A simple methodology for producing super-hydrophobic composite films on various substrates

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Abstract

Various nanoparticles (silicon oxide, tin oxide and aluminium oxide) were mixed with poly (methyl siloxane) (Rhodorsil 224). The mixtures were sprayed on silicon substrates resulting in the formation of a rough, two-length-scaled hierarchical structure surface layer. We report that: (i) Super-hydrophobic composite films were produced with all the particles used, (ii) The effect of the particle's nature on the developed hydrophobicity was examined showing that the maximum static water contact angle is independent of the nature of the polymer-particle binary mixture, (iii) The effect of the particle concentration on the hydrophobic character of the composite film was also examined showing that the static contact angles measured on surfaces which were prepared from dilute dispersions, increase rapidly with particle concentration reaching a maximum value (162 ± 2^{0}) and (iv) When the static contact angle is maximum, the contact angle hysteresis reaches some minimum values (2-4°) providing evidence that the composites prepared with high particle concentration are super hydrophobic and exhibit augmented water repellency. The methodology was also tested on various substrates (glass, marble, concrete, aluminum, silk, wood). The static water contact angle measurements revealed that the substrate has no significant effect on the superhydrophobic character of the applied coatings.

Introduction

Water repellency is important in many biological processes and technological applications. Prevention of snow sticking and metal corrosion, protection of monuments and self cleaning surfaces are only some of the applications where enhanced water repellency is required [1].

In nature, the leaves of lotus (*Nelumdo nucifera)* have been under thorough study showing that the high water contact angle is the result of the combination of the rough microstructure (cells) and the rough nanostructure (wax crystals) with a wax of low surface energy covering them [2-4]. The "lotus effect" has inspired the efforts for the creation of synthetic super-hydrophobic surfaces.

Within this framework the general strategy for the production of super-hydrophobic surfaces includes the use of materials with low surface energy and the creation of rough surfaces. The combination of surface roughness and low surface tension according to the Wenzel and Cassie-Baxter equations [5] enhances the hydrophobic character of a surface.

Most of the developed methodologies include the formation of roughness in the nano-scale, with plasma treatment, sol-gel or by picking suitable solvents for polymers [6-8].

In previous works we presented a simple methodology which was applied on a wide variety of surfaces [9,10]. The methodology included the addition of nanoparticles in

polymeric solutions. The mixture was then sprayed on the substrate. Some of the advantages of the methodology are that: it is a low-cost and very simple method as it is a one step process and includes the use of some very common materials and that superhydrophobicity can be achieved by using different polymers.

In this work we follow the same methodology and evaluate the effect of the addition of the various particles on the hydrophobic character of the polymer/particle composite film. In particular various nanoparticles such as silicon oxide (SiO_2), aluminium oxide (Al_2O_3) and tin oxide (SnO_2) were used for mixing with a poly(alkyl siloxane) (Rhodorsil 224).

Experimental

Poly(methyl siloxane) (Rhodorsil 224, Rhodia Silicones) which is a 7% wt. solution in white spirit, was used for mixing with various nanoparticles. The θ_s of the polymer on smooth substrate after spin coating was 103^0. The nanoparticles were: (i) Silicon oxide (SiO_2) particles (fumed powder, Aldrich) with 7nm mean diameter, (ii) Silicon oxide (SiO_2) particles (fumed powder, Aldrich) with 14nm mean diameter, (iii) Aluminium oxide (Al_2O_3) particles (Alfa Aesar) with 40-50 nm diameter and (iv) Tin oxide (SnO_2) particles with 22-43 nm diameter. Rhodorsil-silica dispersions with particle concentrations 0.1, 0.3, 0.5, 1.0, 1.5 and 2.0 % w/v and Rhodorsil-tin/alumina dispersions with particle concentrations 0.5, 1, 2, 4, 6, 8, 10 % w/v were prepared. Mixtures were subsequently stirred vigorously for 20 min. The polymer-nanoparticles dispersions were immediately sprayed on clean Si wafer substrates. Silicon wafers with <100> orientation containing a native surface oxide were purchased from Siegert Consulting e.K. The spraying system was an airbrush system (Paasche Airbrush) with a nozzle of 733 μm diameter. The coatings were then annealed at 40 ^{o}C overnight in vacuum to remove residual solvent and kept at room temperature for 2-3 days. The morphologies of the film surfaces were investigated by Scanning Electron Microscopy (SEM, Jeol JSM 840A). Contact angle measurements were carried out by the sessile drop method using a Krüss DSA 100 (Krüss) apparatus and distilled water. Water droplets (2-4 μl) were delivered to different points of each specimen and from a height sufficiently close to the substrate, so that the needle remained in contact with the liquid droplet. Then, the delivery needle was withdrawn with minimal perturbation to the drop [11] and the image of the drop was captured immediately for contact angle measurement. The contact angle hysteresis was calculated by the dynamic sessile drop method. The advancing/receding contact angle was the maximum/minimum angle measured while the volume of the droplet was increased/decreased without increasing/decreasing the solid-liquid interfacial area. The reported contact angle values are averages of five measurements.

Results & Discussion

Surface morphology

In figure 1 SEM images of the surface morphologies formed by the Rhodorsil-particle mixtures sprayed on the substrate are presented. Various surface structures are formed on the substrate by varying the particle concentration (Figure 1, a-d). It is also shown that the morphologies formed are similar for all the particles used but there is a significant difference in particle content. The ratio of the surface area covered by the mixture increased with increasing the particle concentration. Apparently, the surface roughness of the treated substrate increased with increasing the particle content in the polymer-particle mixture. The particles were aggregated creating structures with diameter of

about 20-40 μm (Figure 1, a-d). So by varying the concentration of the particles in the polymeric solution different surface morphologies in the micro-scale were formed.

We now turn our attention on the surface structure of the aggregates that protrude above the smooth polymer film. Figure 1 (e-h) show examples of the morphologies of aggregates formed in Rhodorsil-particle films deposited on silicon. It is demonstrated that each aggregate consists of a nanostructure which implies an augmented roughness at the nanoscale. In summary, figure 1 suggests that the randomly distributed protruded aggregates consist of further nanostructures, implying that a two-length-scaled hierarchical structure is formed in the surface. It is known that such structure exists in the lotus leaf which exhibits water repellent properties. In the following, the hydrophobic character and the water repellent properties of the surfaces, described above, are evaluated.
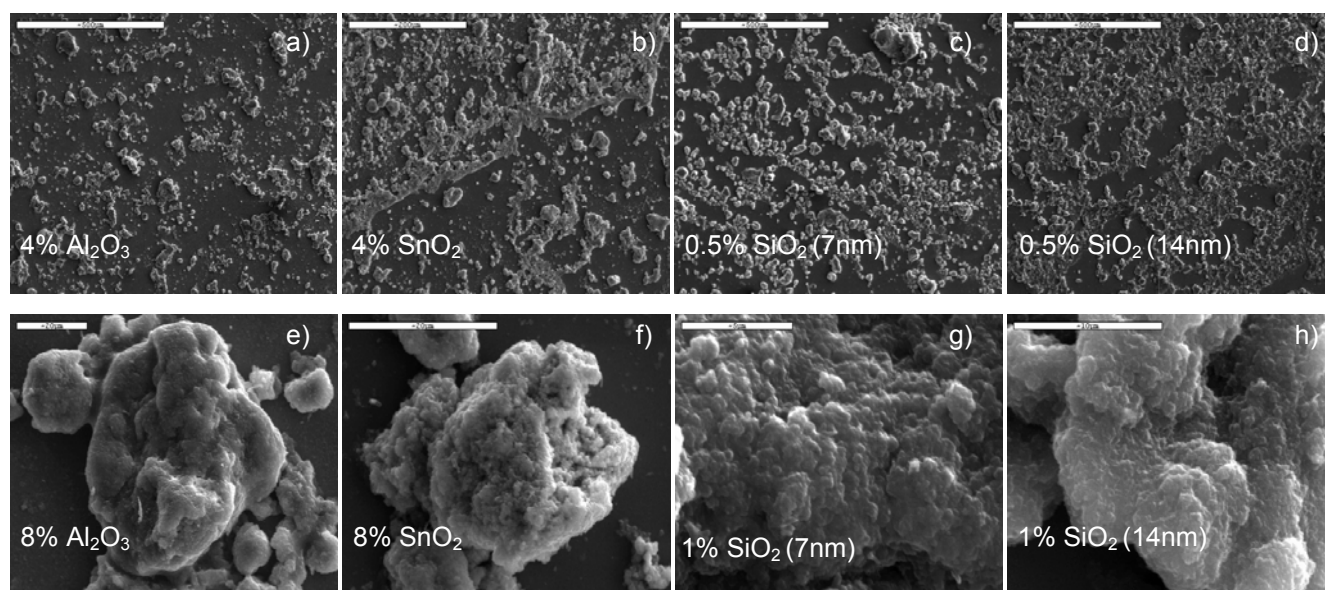

Figure 1. SEM images of Rhodorsil-particle films deposited on Si-wafer. The concentrations (w/v) of the particles in the dispersions which were deposited on the substrates are shown in the lower left corner of each image.

Water contact angle

Figure 2 shows water static contact angle (θ_s) and contact angle hysteresis measurements, defined as the difference of the advancing (θ_a) and the receding contact angle (θ_r), as a function of particle concentration for siloxane-SiO_2 (7nm,14nm) - SnO_2 - Al_2O_3.

The results show a significant enhancement of the hydrophobicity for all the particles used. The increase follows the same tendency. For low particle content a significant increase of static water contact angle is observed. Beyond a "critical point" further addition of nanoparticles does not have a significant impact on the developed hydrophobicity. The static contact angle reaches a plateau of about 162 ± 1^0 for all the particles used. In a previous work, in PMMA/ particles mixture a maximum water contact angle of 154^0 was reported. Therefore it is shown that the maximum water contact angle is determined by the surface tension of the polymer and not by the nature of the particles. As it is obtained from figure 2 there is a significant difference in the particle content where the plateau is reached. It is 0.5%, 1%, 4% and 6% w/v for silicon oxide 7nm, silicon oxide 14nm, aluminium oxide and tin oxide nanoparticles, respectively.

The variation of water contact hysteresis with particle content is more complicated. For low concentration of particles there is a gradual increase of advancing contact angle. The receding contact angle remains practically stable leading to an increase of water contact angle hysteresis. The hysteresis reaches some maximum values, which are 40 ± 4^0 depending on the particle used. The maximum hysteresis was measured at 1 % w/v for tin oxide and aluminium oxide nanoparticles and at 0.3% w/v for silicon oxide nanoparticles.
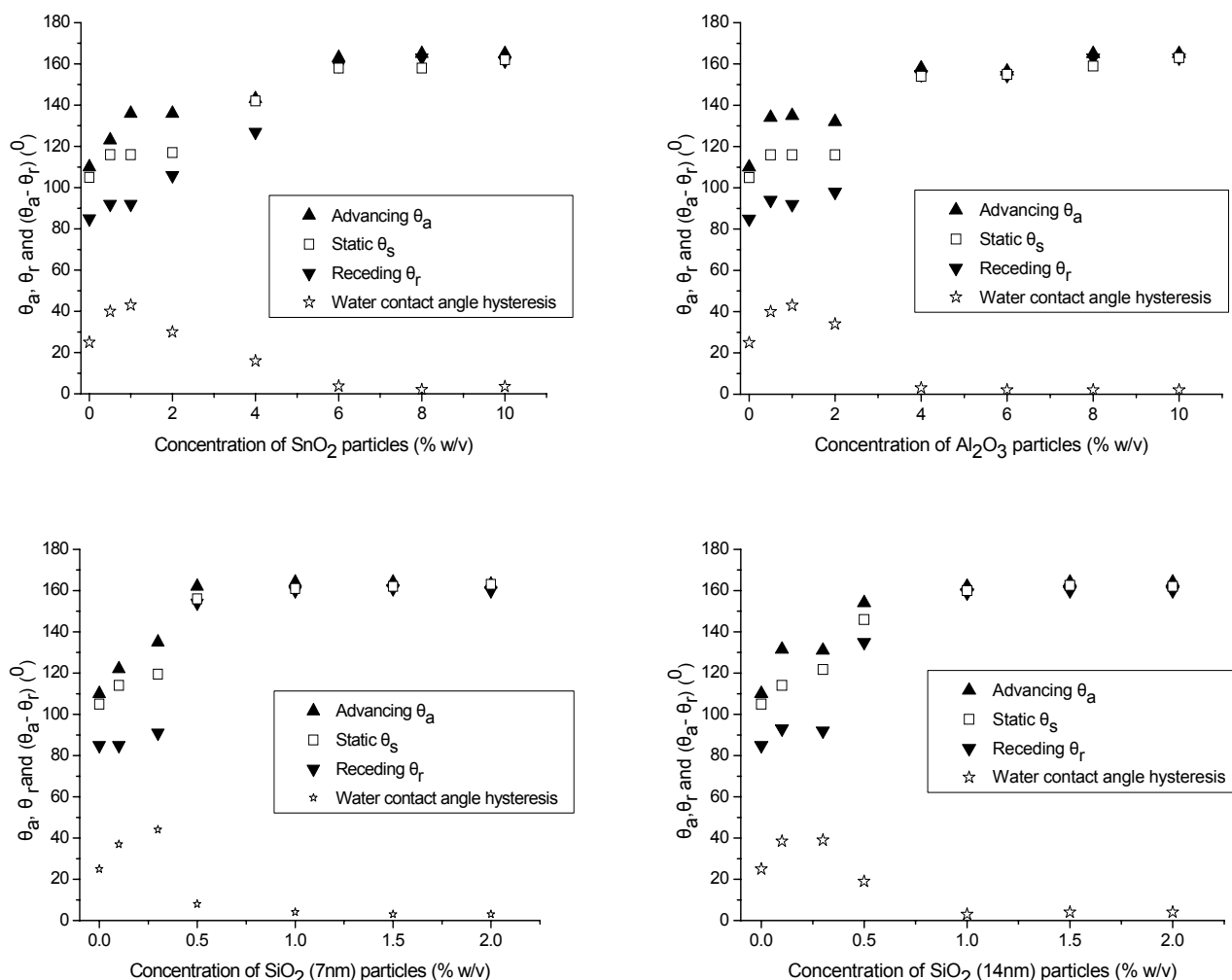

Figure 2. Static water contact angle (θ_s) and contact angle hysteresis ($\theta_a - \theta_r$) vs. concentration of particles.

As it was demonstrated in a previous work the effect of the particle concentration on the contact angle hysteresis ($\theta_a-\theta_r$) resembles to some extent the effect of roughness on wax surfaces [12,13]. In these works the water contact angle hysteresis first increases with roughness, then decreases rapidly and finally becomes constant. The rapid decrease of hysteresis can be attributed to the rapid transition of the surface from the Wenzel regime to the Cassie-Baxter regime.

In the case of Rhodorsil-particle dispersions the advancing contact angle increases but the increase is more rapid compared to the wax (Figure 2). The receding contact angle remains practically stable at low particle concentration before a significant increase. Finally at elevated particle concentration (>0.5% w/v for silica particles and >2%

for alumina and tin particles) hysteresis decreases rapidly and finally becomes constant. Polymer-particle composite films prepared from dispersions of high particle content correspond to the Cassie-Baxter scenario. This is evidenced by the enhanced θ_s values and the dramatic decrease in hysteresis that reflects a transition to a "composite" surface characterized by such a large roughness that a liquid cannot completely wet the crevices. The elevated hysteresis in the case of films prepared from dispersions of low particle content can be explained if we consider that water may fill the large, smooth areas that exist among the aggregates. In summary, the large, smooth areas are filled with water (Wenzel) but not the small nanocrevices that exist on the surface of the particle aggregates (Cassie-Baxter). This is a mixed regime.

The minimum hysteresis values reported were 2-4^0 depending on the particle used. Static water contact angle of over 150^0 and low contact angle hysteresis denotes a super-hydrophobic surface. So figure 2 provides evidence that composites prepared with high particle concentrations are super hydrophobic and exhibit augmented water repellency. This is also confirmed by figure 3. Figure 3 shows consecutive images of a water droplet bouncing on Si wafer covered by siloxane and 10% w/v SnO_2 nanoparticles. The droplet rolls-off and finally is removed from the substrate.
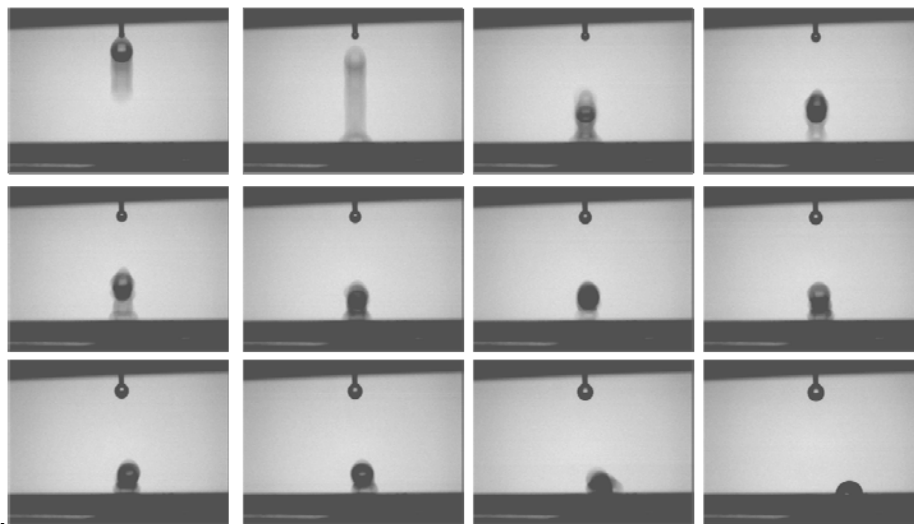
Figure 3. Water droplet bouncing on the substrate which was treated with the siloxane and 10% w/v tin particles.

Application on various substrates

The spray technique has the advantage that it can be easily used to treat various surfaces. Various substrates were treated with Rhodorsil and silicon oxide particles (7nm) and static water contact angle measurements (θ_s) on the treated surfaces of glass, silicon, concrete, aluminum, silk, wood, and marble were carried out. The obtained results are presented in Table 1:

Table 1. Static contact angle (θ_s) of pure siloxane, siloxane-SiO$_2$ (2% w/v), applied on various substrates.

Substrate	Static water contact angle (^{0})	
	No particles	Silicon oxide particles (7nm)
Cement	105	164
Metal (Iron)	136	160
Fabric (Silk)	106	162
Wood (Plywood)	130	162
Marble (Pentelic)	109	160
Glass	103	164

The obtained results show that: (i) The nanoparticles enhance the hydrophobic character of simple polymers applied on various substrate materials, (ii) The static contact angles measured for the polymer-particle composite films are nearly independent of the substrate material.

Conclusions

A commercial siloxane composition was modified by the addition of nanoparticles (silicon oxide, tin oxide, aluminium oxide) and sprayed on different substrates - silica wafer, glass, wood, iron, silk. As a result rough, two-length-scaled hierarchical structure surface layer is formed. The maximum contact angle succeeded (162 ± 2^0) was independent of substrate nature and nanoparticles chemistry. However, it was achieved at different concentrations of nanoparticles in modified composition and in particular at 0.5%, 1%, 4% and 6% w/v for silicon oxide 7nm, silicon oxide 14nm, aluminium oxide and tin oxide, respectively. At the same concentrations the very low contact angle hysteresis ($2-4^o$) was observed. Thus the modified siloxane composition enhance substantially the water repellence of the treated surfaces and render them super hydrophobic and self cleaning. The suggested modification is low cost and the modified composition can be applied for the most effective water protection of large surfaces such as monuments, iron construction and buildings.

Acknowledgements

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