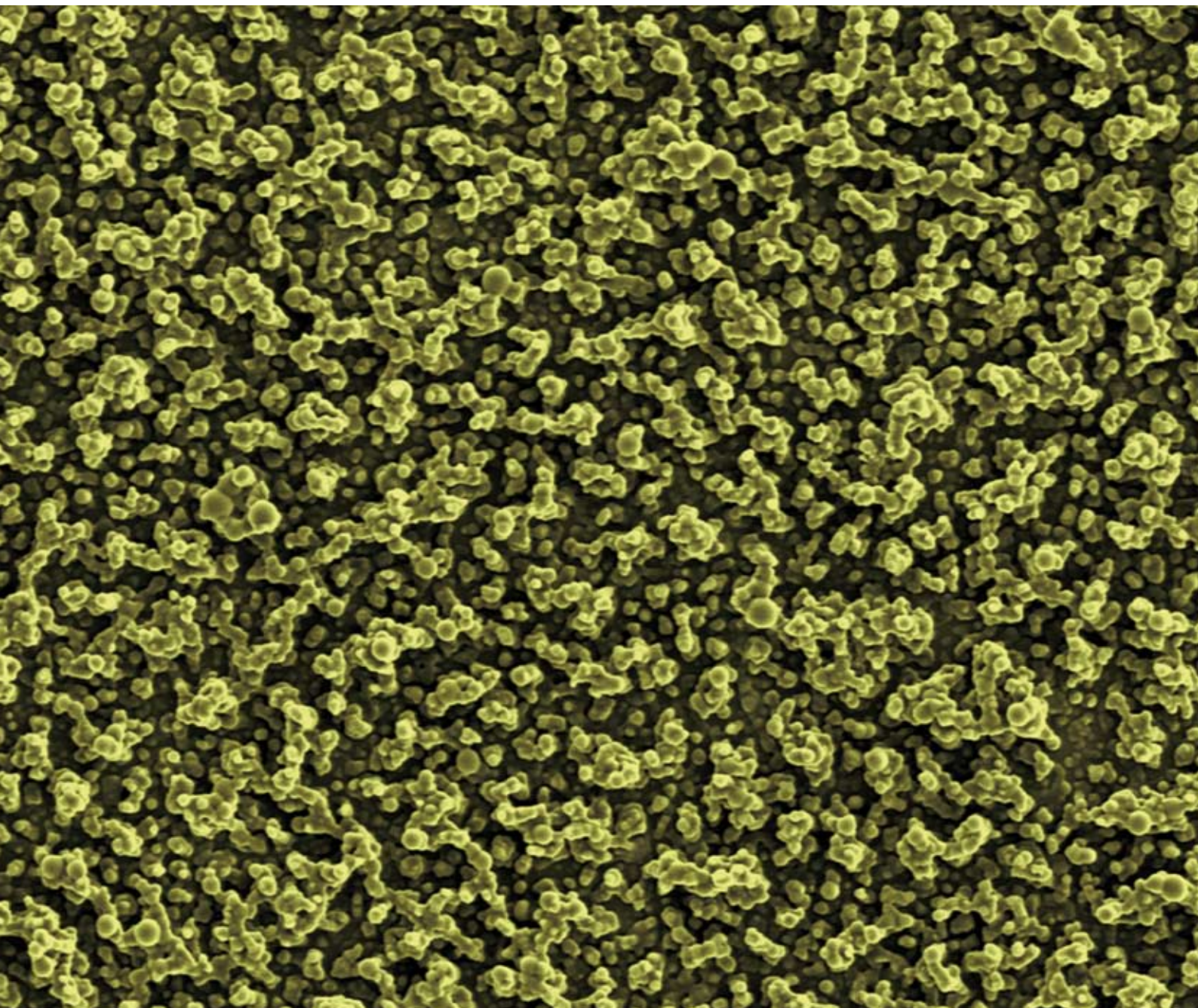


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FEATURE ARTICLE

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A single step route to superhydrophobic surfaces through aerosol assisted deposition of rough polymer surfaces: duplicating the lotus effect

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Superhydrophobic rough polymer surfaces were prepared by aerosol assisted deposition.

The 'lotus effect' is the self-cleaning action brought about by hydrophobic surfaces, where the action of water running over the leaf will wash off dirt and other foreign bodies from the surface. It is named after the lotus plant which has a sufficiently high water contact angle that water on the surface beads, rolls and spins across the surface instead of sliding. The rolling action increases the amount of foreign bodies picked up.¹ The properties of the surface that promote this type of interaction are a waxy coating that lowers the interaction of the water with the surface and a high roughness.² To achieve the lotus effect a surface has to be superhydrophobic, that is one that repels water to the extent where the water contact angle exceeds 140°. Many approaches have been taken to create man-made self-cleaning superhydrophobic films. Invariably this involves two steps, the first is to create a very rough surface, such as aligned carbon nanotubes³ and mechanically constructed "bed-of nails" type surfaces,⁴ to make the nodules followed by coating with a polymer to generate the "waxy" low energy surface. Here we show how a simple one step aerosol mediated process generates a rough polymer surface that is superhydrophobic, with a contact angle of up to 167° and a very low tip angle (5°) that promotes droplet rolling and spinning.

Films were grown by aerosol assisted chemical vapour deposition from a SYLGARD® 184 Silicone Elastomer. This elastomer consists of two parts, the first is the elastomer and the second a curing agent to encourage cross linking and hardening to generate a heat resistant polymer. Both polymer and cross link agent (10:1 ratio) were dissolved in chloroform (50 mL) by rapid stirring for 5 min. To prevent premature curing the solution was immediately used to form a coating. The depositions were carried out in a cold-walled horizontal-bed CVD reactor.^{5,6} The reactor contained a top and bottom plate for deposition to occur, both composed of SiO₂ barrier glass (dimensions: 145 × 45 × 5 mm). The CVD reactor was heated by a carbon block, on which the bottom plate was placed. A top plate was positioned 8 mm above and parallel to the bottom plate and the complete assembly enclosed within a quartz tube. The aerosol of the precursor solution was generated using an ultrasonic humidifier and transported using nitrogen gas. Deposition time was typically 30–35 min. The plates after deposition were removed and handled in air, with the top plate having the deposited film. The reactor

temperature was varied from 90–360 °C and film properties examined on each occasion.

The AACVD grown polymer films on glass were examined by FT-IR, these showed the exactly same IR fingerprint to that of the standard cured polymer with prominent C–H vibrations at 2960 and 2905 cm⁻¹. The polymer films were adhesive to the glass substrate, the majority of samples passed the Scotch tape test and were fairly scratch resistant requiring a metal spatula to mark. The films showed the expected C, O and Si atom% ratios by WDX analysis.

Scanning electron microscopy showed that the polymer deposited via AACVD has a very rough microstructure, Fig. 1, with nodule-like structures protruding from the glass substrate. These nodule-like structures were not as prevalent in low temperature depositions, and became the most prominent feature at deposition temperatures of 270 °C and above. The nodules consisted primarily of one micron sized spherical shaped projections. Together they formed an exceptionally rough surface. At higher deposition temperatures (300 °C and above) the nodules were slightly more interconnected to form *ca.* 50 micron sized ridges.

Contact angle measurements (Fig. 2) were determined by dropping water (30 µL) onto the surface at random. Contact angles were taken from each side of the droplet as they did differ substantially in some cases. They were measured by both the spread of a known water droplet volume (using a microscope) and by side-on optical photographs (Table 1).

Films formed below 240 °C showed some variability in the measured contact angle, whereas the films deposited at 240 °C

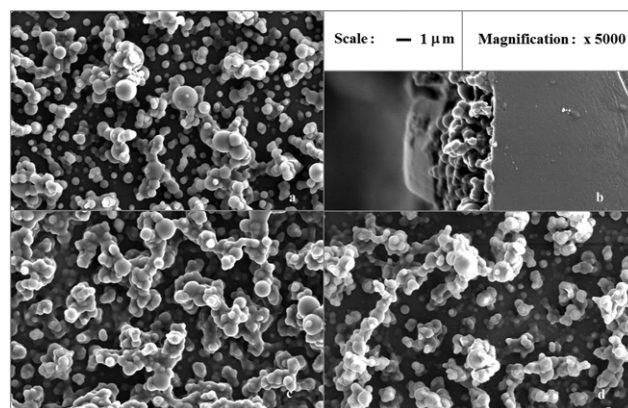


Fig. 1 SEM images of SYLGARD® 184 Silicone Elastomer applied to SiO₂ barrier glasses using AACVD. Using a substrate temperature of (a/b) 270, (c) 300 and (d) 360 °C. (a), (c) and (d) show top-down views of the coating, whereas (b) is a side on profile view. Magnification and scale bar are also shown.

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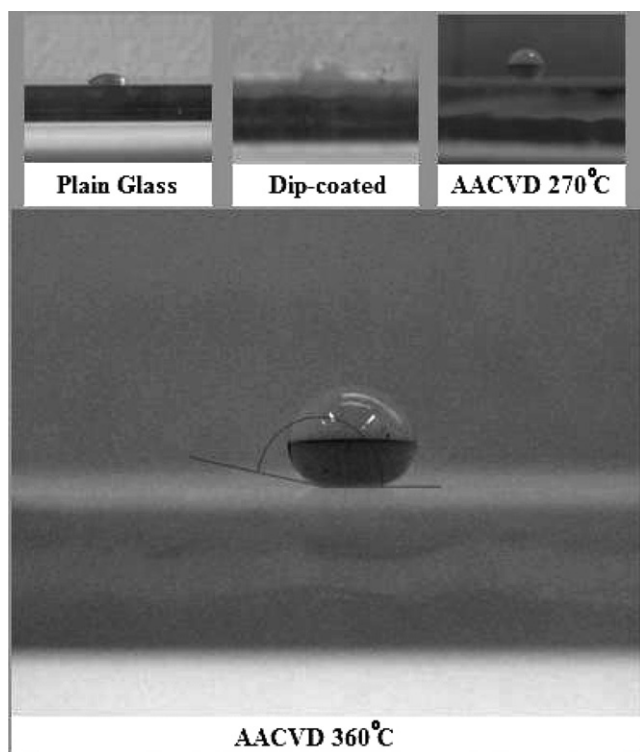


Fig. 2 Photograph used in the determination of the contact angle made of a water droplet with an elastomer film. Top-left is a water droplet placed on the SiO₂ barrier glass with no coating (contact angle = 25°). Top-centre is the dip-coated polymer (contact angle = 95°). Top-right shows an AACVD deposition carried out at 270 °C (contact angle = 158°). The contact angle reached a maximum of 167° on a film deposited using a substrate temperature of 360 °C.

Table 1 Deposition parameters and average (ten separate measurements) and maximum water droplet contact angles for SYLGARD® 184 Silicone Elastomer deposited by an AACVD process and by dip coating

Deposition Type	Average Contact Angle (°)	Maximum
Dip-coated polymer	95	—
AACVD (210 °C)	150	162
AACVD (240 °C)	156	165
AACVD (270 °C)	158	166
AACVD (300 °C)	160	167
AACVD (330 °C)	160	167

showed universally high hydrophobicity (contact angles greater than 145°). The uncoated glass substrate used was a relatively hydrophilic surface, typical contact angle ~25°. The outlying results are a product of having their contact measurements taken at the edges of the substrate (where at low temperature there was some lack of deposited material) and hence the hydrophobicity was reduced. At higher depositions temperatures, total surface coverage was observed, thus reduced outlying results, and an increasing average contact angle was seen.

As well as contact angles to analyse the hydrophobicity of the surface, the slipping angle of water on the surface was also measured. If the slipping angle is low, *i.e.* droplet easily falls off the surface, there is less attraction between the water droplet and the surface. The high

static contact angles measured suggest a high hydrophobicity: surfaces with this magnitude of contact angle have been reported to produce slipping angles of 5–10°. However, the films deposited here at 210 °C temperature would often hold a 60 µL water droplet when held at 90° tip angle, that is the films were examples of sticky hydrophobic surfaces as described by Wenzel.⁸ In marked contrast the films deposited at 240 °C and above consistently (typically ten tests per film) showed low slipping angles of *ca* 10–15°. A decrease in slipping angle was observed for films deposited at higher temperature. The film formed at 360 °C provided the lowest slipping angle recorded at 4°. Noticeably the water droplets placed on the polymer surfaces formed at 240 °C and above adopted a “roll and spin motion” down the surface, the mechanism observed in the lotus effect. This suggested a Cassie–Baxter wetting mechanism⁹ which is used in the self-cleaning of plants in order to remove bacteria and dirt from the plant surfaces.

The process to form the superhydrophobic films was simple, involving a single step. The process used an inexpensive AACVD apparatus, but could be even more simply replicated with a heated surface and an aerosol delivery system such as an artist spray brush. The process involves the transfer of the polymer inside an aerosol to the heated substrate. The aerosol droplets are spherical and it is the evaporation of the aerosol carrier solvent that gives rise to the spherical polymer shapes formed on the surface. The process is not a CVD one in the classic sense as there is no over-riding surface reaction chemistry, however the polymer is cured during the deposition process by having the cross linking agent present and encouraged by the temperature of the process. The film generated has lost the liquid properties of the polymer precursor and forms a “hard” coating. The films formed in the process are exceptionally hydrophobic, with contact angles up to 167°. This exceptionally high contact angle is due to the facts that the native polymer is hydrophobic, a dip coated film of the polymer with a smooth microstructure had a contact angle of 95°, and that the film is very textured consisting of nodule-like polymer projections.

There have been a number of approaches where polymers have been laid down on rough surfaces to generate superhydrophobic materials. Patterned silica spheres (950 nm) have been heat treated with polyvinylidene fluoride to make a surface with a water contact angle of 154°. Fluoroalkylsilane (FAS) moulds have been used to produce a similar contact angle of 167°,¹⁰ however this technique uses high temperature sintering (1100 °C). A very high contact angle of 174° has been achieved by growing alkyl ketene dimer crystals: upon isolation of the compound and resultant solidification, a very rough surface can be observed. These surfaces however need a substantial amount of material placed onto a substrate in order for single crystals to be formed. One of the highest contact angles reported is 178° by placing a water droplet on acid coated cobalt hydroxide crystalline nano-pins.¹¹

The technique reported here uses relatively low temperatures to form superhydrophobic surfaces on glass substrates. It is the mechanism of polymer agglomeration that occurs during the aerosol assisted process that is the key to yielding such highly rough surfaces. The technique is a way to quickly and simply apply a superhydrophobic coating to a range of surfaces (the processes works on steel, copper and alumina substrates as well as glass), and could be scaled up for the polymer to coat a large area. Such a polymer film could find numerous applications from coating surfaces to make them self-cleaning, to anti-adhesive and demisting applications.

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