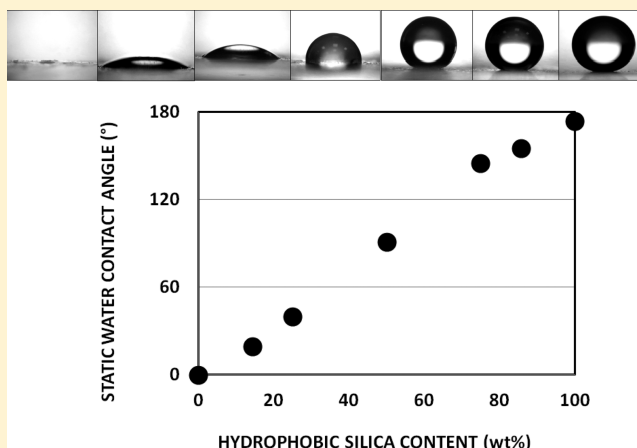


# Tunable Wetting of Polymer Surfaces

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**ABSTRACT:** A simple method was developed for the preparation of polymeric materials with controlled surface wettability or tunable surface wetting. The method is applicable to a large number of polymers, thermoplastic or thermoset. With this method, it is possible to prepare polymer surfaces with static water contact angles ranging from 0° (superhydrophilic) to greater than 170° (superhydrophobic). The method developed is based on spin-coating of a hydrophilic/hydrophobic silica mixture dispersed in an organic solvent or solvent mixture onto the polymer surface. Depending on the hydrophilic/hydrophobic silica ratio in the coating mixture, it is possible to obtain polymer surfaces displaying gradually changing wettability from superhydrophilic to superhydrophobic. In this article, preparation and surface characteristics of polystyrene (PS) and cross-linked epoxy resin (ER) films are provided as general examples. Polymer surfaces obtained were characterized by scanning electron microscopy, white light interferometry, atomic force microscopy, X-ray photoelectron spectroscopy, and static water contact angle measurements. Effects of the type of polymeric substrate and composition of the silica mixture on the surface behavior of the composite systems were investigated.



## INTRODUCTION

Preparation and characterization of materials with superhydrophilic or superhydrophobic surfaces have been extensively investigated during the past 10 years.<sup>1,4</sup> In addition to the scientific curiosity to understand the critical chemical and physical factors and/or parameters leading to the formation of such surfaces, potential technological applications of these materials in various fields, such as biomaterials, microelectronics, microfluidics, coatings, textiles, and so forth, have been the major driving forces behind these studies.<sup>1,4</sup>

It is well-documented that wetting behavior of a surface is controlled by its chemical structure and surface topography or roughness.<sup>5,6</sup> Hydrophobic surfaces (e.g., highly fluorinated or dimethylsiloxane containing systems) that display roughness on the micrometer and/or nanometer scale display superhydrophobicity, which is also usually called the Lotus Effect, since the surface structure of these materials mimics that of the Lotus Leaf.<sup>7,8</sup> The theoretical explanation of the effect of surface roughness on wetting behavior has been provided by Wenzel<sup>9</sup> and Cassie and Baxter.<sup>10</sup> There have been numerous publications that have used these equations or slightly modified versions of them to explain the contact angle behavior of rough surfaces.<sup>11,13</sup>

Very interestingly, when compared with intense efforts and a large number of publications describing the preparation and characterization of superhydrophobic or superhydrophilic surfaces, studies on the preparation of surfaces with controlled wettability or tunable wetting characteristics have been fairly limited. Recently, several articles have been published

describing various approaches for the preparation of surfaces that display tunable wetting behavior. Composto and co-workers<sup>14</sup> studied the wettability of polymeric surfaces obtained by reacting amine-modified silica nanoparticles with diameters from 15 to 230 nm, onto poly(styrene-*random*-acrylic acid) films. Depending on the particle size and surface coverage, they were able to obtain static water contact angle values between 75° and 120°. Stafford and co-workers<sup>15</sup> examined the wettability of UV/ozone-treated and wrinkled PDMS surfaces. As a function of the surface roughness, they were able to obtain static water contact angles between 60° and 110°. A method for the preparation of surfaces with tunable wettability based on multilayer deposition of a polyelectrolyte on a rough substrate, followed by the ion exchange of the counterion was reported.<sup>16</sup> By this technique, static water contact angle of the surface could be switched between 5° and 164°. Complex films displaying tunable wetting behavior, with static water contact angles between 60° and 100°, were reported.<sup>17</sup> Films were prepared by ionic self-assembly approach, where methyl orange and perfluorinated dodecanoic acid was attached to a poly(ionic liquid) backbone. Silica films with tunable wetting behavior that displayed static water contact angles between 10° and 150° were prepared on stainless steel meshes by sol-gel technique followed by surface modification and annealing.<sup>18</sup> Tunable wetting states were controlled by changing the surface

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chemistry and morphology. ZnO-based nanoneedles and nanonails were shown to display static water contact angles between  $90^\circ$  and  $125^\circ$ .<sup>19</sup> Interestingly, upon air annealing these materials displayed superhydrophilicity, whereas when treated with stearic acid, they became superhydrophobic and showed static water contact angles around  $160^\circ$ . Wetting behavior of patterned silicon microchannels coated with positively and negatively charged polyions and hydrophilic  $\text{TiO}_2$  nanoparticles, using the layer-by-layer deposition technique, was investigated. Depending on the coating type and thickness, static water contact angles between  $10^\circ$  and  $160^\circ$  were obtained.<sup>20</sup> Electrochemically tunable wetting property of polypyrrole upon application of very low voltages was also investigated.<sup>21</sup> Static water contact angles of  $107^\circ$  and  $133^\circ$  were observed for the oxidized and reduced samples, respectively. Similarly, Advincula and co-workers investigated the potential-induced wetting behavior of nanostructured polystyrene beads layered on gold or ITO surfaces which were subsequently coated by polythiophene films through electropolymerization.<sup>22</sup> Materials obtained displayed static water contact angles between  $60^\circ$  and  $150^\circ$  for several cycles, upon application of a potential switching between 0 and 1.05 V. Krupenkin and co-workers investigated the electrically controlled, fully reversible wetting–dewetting transitions on nanostructured surfaces. The nature and mechanism of the reversibility was studied both experimentally and theoretically.<sup>23</sup> Preparation of nanostructured surfaces with tunable wetting behavior from superhydrophobic to superhydrophilic upon UV<sup>24,25</sup> and UV-ozone<sup>26</sup> exposure were also reported. In addition to the experimental studies, tunable wetting behavior of biomimetic nanostructured materials under electric field was also investigated by using molecular simulations.<sup>27</sup>

As can be seen from the discussion above, most of the experimental techniques used in the preparation of surfaces that display tunable wetting behavior (i) are based on fairly complex and difficult processes, (ii) are applicable for specific polymer systems, and (iii) only cover a fraction of the superhydrophilic–superhydrophobic range. Here, we report a very simple approach to obtain polymeric surfaces with tunable wetting behavior with static water contact angles from  $0^\circ$  to  $175^\circ$ . In the method developed, a mixture of hydrophilic and hydrophobic silica is spin-coated onto the polymer surface. Depending on the composition of the silica coating, it is possible to obtain surfaces with static water contact angles between  $0^\circ$  and  $175^\circ$ . This process can be applied to almost any polymeric system, thermoplastic or thermoset. It may also be applied to other substrates using a modified coating/curing procedure.

## ■ EXPERIMENTAL SECTION

**Materials.** Bisphenol-A based epoxy resin (DER 331) with an epoxy equivalent weight of 190 g was kindly provided by Dow Chemicals. Amine-terminated poly(propylene oxide) oligomer with amine equivalent weight of 198 g/mol (Jeffamine D 400) was a product of Huntsman Chemicals. Hydrophobic (HDK H2000) and hydrophilic (HDK N20) fumed silica were kindly provided by Wacker Chemie, Munich, Germany. Hydrophobic and hydrophilic silica were coded as H2K and N20, respectively, in the manuscript. Primary particle size for silica is reported to be 5–30 nm, which increases to 100–250 nm after aggregation.<sup>28</sup> The specific surface area is reported to be  $170\text{--}230\text{ m}^2/\text{g}$ .<sup>28</sup> Hydrophobic silica is obtained by the reaction of hydrophilic silica, which is  $>99.8\%$  by weight of amorphous silicon dioxide and has a silanol content of  $2\text{SiOH}/\text{nm}^2$ , with trimethyl chlorosilane or hexamethyldisilazane producing a surface covered with

trimethylsiloxy groups.<sup>28</sup> Polystyrene was synthesized in our laboratories in toluene solution at  $80^\circ\text{C}$  by free radical polymerization, using benzoyl peroxide initiator. Number average molecular weight and polydispersity index values determined by size exclusion chromatography were  $120\,000\text{ g/mol}$  and 1.80, respectively. Reagent-grade isopropanol (IPA) and tetrahydrofuran (THF) were obtained from Merck and used as received.

**Sample Preparation.** Samples were prepared by spin-coating onto glass slides following a three-step procedure. Glass surfaces were cleaned by wiping with IPA and THF successively several times before the coating is applied. Stable silica dispersions with desired silica ratios were prepared in THF, IPA, or THF/IPA mixture, as shown in Table 1. Choice of the solvent or solvent mixture is based on the polarity of

**Table 1. Description of Samples Prepared, Compositions of Silica Dispersions, and Solvent Used**

| sample code |        | silica ratio<br>N20/H2K | H2K content<br>(wt %) | composition of<br>solvent mixture |       |
|-------------|--------|-------------------------|-----------------------|-----------------------------------|-------|
|             |        |                         |                       | solvent                           | (v/v) |
| PS-0        | ER-0   | 1/0                     | 0                     | IPA                               |       |
| PS-14       | ER-14  | 6/1                     | 14.3                  | IPA/THF                           | 6/1   |
| PS-25       | ER-25  | 3/1                     | 25.0                  | IPA/THF                           | 3/1   |
| PS-38       | --     | 5/3                     | 37.5                  | IPA/THF                           | 5/3   |
| PS-50       | ER-50  | 1/1                     | 50.0                  | IPA/THF                           | 1/1   |
| PS-63       | --     | 3/5                     | 62.5                  | IPA/THF                           | 3/1   |
| PS-75       | ER-75  | 1/3                     | 75.0                  | IPA/THF                           | 3/5   |
| PS-86       | ER-86  | 1/6                     | 85.7                  | IPA/THF                           | 1/6   |
| PS-100      | ER-100 | 0/1                     | 100.0                 | THF                               |       |

silica mixture. Concentration of silica in the dispersion was constant at 2.5% by weight, regardless of the composition of the mixture. To obtain a homogeneous distribution, the dispersion was subjected to ultrasound sonication at a frequency of 35 kHz on a Sonorex RK 255H type ultrasonic bath (Bandelin, Berlin, Germany) for 180 min.

**Coating on Polystyrene.** Polystyrene (PS) was dissolved in THF to make a solution with a concentration of 20% solids by weight. Three drops of PS solution was placed onto the glass slide and spin-coated at 1000 rpm. This provides a base film with a thickness of  $25\text{--}30\text{ }\mu\text{m}$ . Immediately afterward, 3 drops of silica dispersion in THF was placed onto the film, and after waiting for 1 min (to allow the solvent to dissolve/swell top polymer layer and penetration and adhesion of silica particles into the polymer matrix to obtain a durable coating), it was spin-coated at 1000 rpm. This step was repeated in order to form a denser silica layer. Samples were dried at  $50^\circ\text{C}$  under vacuum. Table 1 provides a list of the samples prepared, their compositions, and solvents used.

**Coating on Epoxy Resin.** Stoichiometric amounts of DER 331 and D 400 were mixed and spin-coated at 1000 rpm on a glass substrate. Thickness of the films obtained was  $40\text{--}50\text{ }\mu\text{m}$ . Sample was partially cured at  $60^\circ\text{C}$  for 4 h. Three drops of silica dispersion were then placed onto the sample, and after waiting for 1 min (to allow the solvent to dissolve/swell top layer of the resin and provide adhesion of silica particles into the resin matrix), it was spin-coated at 1000 rpm. This step was repeated in order to form a denser silica layer. Samples were cured at  $80^\circ\text{C}$ . Table 1 provides a list of the samples prepared, their compositions, and solvents used.

Sample coding used in Table 1 is as follows: PS and ER denote polystyrene and epoxy resin, respectively. The following numbers indicate the amount of hydrophobic silica H2K (in weight percent) in the silica coating mixture applied.

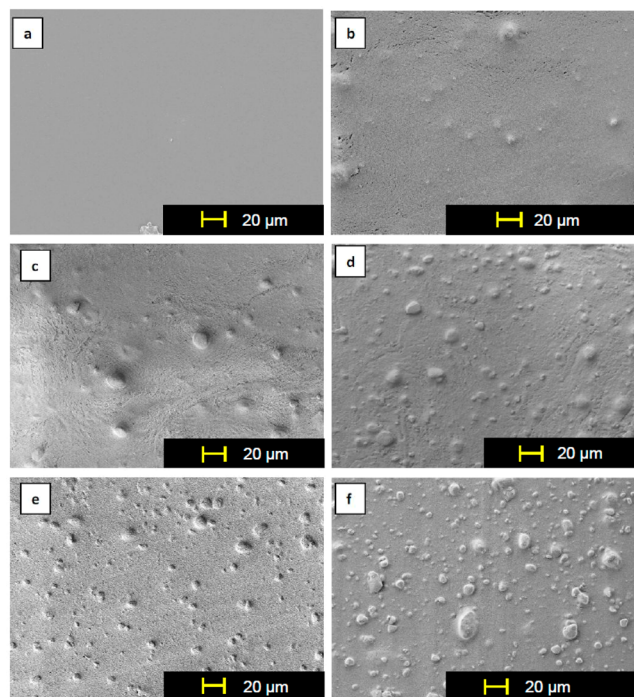
**Characterization Methods.** Static water contact angle measurements were performed on a Krüss G-10 goniometer, fitted with a high-resolution digital camera (Spot Insight Color, by Diagnostic Instruments, Inc.) at room temperature ( $23 \pm 1^\circ\text{C}$ ). During measurements,  $5\text{ }\mu\text{L}$  deionized, triple distilled water was used. The average of 10 readings was reported as the contact angle for each

sample. Surface structures of the samples were examined using a field-emission scanning electron microscope (FESEM) (Zeiss SUPRA 35VP, LEO, Germany) operated at 2 kV. The films were coated with a thin layer of carbon prior to SEM examinations. Atomic force microscopy (AFM) images were recorded by using Nanomagnetics Instruments Multimode atomic force microscope operated in dynamic mode. Au reflective NSG10 silicon tip with a force constant of 11.8 N/m and resonance frequency of 240 kHz was utilized to probe the surfaces. Engagement set points between 0.6 and 0.8 of the free amplitude oscillation were used. Surface chemical compositions of the films were investigated using a ThermoScientific K-Alpha X-ray photoelectron spectrometer (XPS) equipped with a monochromatic Al K $\alpha$  excitation source (1486.6 eV) and hemispherical analyzer. The spot size of the beam was 400  $\mu$ m. The take-off angle was set at 90°. XPS atomic compositions were collected from a depth of  $\sim$ 10 nm and ratios were determined by using the supplied *Avantage* software. A flood gun was employed to reduce surface charging and binding energies were referenced to the carbon 1s primary signal at 284.4 eV.

## RESULTS AND DISCUSSION

Polymer surfaces with tunable wetting behavior may play critical roles in adhesion, selective absorption, biocompatibility, permeability, and so forth. Here, we report a simple three-step spin-coating process for the preparation of polystyrene and cross-linked epoxy resin surfaces with controlled wettability or tunable wetting behavior. Process is based on the use of a silica coating, which is composed of a mixture of hydrophobic and hydrophilic silica. As discussed in detail below, with this approach we are able to obtain polystyrene and epoxy resin surfaces with static water contact angles in the range of 0° (superhydrophilic) to >170° (superhydrophobic). There are a number of reports in the literature which describe the preparation of polymeric surfaces with tunable wetting behavior.<sup>14–27</sup> However, they are (i) usually based on fairly difficult processes, (ii) applicable for specific polymer systems, and (iii) only cover a fraction of the superhydrophilic–superhydrophobic range. On the other hand, with our simple approach it is possible to obtain almost any static water contact angle desired (truly tunable wetting behavior) on almost any polymeric surface, thermoplastic or thermoset. We believe this method can easily be extended to other substrates such as silica, inorganic glasses, and ceramics.

**SEM Studies.** Morphology of the surfaces obtained as a function of the silica composition was investigated by SEM studies. SEM images of uncoated and silica coated polystyrene film surfaces at different hydrophilic/hydrophobic silica concentrations are reproduced in Figure 1a–f. As can be seen in Figure 1a, spin-coated polystyrene film surface is very smooth and featureless, which is expected. When silica coating is applied onto the polystyrene surface using a spin-coating procedure, surface topography gradually changes as a function of silica composition. As shown in Figure 1b, it is interesting to note that 2 layers of hydrophilic silica (N20) coated polystyrene surface (PS-0) is fairly homogeneous and smooth with a few domains of silica 1–10  $\mu$ m in size. Hydrophilic silica particles typically are less probable to agglomerate due to their surface charge. On the other hand, 2 layers of hydrophobic silica (H2K) coated polystyrene surface (PS-100) display a fairly rough surface topography with a large number of silica domains also in 1–10  $\mu$ m size range. As we have already reported, this sample displays a superhydrophobic surface.<sup>29</sup> As can clearly be seen in Figure 1c–e, polystyrene surfaces coated with a mixture of hydrophilic/hydrophobic silica display surface topographies with gradually increasing microroughness as a



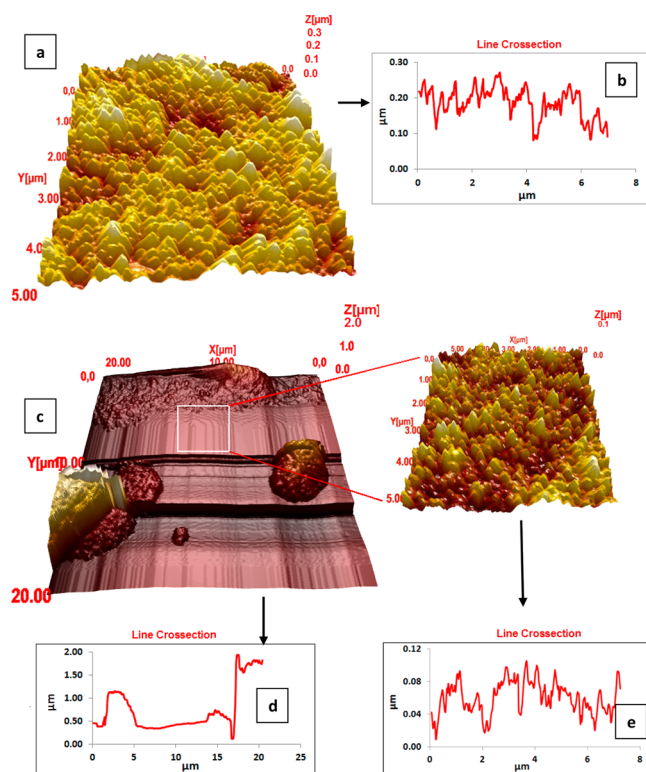
**Figure 1.** SEM surface images of (a) spin-coated polystyrene film, (b) 2 layers of N20 coated (PS-0), (c) 2 layers of 75/25 (N20/H2K) coated (PS-25), (d) 2 layers of 50/50 (N20/H2K) coated (PS-50), (e) 2 layers of 25/75 (N20/H2K) coated (PS-75), and (f) 2 layers of H2K coated (PS-100) polystyrene surfaces.

function of the hydrophobic silica content. Interestingly, the sizes of the silica domains remain constant in the 1–10  $\mu$ m range, but their concentration increases as the content of hydrophobic silica in the coating increases. Gradual increase in the surface roughness as a function of the hydrophobic silica content of the coating plays a critical role in the tunable wettability of the surfaces formed as determined by static water contact angle measurements, discussed later, eventually leading to the formation of superhydrophobic surfaces. On the basis of SEM and white light interferometry studies discussed later, we believe the silica particles penetrate into the polymer film a few micrometers and produce durable surfaces.

**AFM Studies.** In order to better understand the surface topography and the extent of surface roughness on the silica-coated polymer surfaces, AFM studies were performed on several silica-coated polystyrene samples, where height images were obtained and average roughness of the surfaces were determined.

Height images and depth profiles of the hydrophilic and hydrophobic silica coated polystyrene films, which are coded PS-0 and PS-100, respectively, are provided in Figure 2. AFM height image given in Figure 2a shows homogeneous coverage of the PS-0 film surface with hydrophilic silica, (similar to the SEM results) with a fairly low surface roughness of about 0.10  $\mu$ m or 100 nm, as shown in the depth profile provided in Figure 2b. Hydrophobic silica-coated polystyrene (PS-100) displays a fairly rough surface consisting of large silica domains on a fairly smooth matrix as can be seen from 20  $\times$  20  $\mu$ m<sup>2</sup> sections of AFM height images given in Figure 2c. Depth profile indicates domain heights of 1–2  $\mu$ m (Figure 2d), which is an order of magnitude higher, when compared with the smooth matrix, which shows average roughness of about 0.10  $\mu$ m (Figure 2e).





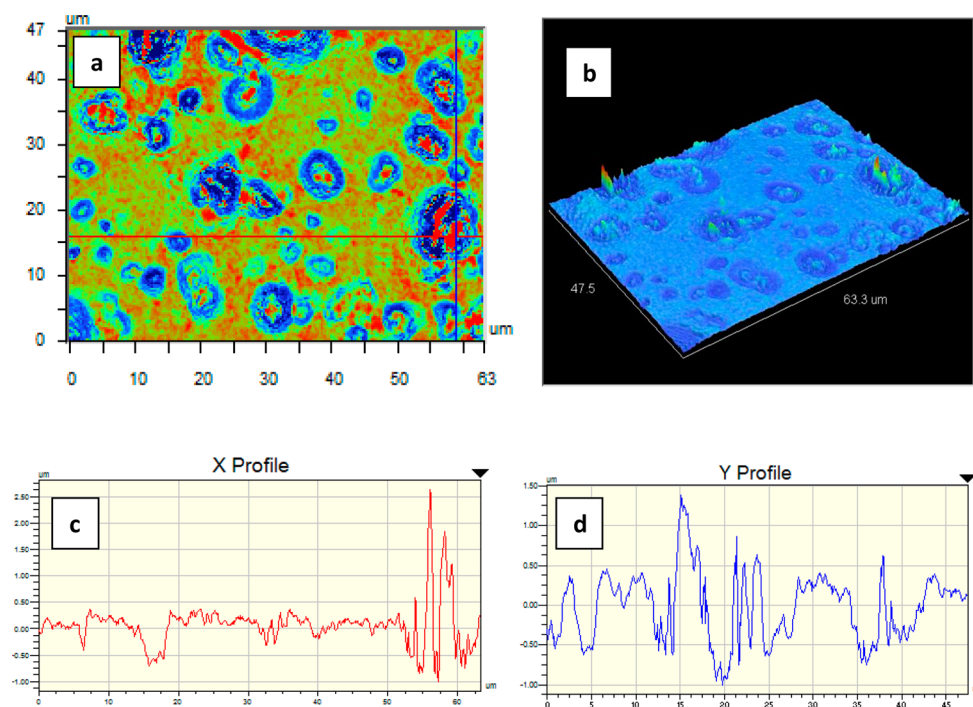
**Figure 2.** AFM height images and depth profiles of silica coated surfaces for PS-0 (a,b), and (b) PS-100 (c,d,e).

**Investigation of the Surface Topography by White Light Interferometry.** Optical interferometry is a simple, noncontact technique based on the analysis of the interference patterns of light waves to obtain quantitative information on the three-dimensional surface topography of materials. As the

name implies, white light interferometers use white light with a broad optical bandwidth and are capable of precisely mapping a variety of surfaces, smooth or rough. Surface heights from nanometer to micrometer scale across areas that range from micrometers to millimeters can easily be mapped by this technique.

Figure 3a provides the topographical image of the PS-100 surface with dimensions of  $63 \times 47 \mu\text{m}^2$ , obtained by white light interferometry. Figure 3b provides the 3D image of the surface. General features of the images obtained are fairly similar to that obtained by SEM and provided in Figure 1f. They show silica domains in the  $1\text{--}10 \mu\text{m}$  range with a fairly homogeneous distribution of the particles on polymer surface. Also provided in Figure 3c,d are the 2D profiles of the silica-coated PS-100 film surface in  $x$  and  $y$  directions, as indicated by the lines in Figure 3a. As provided in Figure 3c, the 2D profile along the  $x$ -axis indicates a fairly smooth surface until reaching the large silica particle located between  $55$  and  $63 \mu\text{m}$ , which has a length of  $8 \mu\text{m}$  and a height of about  $3 \mu\text{m}$ . The 2D profile along the  $y$ -axis, given in Figure 3d, crosses through several silica particles and as a result indicates a fairly rough topography. Particle sizes vary between  $3$  and  $15 \mu\text{m}$  and their heights are in  $0.5$  to  $2.5 \mu\text{m}$  range. These results clearly show that the hydrophobic silica-coated PS-100 surface has a microrough topography with particle sizes in the  $1\text{--}15 \mu\text{m}$  range and particle heights of  $0.5\text{--}3 \mu\text{m}$ .

**Surface Analysis by X-ray Photoelectron Spectroscopy.** In order to better understand the homogeneity of the distribution of the hydrophilic and hydrophobic silica on the surface coating, X-ray photoelectron spectroscopy was utilized and C/Si ratios on the coated surfaces were determined. As discussed in the Experimental section, hydrophilic silica (N20) is  $>99.8\%$  by weight of amorphous silicon dioxide ( $\text{SiO}_2$ ) and has a silanol content of  $2\text{SiOH}/\text{nm}^2$ . On the other hand, hydrophobic silica surface is covered with trimethylsiloxy



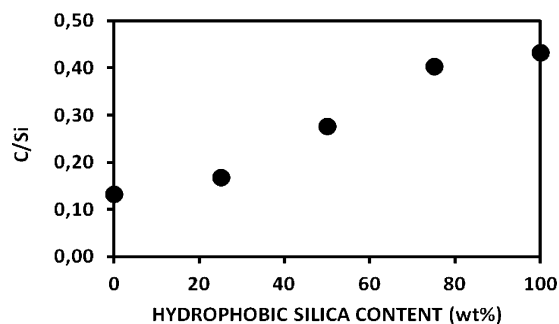
**Figure 3.** (a) 2D and (b) 3D topographical images of the PS-100 surface, and depth profiles of surfaces along (c)  $x$ -axis and (d)  $y$ -axis, obtained by white light interferometry.

–Si(OCH<sub>3</sub>)<sub>3</sub> groups. Since only hydrophobic silica particles contain carbon atoms on their surfaces, the C/Si ratio is expected to display an increase as a function of the hydrophobic silica content of the coating applied, if the silica particles in the coating are homogeneously mixed and distributed on the polymer surface. Therefore, XPS data would provide important information on the composition and the homogeneity of the silica coatings applied onto the polymer surface. Table 2 provides the XPS binding energy values obtained for Si2p and C1s peaks, atom percentages calculated from XPS spectra, and the C/Si ratio for the silica-coated PS samples.

**Table 2. Analysis of Si2p and C1s Peaks of the XPS Spectra for Silica-Coated Polystyrene**

| sample | Si2p    |          | C1s     |          | C/Si  |
|--------|---------|----------|---------|----------|-------|
|        | BE (eV) | atom (%) | BE (eV) | atom (%) |       |
| PS-0   | 102.67  | 49.93    | 284.35  | 6.61     | 0.132 |
| PS-25  | 103.72  | 36.77    | 284.77  | 6.18     | 0.168 |
| PS-50  | 103.66  | 35.22    | 284.62  | 9.76     | 0.277 |
| PS-75  | 103.25  | 34.92    | 284.36  | 14.06    | 0.403 |
| PS-100 | 103.26  | 34.30    | 284.41  | 14.86    | 0.433 |

A plot of the C/Si ratio obtained from the XPS analysis as a function of the hydrophobic silica content of the coatings is provided in Figure 4. Very small C/Si ratio at the origin, for the hydrophilic silica coating only, is most probably due to the polystyrene background. On the other hand, as the amount of hydrophobic silica in the coating increases the C/Si ratio also increases. These results also indicate fairly good mixing and homogeneous distribution of the hydrophilic and hydrophobic silica on the surface of the polystyrene after spin-coating process.



**Figure 4.** Variation of the C/Si ratio as a function of the hydrophobic silica content on the coated PS surface.

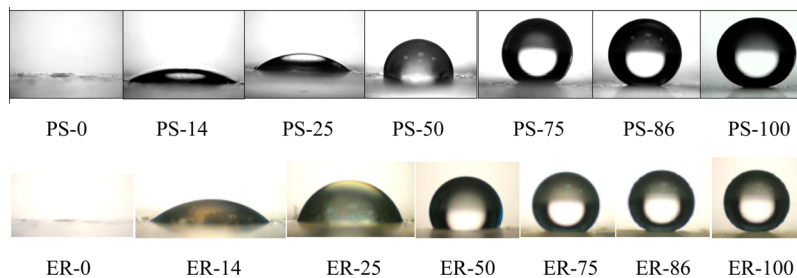
**Static Water Contact Angle Measurements.** Figure 5 provides representative images of the static water contact angles measured on the silica-coated polystyrene (PS) and cross-linked epoxy resin (ER) samples, respectively, as a function of the hydrophobic silica content of the coating mixture. PS-0 and ER-0, which are coated with hydrophilic silica (N20), only display superhydrophilic surfaces. As can be seen in Figure 5, PS-0 and ER-0 surfaces are completely wetted by the water droplet, and it is not possible to measure a water contact angle on these surfaces. On the other hand, surfaces coated with hydrophobic silica (H2K) only (PS-100 and ER-100) display superhydrophobic behavior with static water contact angles well over 170°. Very interestingly, as shown in Figure 5, as the amount of hydrophobic silica (H2K) in the coating mixture increases, coated surfaces become more and more hydrophobic and display well-defined and gradually increasing static water contact angles as a function of the composition of the silica coating applied both for polystyrene and for cross-linked epoxy resin samples. As discussed earlier, an increase in the microroughness of the surfaces as a function of the hydrophobic silica content most probably also contributes to the increase in the measured contact angles.

Tables 3 and 4 provide a summary of the static water contact angles measured on silica coated polystyrene and epoxy resin

**Table 3. Experimentally Measured and Calculated Static Water Contact Angles for Polystyrene Samples as a Function of the Hydrophobic Silica Content of the Coating Mixture**

|        | H2K content wt % | $f_1$ | static water contact angle (°) |            |
|--------|------------------|-------|--------------------------------|------------|
|        |                  |       | measured                       | calculated |
| PS-0   | 0                | 0.000 | 0                              | 0          |
| PS-14  | 14.3             | 0.143 | 19.6 ± 1.3                     | 44.4       |
| PS-25  | 25.0             | 0.250 | 40.0 ± 1.6                     | 60.0       |
| PS-38  | 37.5             | 0.375 | 59.1 ± 2.8                     | 75.5       |
| PS-50  | 50.0             | 0.500 | 91.0 ± 1.4                     | 90.0       |
| PS-63  | 62.5             | 0.625 | 117.6 ± 3.3                    | 104.5      |
| PS-75  | 75.0             | 0.750 | 145.0 ± 3.3                    | 120.0      |
| PS-86  | 85.7             | 0.857 | 155.1 ± 2.8                    | 135.6      |
| PS-100 | 100              | 1.000 | 173.7 ± 0.5                    | 180        |

samples, respectively, as a function of the hydrophobic silica content. Each reported contact angle value is an average of at least 10 measurements. In addition to the experimentally measured water contact angles, theoretical water contact angle values calculated by using the Cassie–Baxter<sup>10</sup> equation are also provided in Tables 3 and 4. Theoretical analysis of the contact angles on a two-component composite solid surface is provided by Cassie and Baxter, who proposed the equation



**Figure 5.** Images of the representative static water contact angles measured on the silica-coated polystyrene (PS) and epoxy resin (ER) samples as a function of the silica composition.

**Table 4. Experimentally Measured and Calculated Static Water Contact Angles for Epoxy Resin Samples as a Function of the Hydrophobic Silica Content of the Coating Mixture**

|        | H2K content wt % | $f_1$ | static water contact angle (°) |            |
|--------|------------------|-------|--------------------------------|------------|
|        |                  |       | measured                       | calculated |
| ER-0   | 0                | 0.000 | 0                              | 0          |
| ER-14  | 14.3             | 0.143 | 32.0 ± 2.0                     | 44.4       |
| ER-25  | 25.0             | 0.250 | 70.4 ± 2.7                     | 60.0       |
| ER-50  | 50.0             | 0.500 | 116.0 ± 1.9                    | 90.0       |
| ER-75  | 75.0             | 0.750 | 137.5 ± 3.0                    | 120.0      |
| ER-86  | 85.7             | 0.857 | 159.1 ± 3.5                    | 135.6      |
| ER-100 | 100              | 1.000 | 175.3 ± 0.8                    | 180        |

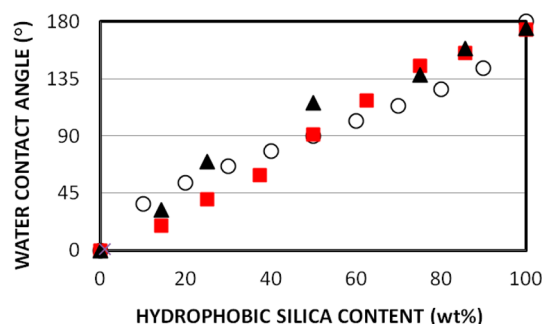
below for estimating the equilibrium contact angle ( $\theta$ ) on solid surfaces with varying degrees of heterogeneity, as well as rough surfaces containing air pockets.<sup>10</sup>

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2$$

In this equation,  $f_1$  and  $f_2$  are the liquid/solid contact area fractions of components (1) and (2) on the surface, and  $\theta_1$  and  $\theta_2$  are the equilibrium contact angles of the liquid on each of the flat surfaces of pure components.

Since the coated samples prepared in this study were based on two different types of silica, and XPS results indicated a homogeneous distribution of hydrophilic and hydrophobic silica in the coating, together with the formation of a microrough topography as demonstrated by SEM studies, the Cassie–Baxter equation was utilized to calculate the theoretical water contact angles on these solid, composite polymer surfaces as a function of silica composition. In the calculations,  $f_1$  and  $f_2$  were taken as the fraction of hydrophobic and hydrophilic silica in the silica mixture, respectively, and are tabulated in Table 3 and Table 4. The value of the static water contact angle on the hydrophobic silica-coated surface ( $\theta_1$ ) was taken as 180° (or  $\cos \theta_1 = -1.00$ ) and on hydrophilic silica-coated surface ( $\theta_1$ ) as 0° (or  $\cos \theta_1 = 1.00$ ), which are the ideal values. Experimentally determined water contact angle values on hydrophilic silica-coated PS and ER surfaces were 0°, identical to the ideal value, and on hydrophobic silica-coated PS and ER surfaces were  $173.7 \pm 0.5^\circ$  and  $175.3 \pm 0.8^\circ$ , respectively, as provided on Tables 3 and 4, which are very close to the ideal value.

When experimentally determined static water contact angle values tabulated on Tables 3 and 4 are plotted against the amount of hydrophobic silica present in the coating mixture, very interestingly, a fairly linear plot is observed for both the thermoplastic polystyrene (PS) and cross-linked epoxy resin (ER) surfaces, as shown in Figure 6. Also provided in Figure 6 is a plot of the static water contact angle values calculated from Cassie–Baxter equation. It is very interesting to note from Figure 6 that experimentally determined contact angles on two different polymers and contact angles calculated using Cassie–Baxter equation are very close to each other. These results indicate that (i) coating applied onto the polymer surfaces using a mixture of hydrophobic/hydrophilic silica is homogeneous, (ii) water contact angles measured on the silica coated surfaces are only dependent on the composition of the silica mixture but independent of the base polymer used, and (iii) the Cassie–Baxter equation is useful in estimating the water contact angles on solid, microrough surfaces composed of a mixture of hydrophilic and hydrophobic silica. Interestingly, we believe that the results provided in Table 3, Table 4, and Figure



**Figure 6.** Plot of experimental and calculated static water contact angles on silica-coated polystyrene and epoxy resin surfaces as a function of the hydrophobic silica content of the coating mixture: (red block) polystyrene, (▲) epoxy resin, (○) calculated from Cassie–Baxter equation.

6, belong to very few experimental supports for the Cassie–Baxter equation in such a wide range of static water contact angles, from 0° to 175°.

## CONCLUSIONS

A simple and versatile method, based on spin-coating of a hydrophilic/hydrophobic silica mixture dispersed in an organic solvent or solvent mixture onto a polymer surface, was developed for the preparation of polymer surfaces with controlled wettability or tunable wetting. It has been demonstrated that with this method it is possible to prepare polymer surfaces with static water contact angles ranging from 0° (superhydrophilic) to greater than 170° (superhydrophobic). In this report, preparation and characterization of surfaces with controlled wettability based on polystyrene (PS) and a cross-linked epoxy resin (ER) are provided as general examples. We believe that the method is applicable to a large number of polymers, thermoplastic or thermoset. Although only a spin-coating process was discussed in this manuscript, we believe it may be possible to obtain polymer surfaces, which display tunable wetting behavior by coating a hydrophilic/hydrophobic silica mixture using a spraying or dipping method or employing doctor-blade coating techniques.

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### Notes

The authors declare no competing financial interest.

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