Production of Superhydrophobic Surfaces by Combining the Rapid Expansion of Supercritical Solutions (RESS) Technique with Electrostatic Deposition

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ABSTRACT

The aim with the study was to create superhydrophobic surfaces by spraying a polymer with the rapid expansion of supercritical solutions- electrostatic deposition (RESS-ED) technique. This combination of spraying techniques implies that an electrical field was applied between the nozzle and the surface during spraying of the polymer particles. A copolymer of poly(vinyl acetate)-*stat*-poly(vinyl pivalate) (PVAc-PVPi) was used in the present study. The polymer concentration and the spray distance between the nozzle and the surface were varied in order to find the most suitable parameters for the production of superhydrophobic coatings. The surfaces were characterized in terms of their morphology and hydrophobic properties by scanning electron microscopy and contact angle measurements, respectively. Superhydrophobic coatings were produced at low spray distances and low polymer concentrations with the RESS-ED technique. These surfaces had water contact angles above 150° and the tilt angles varied between 5-11°. The main morphology of the coatings was particles with a broad size distribution, which is probably a contribution to the roughness of the surfaces and consequently the high contact angles. These results are promising for the creation of superhydrophobic surfaces with non-fluorinated polymers using the RESS-ED technique.

INTRODUCTION

The water repellence and the self-cleaning property is the main reason for the interest in superhydrophobic surfaces. These surfaces need to be rough on both a micro and nano scale for a water droplet to roll off the surface instead of sliding [1]. In order to classify a surface as superhydrophobic, the water contact angle should be above 150°, the contact angle hysteresis should be low (<10°) and the tilt angle (<10°) at which a water droplet rolls off a tilted surface should also be low [2].

Fulton et al. has developed the combined spraying technique of rapid expansion of supercritical solutions (RESS) and electrostatic deposition (ED) with the aim to produce superhydrophobic coatings [3]. They identified the challenge to collect the small particles produced in the RESS technique since some of the particles are lost when the carbon dioxide is expanded during the spraying phase. In their work, they produced superhydrophobic surfaces with RESS-ED on both flat and structured surfaces using fluorinated polymers.

In earlier work, superhydrophobic coatings were produced by spraying a copolymer of poly(vinyl acetate)-*stat*-poly(vinyl pivalate) (PVAc-PVPi) with the RESS technique [4]. The limitation with these surfaces was the poor spreading of the polymer particles since the particles pilled up in the centre under the spray nozzle and a few particles ended up in the outskirts, resulting in uneven coatings. The aid of electrostatic deposition was used in this work to improve the spreading of the polymer particles produced with the RESS technique. A high voltage was applied to the spray nozzle and the surface substrate was connected to ground in the combined RESS-ED spraying technique. The polymer concentration and the spray distance between the nozzle and the surface have been varied in order to find the most suitable conditions to produce superhydrophobic surfaces.

MATERIALS AND METHODS

Materials

Poly (vinyl acetate)- poly (vinyl pivalate) (PVAc-PVPi) of 10.4 kDa, ultra pure carbon dioxide (99.9 %) (AFROX, Johannesburg, South Africa) and acetone (Sigma Aldrich, Darmstadt, Germany) was used as received. Silica wafers (Electronic Materials, Novara, Italy) and aluminium foil were used to spray on for further analysis.

The RESS-ED equipment

The set-up of RESS-ED is schematically illustrated in Figure 1. The copolymer was dissolved in acetone and this solution was placed in a high-pressure vessel that was filled with $scCO_2$ at 40 °C and 300 bars. The nozzle was attached to a high voltage source and 8 kV was applied during spraying. The polymer particles were collected on a grounded surface at a distance of 3, 6 or 9 cm away from the nozzle.

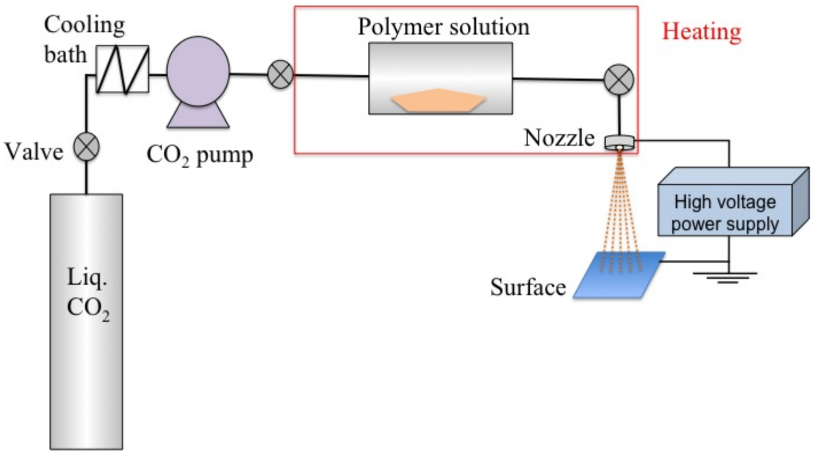

Figure 1: Schematic diagram of the RESS-ED set-up used in the spraying experiments

Characterization methods

A CAM200 contact angle meter (KSV instruments Ltd, Helsinki, Finland) with an automatic dispenser was used for the contact angle measurements. A field emission scanning electron microscope (FE-SEM) (Hitachi S-4800, Tokyo, Japan) was used to study the morphology of the sprayed surfaces.

RESULTS

The advancing and receding contact angles of a 5 μL water droplet, the hysteresis and the tilt angles of all the sprayed surfaces were measured to determine the wetting properties. All surfaces produced with RESS-ED had advancing and receding contact angles above 150°. The hysteresis (the difference between advancing and receding contact angles) was below 10° for all surfaces except a surface sprayed at 9 cm with a low polymer concentration. The surfaces made at a spray distance of 3 cm for all polymer concentrations had tilt angles below 11° at which the water droplet rolled of the surface, meaning that these surfaces have superhydrophobic properties. The surfaces made at higher spray distances had tilt angles of 10-27°. The surface morphology was studied with the aid of SEM. Clusters of particles with a broad size distribution were the main morphology for the surfaces produced by RESS-ED as shown in Figure 2. The smallest particles were less than 1 μm in diameter and the larger particles were in the size range of 2-10 μm. This broad particle size distribution is probably a contribution to the roughness of the surfaces and consequently the high contact angles.

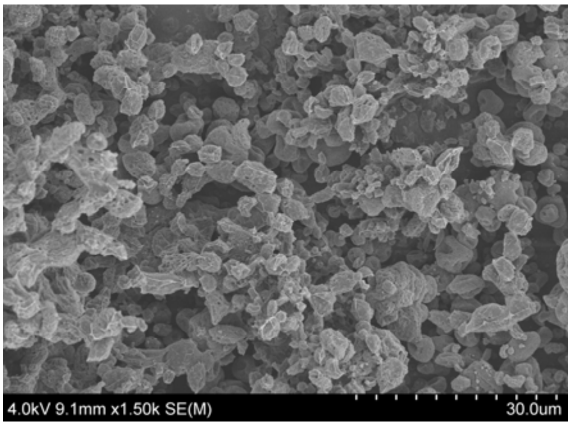

Figure 2: Scanning electron micrograph of PVAc-PVPi sprayed at 6 cm with the RESS-ED technique.

CONCLUSION

The RESS-ED technique has been used to produce superhydrophobic coatings by spraying a copolymer of PVAc-PVPi. Different spray distances and polymer concentrations have been investigated and superhydrophobic surfaces were made at short spray distances for all examined polymer concentrations. These results are promising for the creation of superhydrophobic surfaces with non-fluorinated polymers using the RESS-ED technique.

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