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Investigation of different particle sizes on superhydrophobic surfaces made by rapid expansion of supercritical solution with in situ laser diffraction (RESS-LD)

Oskar Werner[a], Charlotta Turner[b,*]

[a] Department of Physical and Analytical Chemistry, Uppsala University, P.O. Box 599, SE-751 24 Uppsala, Sweden
[b] Department of Chemistry, Centre for Analysis and Synthesis, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden

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ABSTRACT

In situ laser diffraction, scanning electron microscopy (SEM) imaging, and thermography have been used to investigate particle formation and particle size distribution of alkyl ketene dimer (AKD) produced by rapid expansion of supercritical solution (RESS). The investigated RESS process is based on an earlier reported method to prepare superhydrophobic coatings. Spray distance, pre-expansion temperature and pressure have been varied and the results from the methods have been compared. SEM images and light scattering data correlate well, and show that the mean particle size increased and the size distribution became significantly broader with increasing spray distance. Mean particle diameters of above 5 μm were only observed for pre-expansion temperatures at 50 °C or below. Furthermore, results show that by placing the surface to be coated within the cold expansion zone of carbon dioxide (CO_2), i.e. in this study at 55 mm or shorter for a pre-expansion temperature (T_{pe}) and pressure (P_{pe}) of 57 °C and 180 bar, respectively, will produce a surface evenly covered by 3-μm crystalline AKD flake-like particles. Obtained results also indicated, but did not prove, that agglomerates of AKD particles were carried to the surface by liquid CO_2 droplets in the jet.

1. Introduction

As one of the oldest particle formulation techniques involving supercritical solvents, rapid expansion of supercritical solutions RESS [1–3], has been used to produce particles of a wide array of substances. Even though the focus of particle formulation research in recent years has been moved from RESS to supercritical anti-solvent (SAS) and particles from gas-saturated solution (PGSS) [4], the former is still the preferred process in some cases because of its simplicity and organic solvent-free process. One example is when RESS is used for coating [5,6]. In Quan et al. [5], it is described how alkyl ketene dimer (AKD), a wax, was dissolved in supercritical carbon dioxide ($scCO_2$) and sprayed onto paper surfaces, in order to make them superhydrophobic. By spraying onto surfaces in ambient conditions rather than placing the objects to be treated in a depressurization chamber, treatment of larger surfaces is made possible. Furthermore, this enables the process to be continuous, for example as an extra step in a paper conversion plant. The solubility of AKD in $scCO_2$ varies heavily with pressure and density, but is in the region of a few mg/g for the conditions applied in this study. A thorough investigation of solubility of AKD in $scCO_2$ can be found in Rodríguez-Meizoso et al. [7].

Our earlier works [5,6] showed that the produced surfaces had at least two levels of roughness. The smallest observed particles constituting the surface were flake-like and of the approximate size of 5 μm × 5 μm × 0.1 μm. Some of these particles appeared to be merged into larger agglomerates. The aim of the present study was to investigate the formation of these particles and particle agglomerates, as well as the resulting coated surfaces. In order to investigate the particle formation in the jet-cone between the nozzle and the surface, as well as the produced surfaces, the off-line method of SEM has been complemented with the in situ method of laser diffraction size measurements.

In situ methods to investigate the formulation of particles using supercritical techniques have earlier proved fruitful. Braeuer et al. [8] used Raman and elastic light scattering to obtain information on the formation of particles in a SAS process. The use of light scattering for the characterization of already produced particles, is frequently found in the literature, see e.g. [9]. However, light scattering as an in situ technique is less commonly used [10].

In this work, measurement at different pre-expansion conditions but also at different distances from the nozzle is performed to gain understanding of the time evolution of the jet, and thereby investigate if the aggregates mentioned above are really aggregates from smaller particles and if so, where in the jet they are formed [11]. Obtained data was complemented with SEM images and thermal imaging.

* Corresponding author. Tel.: +46 46 222 8125; fax: +46 46 222 8209.
E-mail address: Charlotta.Turner@organic.lu.se (C. Turner).

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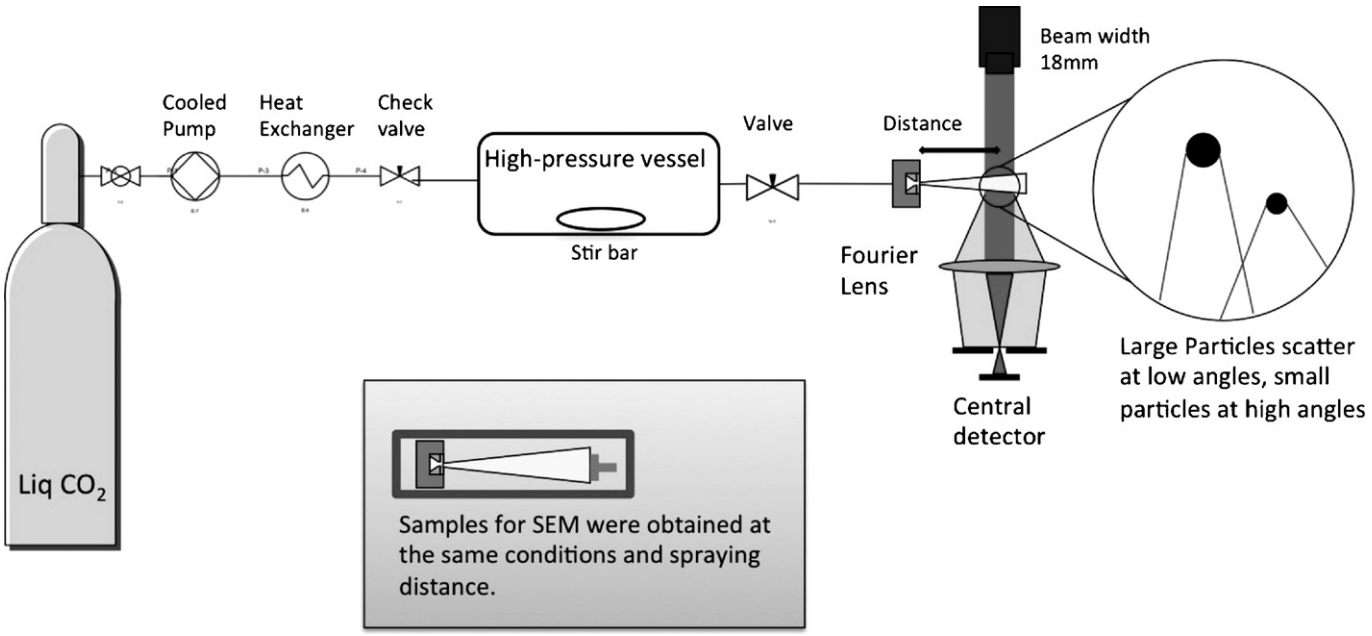

Fig. 1. Schematic of the RESS system used.

2. Materials and methods

The AKD used was SF-300, in pellet form, obtained from EKA Chemicals, Sweden. Carbon dioxide was of N-40 grade from Air liquid. The surfaces used were ca. 15 mm × 15 mm 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.

2.1. RESS system

The RESS system used in this study was a simple in-house made 50 ml horizontal cylindrical pressure vessel connected to a conical sapphire nozzle of inner diameter 0.10 mm and inner length/diameter (L/D) ratio of 1 (Thar Technologies, USA) via a valve into ambient conditions. The pump used was a P-50 pump from Thar Technologies with a maximum flow rate of 50 g/min. The pump was set in pressure control mode. Prior to each experiment the vessel was loaded with an excess of AKD, pressurized, and heated. When pre-expansion conditions were reached the AKD was dissolved under stirring using a magnetic stir bar. The nozzle and the tubing were during the whole experiment heated to a temperature slightly above that of the vessel. The vessel was continuously fed with $scCO_2$ during the spraying via a check valve, and in this way the pressure and temperature were maintained at the cost of a slight (less than 15%) decreasing AKD concentration in the AKD/$scCO_2$ mixture during the 10 s of spraying. As a rough estimate, the AKD concentration was at or near saturation in $scCO_2$ during the spraying, i.e. between 1 and 3 mg/g [7], depending on the P_{pe} and T_{pe}. The setup is shown in Fig. 1.

2.2. Laser diffraction system

The laser diffraction system used was a Malvern 1000 E with a 100 mm Fourier lens (Malvern Instruments, Ltd.). The RESS jet was directed through the laser beam. With the Fourier lens of 100 mm, particles with optical diameter between 0.2 and 120 μm can be detected. The evaluation software was Mastersizer X v2.19. The instrument can also detect the obscuration level of the laser, i.e. how much the sample, in this case the jet, lessens the light intensity measured at the detector as compared to when no sample is present.

2.3. Thermography

Temperature has been measured in the jet cone. This has been done by spraying along an approximately 7 cm × 12 cm piece of thin sheet-metal mounted approximately 2 mm from the nozzle exit, parallel to and in the center of the jet. From this metal sheet, snapshots were taken with a handheld Thermal Imager Ti30 by Fluke (Everett, Washington, USA) with the possibility to read temperatures from −15 °C to 200 °C. The metal sheet was 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. A simple sketch of the setup is shown in Fig. 2.

2.4. Scanning electron microscopy (SEM)

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.

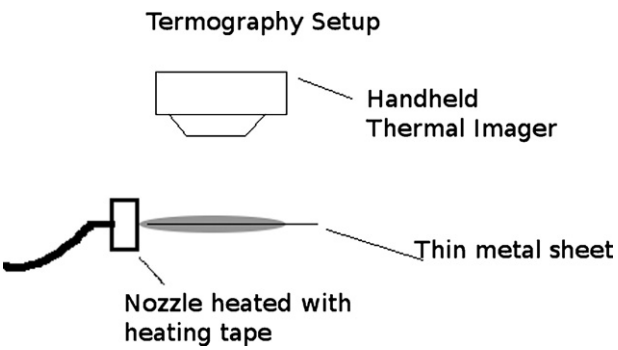

Fig. 2. Schematic of the thermography setup used.