Superhydrophobic polymeric coatings produced by rapid expansion of supercritical solutions combined with electrostatic deposition (RESS-ED)

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1. Introduction

Superhydrophobic surfaces have gained a lot of interest due to their water repellent and self-cleaning properties which are also commonly identified as the “lotus-effect” [1]. A roughness on both a micro- and nanoscale and a low surface energy material are necessary conditions in order to mimic the properties of the lotus leaf found in nature [2]. Superhydrophobic surfaces are usually characterized by a water contact angle above 150°, a low contact angle hysteresis (<10°) and a low roll-off angle (<10°) at which a water droplet rolls off a tilted surface [3].

Electrospinning is a commonly used technique that relies on repulsive electrostatic forces to draw a polymer solution or melt into fibers [4]. An electrical field is applied between a spray nozzle and a collection plate and during spraying the solvent evaporates and the polymer solidifies on the collection plate. The process is called electrospaying when only particles are produced instead of fibers [5].

There are many examples in the literature on how to make superhydrophobic coatings from polymers by using the electrospinning process and one approach is to deposit a hydrophobic polymer, for example polysacrylene (PS) or a fluorinated polymer by electrospinning [6–10]. Kang et al. [7] produced superhydrophobic fibers of PS whereas Zhan et al. [6] electrospun PS from dimethylformamide (DMF) and produced mats which consisted of a mixture of fibers and particles having static water contact angles of above 150°. Other authors have succeeded in producing superhydrophobic surfaces by electrospinning hydrophilic polymers, for instance poly(hydroxybutyrate–co-hydroxyvalerate) (PHBV) from chloroform [11]. Smooth surfaces of PHBV had static water contact angles of 76° indicating that the polymer is rather hydrophilic. Rough surfaces with water contact angles of up to 158° were however produced by electrospinning this polymer [11]. It is also possible to incorporate nanoparticles or other additives in the polymer solution in the electrospinning process to increase the roughness and durability of the coating. For example, Menini and Farzaneh [12] dispersed polytetrafluoroethylene (PTFE) nanoparticles in poly(tetrafluoroethylene-co-vinylidene

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fluoride)-co-propylene] (PTVFP) and used electrospinning from ethyl acetate which resulted in static water contact angles of above 150°.

The use of supercritical carbon dioxide (scCO₂) as a processing aid in the electrospinning process has been modestly explored. Shen et al. [13] performed electrospinning of poly(vinylpyrrolidone) (PVP) from a dichloromethane (DCM) solution into a subcritical CO₂ environment at pressures below 5.5 MPa. Wahyudiono et al. [14] also performed electrospinning of PVP from DCM into near critical and supercritical CO₂ (40°C and up to 8 MPa) and found that CO₂ at these conditions improved the removal of DCM to produce dry fibers. Levit and Tepper [15] have also developed a method for electrostatically supported polymer fiber formation in a compressed CO₂ environment of polydimethylsiloxane (PDMS) and poly(L,L-lactic acid) (PLA). Fulton et al. [16,17] have developed a spraying technique of combining the rapid expansion of supercritical solution (RESS) with electrostatic deposition (ED) with the aim to spray different fluorinated polymers from scCO₂. The spraying conditions were varied depending on the polymer that was used, for example 245°C and 100 MPa were used when tetrafluoroethylene/hexafluoropropylene (TFE/HFP) was sprayed. The set-up was further improved by adding an emitter that gives the already charged particles in the nozzle an increased charge in order to increase the potential differential between the particles and the substrate [18].

In this work, we have used the same principle of applying an electrical field when spraying from RESS and we have used acetone as a co-solvent in the process to spray a specially prepared non-fluorinated copolymer. A charge emitter is not needed to increase the charge in the nozzle since acetone has higher electrical conductivity than neat scCO₂. The solubility of the copolymer is improved by using acetone as a co-solvent, which means that milder processing parameters (40°C and 30 MPa) can be used.

The aim of this project was hence to produce superhydrophobic coatings by using the RESS-ED technique by spraying a copolymer of poly(vinyl acetate)—poly(vinyl pivalate) (PVAc–PVPi). The RESS technique has been used in earlier work to produce superhydrophobic coatings by spraying a wax, alkyl ketene dimer (AKD) [19]. Since the wear resistance is an important factor to produce durable superhydrophobic coatings, the work was further developed to spray PVAc–PVPi with a continuous RESS process [20]. Superhydrophobic surfaces were produced [20] but it was a challenge to collect all of the sprayed polymer particles on the treated surface. As a consequence of this, it was not possible to coat areas larger than about 1 cm² with the copolymer. By combining the RESS spraying technique with electrostatic deposition, all of the sprayed particles should be attracted to the surface by the electrostatic forces. Secondly, since the particles are charged they will repel each other on the surface resulting in a thinner deposited layer and larger covered area for a certain amount of added polymer. Thirdly, since smaller solvent droplets are produced from the nozzle, evaporation of the solvent is more efficient, thereby avoiding organic solvent residues on the coating. In the present work, we investigate the factors controlling the morphology and coating appearance and how they can be suitable for creating a structured surface where the different length scales of the roughness can create a superhydrophobic surface in combination with the surface energy of the used polymer.

2. Materials and methods

2.1. Material

A block copolymer of poly(vinyl acetate)—poly(vinyl pivalate) (PVAc–PVPi), M₅₀ = 10.4 kDa (51:49) was specially prepared at the University of Nottingham and used as received [21,22]. Ultra pure carbon dioxide (99.9%) purchased from AFROX (Johannesburg, South Africa) and acetone from Sigma Aldrich (Darmstadt, Germany) were used as received. Silica wafers (type 150 mm/CZ/1-0-0) BORON/P-type, MEMEC Electronic Materials, Novara, Italy) were used as coating substrates and aluminium foil was used as the underlying substrate during spraying. The silica wafers were cleaned in MilliQ water, ethanol and acetone before use.

2.2. Equipment and experimental procedure

2.2.1. RESS-ED equipment

The set-up of the combined spraying techniques, rapid expansion of supercritical solutions and electrostatic deposition (RESS-ED) is schematically illustrated in Fig. 1. A stainless steel vessel (Applied porous technologies, Dalco Chromtech, Mästa, Sweden) of 2.4 mL capacity was used for the spraying experiments. The vessel was heated by a heating tape (type ELW-HS, IHP International Heating Products AB, Sävedalen, Sweden) and the temperature was controlled by a heat controller (ATR 243, PIXSYS Electronics, Venice, Italy). ScCO₂ was pressurized and delivered to the vessel by a syringe pump (Model 260D, ISCO, Teledyne, Lincoln, USA) which was cooled to approximately 5°C by a water bath. A piece of stainless steel tubing (Scan Tec Lab, Sävedalen, Sweden) with a length of 6 cm and an inner diameter of 0.12 mm was used as a nozzle. The nozzle was heated with the same heating tape as the vessel so that the temperature was kept constant throughout the entire experimental set-up. The nozzle was connected to the anode of a high voltage supply (EL40P1, Glassman High Voltage Inc., High Bridge, USA) and a voltage of 8 kV was applied during the spraying period. A stainless steel jack (20 cm × 20 cm) covered with aluminium foil was connected to ground and used as a collector.

2.2.2. Spraying of PVAc–PVPi with the RESS-ED set-up

Solutions of PVAc–PVPi dissolved in acetone were prepared at concentrations of 7.5, 15 and 25 wt% and approximately 0.5 mL of this mixture was placed in the vessel. The vessel was heated to 40°C and at a stable temperature, CO₂ at 30 MPa was then added to the vessel. This temperature and pressure were chosen based on a previous study [20] showing that PVAc–PVPi is soluble under these conditions. The valve before the vessel was closed and the connection from the pump was removed in order to avoid charge accumulation throughout the system as a preventive measure against damaging the syringe pump. The system was then left to equilibrate for approximately 30 min. After this time, a voltage of 8 kV was applied and the spraying was initiated by opening a valve to the nozzle. Silica surfaces of about 1 cm² were taped onto the aluminium foil that was wrapped on a stainless steel jack and were used to collect the particles on. The spraying was ended when the vessel was emptied. The spray distance between the
2.3. Mass balance of sprayed amount of polymer

The amount of polymer collected on the surfaces for both RESSED and RESS were investigated by weighing the surface substrates before and after spraying. Initially, 30 mg of PVAc–PVPi was dissolved in 0.5 mL acetone (7.5 wt% of polymer concentration) and this solution was placed in the vessel. The spraying experiment was then carried out as described earlier. A spraying distance of 6 cm was used for both spraying techniques. Aluminum foil was used as the collecting surface and was weighed before and after spraying. The experiments were repeated three times and the results are expressed as an average of these measurements. The standard deviation with a 95% confidence interval is also presented.

2.3. Characterization methods

2.3.1. Contact angle measurements (CAM)

A CAM200 contact angle meter (KSV Instruments Ltd., Helsinki, Finland) with an automatic dispenser was used for the contact angle measurements. A MilliQ deionized water droplet of 5 μL was initially placed on the coated surface with the syringe attached to the droplet. The measurements started with expanding the droplet by approximately 15 μL at a rate of 0.5 μL/s, and then the droplet was drained at the same rate. The droplet was expanded and drained during 70 s and one image per second was recorded by the CCD camera of the instrument which uses a mono-chromatic light source. The images were processed using the CAM200 software, applying the Young–Laplace fitting method to calculate the contact angles. The mean values of the left and the right contact angles of each measurement were used in a plot against the base diameter to obtain the advancing and receding contact angles.

The roll-off angles were measured by placing a 5 μL water droplet on the surface and then the stage was tilted until the water droplet rolled off the surface. A trigger function was used for the camera that captured an image when the droplet just started rolling. This image was processed in the software program by fitting a base line to the tilted surface and manually reading the roll-off angle of the base line. The base line can be tilted at steps of 0.1° so any error lies within this range. The contact angles and the roll-off angles were measured on three different places on the sprayed surfaces.

2.3.2. Scanning electron microscopy (SEM)

A field emission scanning electron microscope (FE-SEM) (Hitachi S-4800, Tokyo, Japan) was used to study the morphology of the sprayed surfaces. The samples were coated with a Pt/Pd layer of 12–28 nm thickness by an Agar High Resolution Sputter Coater (Model 208RH) before examination. The size of the particles was determined from the SEM images by using an image analysis software (NI Vision Assistant, Version 8.6.0, National Instruments).

2.3.3. Optical profilometer

An FRT MicroProf 200 noncontact optical profilometer (Fries Research & Technology GmbH, Bergisch Gladbach, Germany) was used to measure the thickness of the sprayed coatings. The instrument uses a high-resolution sensor based on confocal microscopy with chromatic aberration. White light is refracted on the sample surface and the reflected light is translated into a height position. A piece of tape was put on the half side of a silica surface to prepare the samples for the thickness measurements. After spraying on the taped silica surface, the tape was removed and the thickness was measured along the edge of the coating in an area of 2 × 2 mm². A software program, FRT Mark III (Fries Research & Technology GmbH, Bergisch Gladbach, Germany) was used to process the received data. A line fitting was done perpendicular to the coating edge in the surface topography image and height data was received as a function of the scanning distance over the surface. The line fitting was repeated five times for each scanned surface and the thickness of the coatings are expressed as an average of these five measurements with a standard deviation of 95% confidence interval.

3. Results and discussion

3.1. RESSED process considerations

Acetone was used as a co-solvent in this work since the solubility of polymers in general is very low in scCO2 [23,24]. An earlier study has been conducted showing that the PVAc–PVPi is soluble in a mixture of scCO2 and acetone at 30 MPa and 40 °C [20]. Vapor–liquid equilibria for carbon dioxide–acetone mixtures have previously been described with the Peng–Robinson equations of state (PR-EOS) [25]. This study showed that at 40 °C and a mole fraction of about 0.8 of CO2 (which corresponds to the amount of CO2 used in this work), the critical pressure for the mixture is slightly above 6 MPa. This means that the spraying experiments (30 MPa and 40 °C) were performed from a single phase of scCO2 and acetone. Kiran and Pöhler [26] have also examined the binary mixture of carbon dioxide and acetone and concluded that at high carbon dioxide content and pressures above the critical pressure for the mixture (12 MPa), the mixture is at the supercritical state. The spraying was done batch-wise to avoid charge accumulation through the system since 8 kV was applied to the nozzle. Consequently, the pressure in the vessel will decrease during spraying since the amount of scCO2 in the vessel is decreasing during the spraying process. This will lead to a phase separation of the scCO2/polymer/acetone in the vessel. After each spraying, there was a residue of acetone and polymer in the vessel, which indicates a phase separation. However, a significant proportion of the polymer was sprayed through the nozzle and the amount of polymer that was collected on the surface substrates was still enough to create coatings with superhydrophobic properties. In the RESSED process, the scCO2 undergoes a phase transition from the supercritical state to gas phase when leaving the nozzle. This transition occurs fast, close to supersonic velocities [27], with the effect that small particles are carried away with the gas. In this work, a voltage was applied to the nozzle and a charge is hence transferred through the liquid phase to the formed particles. When the particles leave the nozzle, they are forced to the earthed substrate by the charge gradient and will there form a thin film. As mentioned earlier, Fulton et al. [18] patented a nozzle that provides a second charge to the formed particles to improve the charge density due to the low electrical conductivity of scCO2. Since acetone was used as a co-solvent in the spraying experiments and since it has a higher electrical conductivity than scCO2, a better charge transfer to the particles can be assumed than when spraying from pure scCO2.

3.2. Mass balance of sprayed amount of polymer

The amount of polymer collected on the surfaces after spraying with RESSED and RESS are presented in Table 1 with the standard deviation (95% confidence interval) of the three measurements. On average, 5 mg of polymer ended up on the surfaces when using the RESSED technique. Only 0.7 mg of polymer was collected.
Table 1
The amount of polymer collected on a surface when spraying a 7.5 wt% solution of PVAc–PVPi at a spray distance of 6 cm for the RESS-ED and RESS process (30 MPa and 40°C). The amounts of polymer are an average of three measurements and the standard deviation (95% confidence interval) of these measurements is also presented.

<table>
<thead>
<tr>
<th>Process</th>
<th>Average amount of polymer on surface (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RESS-ED</td>
<td>4.9 ± 2.5</td>
</tr>
<tr>
<td>RESS</td>
<td>0.7 ± 0.4</td>
</tr>
</tbody>
</table>

when spraying was carried out with the RESS process. This is a low amount of polymer for both processes since 30 mg of polymer was initially placed in the vessel. After each spraying experiment a small amount of polymer solution was left in the vessel and most likely some polymer could also have precipitated in the tubing between the vessel and the nozzle as well as in the nozzle. The heating of the nozzle was disconnected just before spraying with RESS-ED in order to apply the voltage and this caused the nozzle to cool down during the spraying period. This needs to be improved in order to keep a constant temperature over the whole set-up during the spraying with the RESS-ED technique. Despite the lack of efficient heating, a larger amount of polymer ended up on the surface when spraying with the aid of electrostatic deposition compared to RESS.

A second reason for the lower amount of polymer on the surfaces could be that some of the polymer particles are lost somewhere in between the nozzle and the surface. The phase transition of scCO₂ is very rapid as mentioned earlier and this may cause the polymer particles to drift away with the CO₂ during the gas expansion. Since the solubility of the polymer in acetone and scCO₂ does not depend on the spraying technique, the loss of particles in the spray could be a reason for the lower amounts of sprayed polymer with RESS technique. It could also be that some particles are lost in the spray for the RESS-ED technique but since the applied voltage is the only difference between the two spraying techniques, it is very likely that the electrical gradient between the nozzle and the surface improves the collection of particles. Although not all of the polymer ended up on the surfaces during the RESS-ED spraying process, the amount of particles and the morphology of the coatings were still enough to produce superhydrophobic coatings.

3.3. Surface morphology

The main morphology for surfaces made with both RESS and RESS-ED were a mixture of agglomerates and particles. The particle size distributions were very broad for all sprayed surfaces and the smallest particles were in the size of 0.5–1 μm and the larger particles were 2–8 μm. The spray center of a RESS sprayed surface consists of large agglomerates covered with particles as shown in Fig. 2A (see Fig. 2B for a higher magnification). The RESS-ED coatings consist of agglomerates which are smaller in size and are more spread over the entire surface as can be seen in Fig. 2C and D. The agglomerates may either arise from particles stacking up together to form agglomerates or by acetone also ending up on the surface, which causes the polymer to dissolve again and then solidify in larger agglomerates.

The main difference for the two processes is the spray pattern that appears when spraying with RESS, with particles ending up in a pile directly under the nozzle. The RESS surfaces show larger polymer agglomerates in the center of the surface and a few polymer particles end up in the outskirts of the surface. A SEM image taken at this interface is shown in Fig. 3A. This spray pattern was also observed when spraying with RESS-ED at a spray distance of 3 cm and for a few times at 6 cm. However, the polymer particles are more spread out on the RESS-ED sprayed surfaces which creates a more even surface structure compared to RESS sprayed surfaces as shown in Fig. 3B.

More particles were collected at short spray distances for both processes but at a 9 cm spray distance, the surfaces made by the different processes differ significantly. More particles were collected at 9 cm when spraying with RESS–ED (Fig. 4A and B) and very few polymer particles ended up on the surface when spraying with RESS as can be seen in Fig. 4C and D. For the RESS sprayed surfaces

![Fig. 2. Scanning electron micrographs of PVAc–PVPi at a polymer concentration of 15 wt% and a spray distance of 6 cm, sprayed with RESS (30 MPa and 40°C) in (A) and (B) and sprayed with RESS-ED in (C) and (D). The left images show a magnification of ×150 and the right images show a magnification of ×1500.](image-url)
it seems like the polymer particles have been carried to the surface with the acetone as evidenced by the circular patterns seen in Fig. 4D. In an earlier study, the collection of wax particles sprayed from scCO2 with RESS was investigated [28]. It was concluded that few particles would be collected at large spray distance (>7.5 cm) since the CO2 is in the gas phase and formed particles are easily carried away with the gas. It is possible to collect small amounts of polymer particles when spraying with RESS at a distance of 9 cm while using acetone as a co-solvent in the process. Combining the RESS technique with electrical deposition is clearly an advantage to further improve the collection of sprayed polymer particles at high spray distances as can be seen in Fig. 4A. In this image it is also possible to see that there is no solvent pattern from the acetone, which indicates that the solvent has evaporated during the spraying.

All sprayed surfaces for both RESS and RESS-ED consist of collapsed particles as shown in Fig. 5A. The formation of these particles is due to differences in the concentration of the droplets in the spraying jet. The solvent evaporation is of course faster on the outer surface of the polymer/solvent drop than on the inside, which leads to the formation of a dry polymer layer on the outside. Further solvent diffusion causes the outer layer to wrap and forming the collapsed structures [11,29]. Spraying at 3 and 6 cm for the 7.5 and 15 wt% polymer concentration with RESS-ED resulted in a mixture of collapsed particles and particles with an uneven surface as shown in Fig. 5B. A few particles with this skin formation were observed for the RESS produced particles at the same parameters although collapsed particles were the main morphology. This morphology is most likely also an effect of solvent evaporation due to the fact that this skin formation was not observed at the highest polymer concentrations and at the largest spray distance. The fact that the particles showed a large variation in size and shape is no doubt an advantage when the aim is to produce superhydrophobic coatings [1]. This causes the desired roughness on both a micro- and nanoscale that has earlier been shown to be necessary to achieve a heterogeneous state of wetting [30].

3.4. Evaluation of wetting properties

The advancing and receding contact angles of a 5 μL water droplet, the hysteresis and the roll-off angles of all the treated surfaces are presented in Table 2 as mean values of three separate measurements on different positions on each surface as well as the
standard deviation (with a 95% confidence interval) for the average values. All the coatings sprayed with the RESS-ED technique at a distance of 3 cm showed superhydrophobic properties as can be seen in the high contact angles, low hysteresis and low roll-off angles of these coatings. Spraying at a distance of 6 cm with the RESS-ED technique resulted in a superhydrophobic coating for the 7.5 and 15 wt% polymer concentration but at the high polymer concentration (25 wt%), the water droplet got pinned to the surface and showed higher roll-off angles. Fig. 6 shows an example of a 5 μL water droplet on the surface with 7.5 wt% polymer concentration sprayed at 6 cm when measuring the contact angle. This increase in the roll-off angle is probably due to the creation of large aggregates with a sub-micrometer roughness that is too low and causes the droplet to pin to the surface. The surface with a polymer concentration of 15 wt% at a spray distance of 9 cm prepared with RESS-ED can also be classified as superhydrophobic whilst the coatings made at the other polymer concentrations also resulted in pinning of the water droplet when measuring the roll-off angle.

It was also possible to produce superhydrophobic coatings when spraying from RESS. All the surfaces made with a spray distance of 6 cm had high contact angles and low roll-off angles as well as the coating sprayed at 3 cm and a polymer concentration of 25 wt%. However, the coatings sprayed from RESS at a distance of 3 and 6 cm were not uniform. These coatings had a pattern from the spray-geometry resulting in a pile of polymer in the center of the jet leaving the nozzle. Due to this, the contact angles were measured outside the center of the surfaces since the spray center was not flat and uniform. The surfaces made with RESS at 9 cm spray distance contained a low concentration of polymer and the contact angles are therefore much lower for these surfaces. Consequently, the water droplet did not roll off at angles below 35°. It can also be observed in Table 2 that for the RESS technique, in general the

**Table 2**
The wetting properties (advancing and receding contact angles, hysteresis and the roll-off angles of water droplets) of the sprayed surfaces at different polymer concentrations and spray distances produced with the RESS-ED and RESS technique at 30 MPa and 40 °C. The values of the wetting properties are an average of three measurements and the standard deviation (95% confidence interval) of these measurements is also presented.

<table>
<thead>
<tr>
<th>Process</th>
<th>Spray distance (cm)</th>
<th>Polymer conc. (wt%)</th>
<th>Adv. CA (°)</th>
<th>Rec. CA (°)</th>
<th>Hysteresis (°)</th>
<th>Roll-off angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RESS-ED 3</td>
<td>15</td>
<td>7.5</td>
<td>165 ± 1</td>
<td>162 ± 1</td>
<td>3 ± 1</td>
<td>5 ± 0</td>
</tr>
<tr>
<td>RESS-ED 3</td>
<td>25</td>
<td>7.5</td>
<td>159 ± 2</td>
<td>157 ± 2</td>
<td>2 ± 0</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>RESS-ED 6</td>
<td>15</td>
<td>7.5</td>
<td>161 ± 2</td>
<td>159 ± 1</td>
<td>2 ± 1</td>
<td>10 ± 1</td>
</tr>
<tr>
<td>RESS-ED 6</td>
<td>25</td>
<td>7.5</td>
<td>153 ± 6</td>
<td>149 ± 7</td>
<td>4 ± 1</td>
<td>11 ± 5</td>
</tr>
<tr>
<td>RESS-ED 9</td>
<td>15</td>
<td>7.5</td>
<td>171 ± 2</td>
<td>157 ± 4</td>
<td>14 ± 5</td>
<td>18 ± 3</td>
</tr>
<tr>
<td>RESS-ED 9</td>
<td>25</td>
<td>7.5</td>
<td>162 ± 3</td>
<td>159 ± 1</td>
<td>3 ± 2</td>
<td>11 ± 2</td>
</tr>
<tr>
<td>RESS 3</td>
<td>15</td>
<td>7.5</td>
<td>167 ± 2</td>
<td>160 ± 5</td>
<td>7 ± 4</td>
<td>18 ± 6</td>
</tr>
<tr>
<td>RESS 3</td>
<td>25</td>
<td>7.5</td>
<td>164 ± 1</td>
<td>161 ± 1</td>
<td>3 ± 1</td>
<td>6 ± 2</td>
</tr>
<tr>
<td>RESS 6</td>
<td>15</td>
<td>7.5</td>
<td>163 ± 3</td>
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<td>12 ± 3</td>
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<td>RESS 6</td>
<td>25</td>
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<td>162 ± 5</td>
<td>159 ± 5</td>
<td>3 ± 2</td>
<td>10 ± 4</td>
</tr>
<tr>
<td>RESS 9</td>
<td>7.5</td>
<td>7.5</td>
<td>97 ± 5</td>
<td>77 ± 4</td>
<td>20 ± 8</td>
<td>-</td>
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<tr>
<td>RESS 9</td>
<td>15</td>
<td>7.5</td>
<td>110 ± 4</td>
<td>83 ± 3</td>
<td>27 ± 1</td>
<td>-</td>
</tr>
<tr>
<td>RESS 9</td>
<td>25</td>
<td>4.5</td>
<td>122 ± 21</td>
<td>96 ± 21</td>
<td>26 ± 3</td>
<td>-</td>
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</tbody>
</table>

* The 5 μL water droplet did not roll off at tilt angles up to 35°.
higher the polymer concentration (25 wt%) the better the wetting properties. This is probably linked to the amount of collected particles on the surface, and the same trend cannot be seen for RESS-ED.

3.5. Thickness measurements of the coatings

A selection of surfaces was analyzed by optical profilometer to determine the average coating thickness. A line fitting was made in the topography images received from the profilometer measurements in order to get the height data over the coating edge. Fig. 7 shows an example of a typical height plot for a RESS-ED sprayed surface at 3 cm and 15 wt% polymer concentration of PVAc–PVPi. An average value was calculated for the coating thickness of the height measurements from about 0 to 0.2 mm in the x-direction. As seen in the height plot, there is a deviant value close to the edge of the coating and this is probably attributed to the fact that the tape was removed manually, therefore the measuring points close to the edge were not included in the calculations. The height of the silica surface was also calculated as an average, over a number of data points in the right region of the plot. The number of data points used in the fitting varied depending on how the topography over the coating edge appeared but the aim was to use data with as little deviation as possible since some surfaces had some tape residuals or other impurities on the silica substrate that gave rise to height differences. Five different fittings were done for each surface and finally an average of these five heights were calculated as the coating thickness, as displayed in Table 3 together with the standard deviation (95% confidence interval) for the five thicknesses.

The coatings made by RESS-ED were thinner than the coatings made by RESS. The spray distance seems to affect the coating thickness for both spraying processes as the coating is thicker at short distances. The RESS sprayed surface at 3 cm has the highest thickness, which is probably due to the spray pattern that is created when spraying without an applied voltage. These measurements show that thinner coatings are produced when spraying under an applied voltage.

<table>
<thead>
<tr>
<th>Process</th>
<th>Spray distance (cm)</th>
<th>Thickness of coating (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RESS-ED</td>
<td>3</td>
<td>2.2 ± 0.4</td>
</tr>
<tr>
<td>RESS-ED</td>
<td>6</td>
<td>0.9 ± 0.6</td>
</tr>
<tr>
<td>RESS</td>
<td>3</td>
<td>7.3 ± 0.6</td>
</tr>
<tr>
<td>RESS</td>
<td>6</td>
<td>2.1 ± 0.3</td>
</tr>
</tbody>
</table>

4. Conclusions

In this work we have combined the RESS technique with electrical deposition to produce superhydrophobic surfaces by spraying a specially prepared non-fluorinated copolymer. Surfaces with superhydrophobic properties were produced when spraying at a distance of 3 cm with the RESS-ED technique for all investigated polymer concentrations. Spraying at 6 cm also resulted in superhydrophobic coatings for the polymer concentrations of 7.5 and 15 wt%. All these surfaces had advancing and receding contact angles of above 150° and roll-off angles below 11° at which a water droplet rolled of the surface. Mainly hydrophobic surfaces were produced at higher spray distances, demonstrated by the fact that the water droplet got pinned to the surface when measuring the roll-off angles although the contact angles were high. This was explained by the creation of large aggregates with low submicrometer roughness at these spraying distances, which caused droplet pinning, and loss of superhydrophobic properties. Superhydrophobic surfaces were also produced when spraying with the RESS technique (without an applied voltage) at a spray distance of 6 cm for all polymer concentrations. The limitation with the surfaces produced in RESS is that the coating is non-uniform since a spray pattern is developed during spraying resulting in a pile of polymer in the center and less polymer outside the center. More uniform coatings are produced with the RESS-ED technique and also larger areas can be coated with a certain amount of added polymer. Another advantage with the RESS-ED technique is that it is possible to spray at larger distances between the nozzle and the surface. Very few polymer particles ended up on the surface when spraying with RESS at 9 cm. Using the RESS-ED technique resulted in high contact angles for all polymeric surfaces sprayed at 9 cm. This work shows that applying a voltage during the spraying with the RESS technique can improve the collection and the spreading of the polymer particles and superhydrophobic surfaces can be produced.

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References


