Polystyrene/octadecyltrichlorosilane superhydrophobic coatings with hierarchical morphology†

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Sanjay S. Latthe‡* and A. Levent Demirel*

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A simple, one pot dip-coating process for the fabrication of superhydrophobic coatings using polystyrene (PS) and octadecyltrichlorosilane (OTS) is introduced. The hierarchical coating morphology and the resulting surface wettability were controlled by OTS concentration and by the number of dipping cycles. The coatings showed good durability for applications.

The quest for surfaces having the desired wettability has speeded up in the last decade.^{1–4} Surface wettability has long been known to depend on the chemical composition and morphology of the surface.^{5,6} Recently, the focus has been on controlling the surface composition and/or morphology of coatings in various composite material systems easily and reproducibly while understanding the fundamental processes in morphology formation.^{7–10}

Water-repellent surfaces having water contact angles (WCA) of $\sim 150^\circ$ or higher are known as superhydrophobic surfaces. A water droplet beads on such surfaces, rolls off the surface easily and collects the dust particles as it rolls. Inspired by natural superhydrophobic surfaces such as lotus leaves and water-striders' legs, similar surface morphologies and wetting properties were obtained in various material systems.^{11,12} The common features in these surfaces are the presence of a hydrophobic component and roughness at different length scales formed by hierarchical structures.^{13,14} Generally, two primary approaches were used: creating hierarchical micro/nanostructures on hydrophobic material surfaces^{15,16} or chemically modifying a micro/nanostructured surface with low surface energy materials.¹⁷ Among various methods, dip coating¹⁸ has been preferred for its simplicity, short processing times, coating uniformity in large areas, applicability to various substrates and geometries.

OTS has frequently been used to obtain hydrophobic (in the case of smooth surfaces, especially silicon)¹⁹ or superhydrophobic (rough or patterned) surfaces¹⁷ by self-assembled monolayer formation. Though the post-hydrophobization by OTS self-assembled monolayers can be applied to many substrates, the lifetime of such modified surfaces is poor. The durability is significantly enhanced, compared to post-hydrophobization, when a compound or mixtures of several components are allowed to self-assemble into hierarchical structures at the surface. OTS was reported to form superhydrophobic nanosheet morphology below $\sim 50\%$ relative humidity.²⁰ Depending on the water content in the solutions, OTS showed various morphologies.²¹ The mixture of silica nanoparticles and OTS also formed superhydrophobic surfaces with hierarchical structures.²²

Polymers have better thermo-mechanical properties compared to small molecule surfactants like OTS and are preferred for superhydrophobic surface applications.²³ Superhydrophobic polymer coatings have previously been obtained by the addition of nanoparticles,¹⁴ and the addition of a co-solvent to obtain porous surface morphology¹⁶ followed by appropriate film casting. PS is a commercially available amorphous hydrophobic polymer (WCA $\sim 93 \pm 2.5^\circ$ (ref. 14)) having a glass transition temperature of $\sim 100^\circ\text{C}$. In this paper, we report the formation of hierarchical surface morphology and superhydrophobic coatings by dip-coating from PS/OTS solutions in an organic solvent. The *in situ* one pot synthesis procedure is simple and versatile for obtaining coatings having desired wetting properties by tuning the hierarchical surface morphology through the process parameters such as OTS concentration and the number of dipping cycles. In addition, the coatings are homogeneous, have good adherence to the glass substrates and long-term stability.

The wettability of dip coated PS/OTS films on glass substrates depended both on the concentration of OTS in the solution and on the number of dipping cycles (each cycle consisted of 5 min immersion time and air drying). For a superhydrophobic coating, an optimum OTS concentration and at least 4 dipping cycles were required. Fig. 1 shows the change of the WCA on the coatings as a function of OTS concentration for a different number of dipping

Koc University, Chemistry Department, Sariyer 34450, Istanbul, Turkey. E-mail: ldemirel@ku.edu.tr; Fax: +90 212 3381559; Tel: +90 212 3381350

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‡ Present address: Korea University, School of Mechanical Engineering, Seoul, South Korea. E-mail: sanjaylatthe@yahoo.com

Fig. 1 The dependence of water contact angle on OTS concentration after one (squares), two (circles), four (up triangles), and six (down triangles) dipping cycles. The horizontal axis shows the OTS volume for 4 ml THF and 120 mg PS. The solid lines were drawn to guide the eyes.

Fig. 2 SEM images after four dipping cycles in solutions containing 120 mg PS, 4.0 ml THF and varying volumes of OTS: (a) 0 ml, (b) 0.1 ml, (c) 0.2 ml, (d) 0.3 ml, (e) 0.4 ml, and (f) 0.5 ml.

cycles. The coatings prepared without OTS (from PS solutions in THF) showed a WCA of $89.5 \pm 1^\circ$ independent of the number of dipping cycles as expected from smooth PS surfaces.¹⁴ At a fixed number of dipping cycles, the WCA and thus surface hydrophobicity initially increased with increasing OTS concentration, peaked and decreased slightly when OTS concentration was further increased. The lowest WCA measured in the presence of OTS was $113 \pm 1^\circ$. Though this value is similar to WCA on smooth self-assembled OTS monolayers on silicon,¹⁹ here it does not indicate a smooth OTS layer at the top surface of the coating. The surface roughness also contributes as observed by SEM (Fig. 2).

One dipping cycle (5 min immersion time) was not sufficient to render a superhydrophobic surface. At the OTS concentration of 0.3 ml/4.0 ml THF/120 mg PS, the peak WCA value for a single dipping cycle was measured as $128 \pm 2^\circ$. Further deposition and restructuring by discrete dipping cycles were required to obtain superhydrophobic surfaces having WCAs of $\sim 150^\circ$. The peak WCA value increased to $142 \pm 2^\circ$ after the second dipping cycle and to $151 \pm 1^\circ$ after the fourth dipping cycle. Further dipping cycles did not increase the WCA and it stayed stable at $\sim 145\text{--}150^\circ$. The lowest

effective surface energy was determined to be $\sim 4.0 \text{ mN m}^{-1}$ after four dipping cycles (see Table S1 in the ESI†).

Since the WCA of smooth PS films and smooth OTS monolayers is $\sim 90^\circ$ and $\sim 110^\circ$, respectively, the increase of the WCA of coatings above 110° both with OTS concentration and with the number of dipping cycles indicates that the surface morphology and surface roughness are dominant factors in the enhanced hydrophobicity of coatings.

In order to understand the effect of OTS concentration and the number of dipping cycles on surface wettability, the surface morphology of the coatings has been characterized by SEM. Fig. 2 shows the SEM images of the coatings after the fourth dipping cycle deposited from solutions having different OTS concentrations. The insets show the shape of the water drops on the surfaces. The PS coating without any OTS showed a smooth surface morphology with plateaus and holes having a WCA of $89.5 \pm 1^\circ$ (Fig. 2a). The observation of plateaus and holes indicates that the surface morphology is kinetically trapped as a result of fast solvent evaporation and surface flow typical of dip coating processes. With the addition of OTS, a significant change in surface morphology was observed (Fig. 2b–f). OTS caused hierarchical surface morphology and significant surface porosity at different length scales by intersection of randomly distributed curved sheets. As the OTS volume was increased, the surface structures branched out further and resulted in a network of intersecting curved sheets. The top surface shows the 2D projection of these sheets which looks like a combination of fiber-like structures and pores (see Fig. 3e–f for the SEM image of tilted samples). The WCA on the surface morphology of Fig. 2d was measured to be $151 \pm 1^\circ$. When the OTS concentration was increased further, the curved sheets were seen to orient more in

Fig. 3 SEM images of coatings from a solution containing 0.3 ml OTS, 4.0 ml THF, 120 mg PS after (a) one, (b) two, (c) four and (d) six dipping cycles. (e) The image of (b) at 45° tilt. (f) The image of (c) at 45° tilt.

the plane of the top surface (Fig. 2e–f) which coincided with the corresponding decrease in WCA. The formation and growth of these curved sheets at the top surface increased the solid (PS and OTS) fraction (bright regions) and decreased the surface porosity (dark regions) which can be clearly seen in Fig. 2f. (See Fig. S1† for the change of the amount of dark and bright regions in SEM pictures by OTS concentration.)

The change of the surface morphology with OTS concentration (Fig. 2) clearly explains the dependence of WCA on OTS concentration (Fig. 1). For water drops, rough hydrophobic surfaces can be considered as smooth composite surfaces formed of solid (PS and OTS in this case) and air, according to the Cassie–Baxter model.⁶ Since the WCA in air is 180°, the WCA on rough hydrophobic surfaces increases as the surface fraction of air (f_{air}) increases. In Fig. 2, the fraction of pores in the hierarchical morphology increases with OTS concentration. The air trapped in these pores beneath the water drop results in the increase of WCA. At higher OTS concentrations (Fig. 2e–f), WCA decreases due to the orientation of the curved sheets in the plane of the top surface, which decreases f_{air} .

The effect of the number of dipping cycles on WCA can similarly be understood in terms of the resulting surface morphology. Fig. 3 shows the SEM images of the coating surfaces after a different number of dipping cycles at a fixed OTS concentration. The top surface after a single dipping cycle mainly consisted of nearly circular holes having crater-like perimeters (Fig. 3a). These structures were on top of a dense and nearly smooth ~500 nm thick film as measured by SEM of tilted samples (see Fig. S2 in the ESI†). After the second dipping cycle on top of this coating, the dense film in touch with the glass substrate was ~6 μm thick with rough (few microns peak-to-peak) and porous morphology on top (Fig. 3e). The SEM image of Fig. 3b shows that the number of crater-like circular holes decreased, and fiber-like structures (projection of intersecting curved sheets at the top surface) formed. After the fourth dipping cycle, the fiber-like structures branched out further, resulting in a highly porous surface structure (Fig. 3c). This morphology goes down to the substrate without the presence of any dense and smooth layer underneath as shown in the SEM image of the tilted sample in Fig. 3f. The peak-to-peak roughness as determined from the image is ~4 μm . The surface structure after the sixth dipping cycle (Fig. 3d) looked similar to that after the fourth dipping cycle, but with curved sheets orienting more in the plane of the top surface similar to those observed in Fig. 2e. The increase in WCA with an increased number of dipping cycles is due to the increased surface porosity, as discussed above along the Cassie–Baxter model.

The SEM images of Fig. 3, especially those of the tilted samples, clearly show that the effect of consecutive dipping cycles was not only to increase the coating thickness. The coating thickness increased up to ~10 μm (peak-to-peak) after the second cycle. Further dipping cycles just caused the evolution of the morphology (changes in morphology) together with propagation of the morphology down to the underlying glass substrate. To obtain the observed hierarchical morphology, going through discrete dipping cycles was required. When the glass substrates were dipped in PS/OTS solutions and kept continuously in solution for 24 hours, a similar dependence of WCA on OTS concentration was observed (see Fig. S3 in the ESI†) but the peak WCA was only ~120°. In accordance with the WCA values, the

resulting surface morphologies were rather smooth with holes and did not contain any hierarchical morphology (see Fig. S4 in the ESI†).

Hydrolysis and condensation of OTS seem to be the dominant mechanism in the formation of such hierarchical morphology. FTIR spectra of the coatings (see Fig. S5 in the ESI†) indicated the presence of Si–O–Si bonded OTS chains. The morphology was similar to previously reported OTS nanosheets²⁰ but in our case the curved sheets were continuous throughout the whole coating and had much larger sizes compared to reported nanosheets. This indicates that PS took part in these planar structures stabilized by OTS condensation. This should also be the reason for the flexibility and significant bending of the observed planar structures. The morphology that gave the peak WCA at an OTS volume of 0.25 ml (Fig. 1) corresponds to ~1 OTS molecule per 2 PS monomers. This is almost an upper limit considering the conformation of PS chains and the resulting steric hindrance. The additional OTS molecules cannot interact with PS anymore. These free OTSs might be inducing the orientation of the sheets more in the plane of the substrate which coincides with the corresponding decrease in WCA.

The coated glass substrates up to a mass of ~3 g floated on top of the water surface showing their water repellency and indicating their effectiveness to function similar to the legs of water striders.²⁴ Even after a 1 week observation period, the coated substrates continued floating on top of the water. Up to 20 months in ambient atmosphere, the coatings maintained their morphology and wetting properties. Coatings soaked in water at room temperature recovered their initial WCAs after drying. This also shows that the adhesion of coatings to the glass substrate is strong. (See the ESI†, Fig. S6 and S7 for details of durability characterizations.)

The fabrication of superhydrophobic coatings having hierarchical morphology and good durability by a simple one pot dip coating process and using common chemicals (PS, OTS and THF) has important practical implications. The evolution of hierarchical morphology through kinetically trapped states after discrete dipping cycles is also important fundamentally and deserves further investigation.

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