a porous structure, which together with the high intrinsic contact angle of the AKD, induced superhydrophobic properties to the target surface. The average contact angles to water were above 150 degrees for all the different conditions tested in the experiments. Furthermore, the method showed high reproducibility as more than 80 experiments were performed, all giving surfaces with contact angles above 150 degrees. Preliminary tests has also been performed with stearic acid [$C_{18}H_{35}O_2$] and stearine [$C_3H_5(C_{18}H_{35}O_2)_3$] with good results.

This is, to the knowledge of the authors, the first time that RESS technique has been used to produce superhydrophobic micro-structured surface textures. The new method is fast and more environmentally sustainable than most other current techniques for producing superhydrophobic surfaces, as it utilizes no fluorine compounds and no organic solvents.

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