Modification of the wettability of polymer surfaces using nanoparticles

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ABSTRACT

The effects of nanoparticles, embedded into the matrices of polymer films, on the wettabilities of the surfaces of the composite films are investigated following a two-fold procedure. First, five particles such as silica (of two sizes), tin oxide, alumina and zinc oxide ranged from 7 to 100 nm are mixed with a poly(methyl siloxane). Second, silica nanoparticles (7 nm) are embedded in five different polymers such as poly(methyl methacrylate), polystyrene and three poly (alkyl siloxane) products. Nanocomposite films are produced by adding nanoparticles in the polymer solutions which are then sprayed on silicon substrates.

In the first study, which includes the use of different nanoparticles, the contact angle hysteresis is monitored as a function of particle concentration. It is shown that similar water repellency that corresponds to hysteresis <5° is achieved using any of the five tested particles when these are mixed with the siloxane at elevated concentrations. However, the wettability of film surfaces prepared using dispersions of low particle concentration, is highly affected by the particle size and concentration: (i) water repellency of the modified polymer surfaces is enhanced when nanoparticles of small sizes are used i.e. films prepared using particles of small sizes correspond to lower hystereses compared to films produced using bigger particles. (ii) As the particle concentration increases, we first notice an increase in hysteresis, which then decreases. This result is explained with respect to the surface morphologies of the films which are revealed using Scanning Electron Microscopy (SEM).

In the second study, which includes the use of different polymers, it is shown that superhydrophobicity can be achieved using any of the previously mentioned organic materials. According to SEM images, similar continuous rough structures are formed on the surfaces of the films, prepared using different polymers and (the same) silica nanoparticles. This is supported by the Cassie-Baxter equation which suggests that comparable surface porosity factors correspond to the different composite films.

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1. Introduction

Polymers are very often blended with nanoparticles and nanofillers to produce nanocomposites with improved mechanical, thermal, electronic or optical properties [1,2]. With the increased interest on water-repellent surfaces, expressed in the last decade, the wettability of surfaces of polymer-nanoparticle composites has recently attracted considerable attention [3–21]. Nanoparticles, used as additives, can modify the wettability of polymer surfaces with two mechanisms: (i) they can be used to modify the chemical composition of the surface, affecting thus directly the

intermolecular interactions between solid and water, i.e. the wettability of the surface. (ii) Nanoparticles can be used to modify the surface morphology enhancing, for instance, surface roughness. The latter is a key parameter to achieve superhydrophobicity and water-repellency which were first evidenced on surfaces of plants and small animals [22,23].

Superhydrophobicity implies that the shape of a resting water drop is almost spherical, as it is for instance in Fig. 1, which shows water drops placed on the leaves of a common plant from the Greek flora. Cassie and Baxter provided a simple formula, which correlates the elevated apparent contact angle (θ^*) observed on a superhydrophobic surface of augmented roughness, and the contact angle (θ) measured on a smooth surface [24]:

$$\cos \theta_* = -1 + f_s(\cos \theta + 1) \qquad (1)$$

where f_s is the surface porosity factor, i.e. the fraction of the superhydrophobic surface which is in direct contact with water. It is

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Fig. 1. Superhydrophobicity is observed on various natural surfaces. An example is shown in the photograph: water drops resting on the leaves of a plant, found in Mount Olympus (Greece), exhibit almost spherical shapes.

Table 1
Nanoparticles included in the study were purchased from various suppliers as described in the table.

Particle	Diameter (nm)	Supplier
SiO$_2$	7	Aldrich
SiO$_2$	14	Aldrich
SnO$_2$	22–43	Alfa Aesar
Al$_2$O$_3$	27–43	Nanostructured & Amorphous Materials
ZnO	40–100	Alfa Aesar

noted that both θ^* and θ, included in Eq. (1), are static contact angles, measured for resting water drops.

Superhydrophobicity is usually, but not always, accompanied by water repellency which implies low droplet adhesion [25]. Water repellency can be evaluated through either tilt contact angle or contact angle hysteresis, defined as the difference of the advancing (θ_A) and receding contact angle (θ_R). Hysteresis is directly related to the force needed to start a drop moving over a solid surface [26]:

$$F = \gamma_{lv}(\cos \theta_R - \cos \theta_A) \tag{2}$$

where F is the critical line force per unit length, and θ_R and θ_A are the receding and advancing contact angles, respectively. According to Eq. (2), as the contact angle hysteresis ($\theta_A - \theta_R$) decreases, the critical force needed to make the drop to move decreases. Consequently, superhydrophobic surfaces of enhanced water repellency must correspond to small $\theta_A - \theta_R$.

We investigate the effects of particle concentration and size on the wettability of siloxane-nanoparticle composites. The effect of particle concentration has been previously investigated for some polymer-nanoparticle systems [5–8,13,14,19,21]. Our results are discussed in light of these previously published reports. To the best of our knowledge a systematic investigation on the effect of particle size, however, has not been reported yet. Five different in size (and nature) nanoparticles, described in Table 1, are dispersed in poly(methyl siloxane) solutions at various concentrations. Dispersions are afterwards sprayed on silicon surfaces and the wettabilities of the resulting composite siloxane-nanoparticle films are investigated with contact angle measurements of water drops and Scanning Electron Microscopy (SEM). In another set of experiments, the aforementioned method is used to prepare composites of five different polymers enriched with the same silica nanoparticles (7 nm). Spraying techniques, such the one employed herein, are simple and cost effective methods which can be therefore used to apply superhydrophobic and water repellent polymer coatings on large-scale surfaces [3,6,8,10,13–16,19,21,27,28].

It is important to note that in our work particles are embedded into the polymer matrix, producing thus a nanocomposite system where particles are randomly distributed. This is a major difference with previous detailed studies which investigated the wettability of surfaces prepared by controlled, layer-by-layer deposition of nanoparticles [29–31].

2. Experimental

A poly(methyl siloxane) (Rhodorsil 224, Rhodia Silicones) which is a 7 wt.% solution in white spirit was used as received. Nanoparticles, described in Table 1, were dispersed in siloxane solutions in various concentrations which are described in % (w/v) i.e. grams of nanoparticles per 100 ml of solution. Siloxane-nanoparticle dispersions were stirred vigorously for 20 min and sprayed on clean silicon (Si) wafers (Siegert Wafer) for 2 s using an airbrush system (Paasche Airbrush) with a nozzle of 733 μm in diameter. The orientation of the wafers was ⟨1 0 0⟩. The produced coatings were annealed at 40 °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 using 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 (4 μl or less) were delivered to five 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 and the image of the drop was captured immediately to measure the static contact angle. 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 angles (static, advancing and receding) are averages of five measurements and varied within ±2°. The same, narrow variation was recorded for different samples prepared using the same coating composition.

In the second part of the study, silica nanoparticles (7 nm) were dispersed in four more polymer solutions which were prepared as follows. Poly(methyl methacrylate) (PMMA, Aldrich) and polystyrene (PS, Poole) with molecular weights 120,000 and 100,000 g/mol, respectively, were dissolved in toluene to prepare solutions of 5 wt.%. Poly (alkyl siloxane) products such as Porosil VV plus (AquaBarta) and BS 290 (Wacker Chemie) were dissolved in white spirit to prepare solutions of 10 and 7 wt.%, respectively. Dispersions were sprayed on Si wafers and the wettabilities of the film surfaces were evaluated with contact angle measurements and SEM, which were carried out according to the above described processes. The influence of evaporation on contact angle was monitored for sessile drops placed on Posoril-silica film.

Finally, polymer solutions (without particles) were spin coated onto Si wafers to produce smooth surfaces, which were used to evaluate the inherent wetting properties of the organic materials, through contact angle measurements.

3. Results and discussion

3.1. Films produced using various nanoparticles

Fig. 2a shows contact angle hysteresis measurements, as a function of particle concentration for five siloxane-nanoparticle composite films, prepared using Rhodorsil and the particles of Table 1. A similar qualitative variation of $\theta_A - \theta_R$ is observed for all five composites: as the particle concentration increases we first notice an increase in hysteresis, which reaches a maximum value