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Superhydrophobic and low-hysteresis coating based on rubber-modified TiO₂/SiO₂ nanoparticles

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Abstract. In this article, the wettability of a superhydrophobic layer from rubber-modified TiO₂/SiO₂ nanocomposite is studied. The nanocomposites were prepared with various ratios of TiO₂ and SiO₂ nanoparticles (NPs) and then studied the effect of annealing, UV irradiation and aging after coating on a substrate. Results show that the average contact angle of deionized water droplets on the most hydrophobic coating is 129.5°, which increases up to 151.0° by UV irradiation. In addition, the lowest surface energy of the prepared layers was measured as 29.61 mJ m⁻². The hydrophobicity of the coating surface was investigated after annealing (at temperatures up to 300°C), and results show that the maximum contact angle is about 150°. The dynamics of water droplets on the most hydrophobic coating were investigated by rapid imaging, and results show no hysteresis for surface wetting. Fourier transform infrared spectroscopy shows that UV irradiation causes the formation of C–H functional groups on the surface without considerable change in the hydrophobicity, while the annealing process has no significant effects on the functional groups. The morphology of the coatings was investigated by scanning electron microscopy, and results reveal that the roughness of surfaces increases due to annealing and UV radiation. In addition, a minimum increase in the roughness coefficient is estimated as 73% of the initial value after annealing, which is in agreement with atomic force microscopy results.

Keywords. TiO₂ nanoparticles; silica; superhydrophobic; surface energy.

1. Introduction

Fabrication and characterization of surfaces with a favourable degree of wettability has attracted remarkable interests in recent years due to their potential for nanotechnology applications, such as self-cleaning [1], anti-icing and gradient surfaces [2–4]. Generally, four main features can affect the wettability of a surface, including surface texture, surface chemistry, coating condition and post-processing treatment [2]. Hydrophilic and hydrophobic expressions define the adhesion level of water droplets to the surface [4,5]. The surface energy of a hydrophilic coating is higher than the hydrophobic surfaces, and a water droplet can move on it due to solid–liquid interactions [6,7], arising from the gradient in surface energy. A gradient surface is a coating, in which its wettability varies from superhydrophobic to superhydrophilic [8]. These surfaces can be achieved by controlling the wettability of the coatings layer on a substrate [6,7]. Wettability surface texture and surface chemistry can be modified by coating condition and post-processing treatment.

Fabrication of the superhydrophobic surface with favourable properties is a challenge in the field of surface and interface science [9,10]. As reported, Wenzel–Cassie

coexist state can be fabricated by porous surface, which improves catalysing due to maximizing the interface of electrode coating [11]. Extensive application of non-wetting surfaces requires a facile and cost-effective method to fabricate these coatings [4]. For instance, Ganne and co-workers [7] have reported a superhydrophobic mesh by multimodal roughness with high stability and anti-icing performance, which shows hours of freezing delay for water droplets. Water repellency of the coating surface could be significantly enhanced by the use of SiO₂ and TiO₂ NPs due to coating porosity [12]. Hydrophobic TiO₂–SiO₂ porous composite can be synthesized by several methods [13]. For instance, Kim *et al* [14] reported a cost-effective SiO₂–TiO₂ composite using titanium oxychloride as a TiO₂ precursor, which can be applied for the purification of the contaminated air and this degradation of organic contaminations [12,15,16]. Moreover, crystal stability can be enhanced by the addition of SiO₂ as a dopant for TiO₂ [17], and combining silica and titania NPs can provide a significant stable coating with a larger surface area [18]. Anitha *et al* [19] prepared mesoporous superhydrophobic silica without fluorine, which guides for the use of nanoparticles (NPs) in the composite for easily controlling the coating quality and process. The porosity and coating technology are important

for the fabrication of a superhydrophobic surface and the use of NPs is promising for this purpose. Fabrication of a coating with an arbitrary degree of wettability and studying of water droplet dynamics on a hydrophobic surface is still a challenge for NP-based composites [19,20]. The stability of these coatings against hazard conditions is another challenge that should be addressed for further applications. Using hydrophilic particles and silicone elastomeric materials one can fabricate a superhydrophobic surface with excellent stretchability [21]. In addition, desirable stability can be achieved for myriad-lined protrusions on the surface of the TiAl-based composite [20]. The durability of submerged hydrophobic coating with flat and patterned cross-linked polydimethylsiloxane surfaces was studied and results show that the positive replica remains hydrophobic for a month [22]. Coating technology and post-processing treatments, which can convert a hydrophobic composite to superhydrophobic, is essential for porous composite based on NPs to fabricate a stable and optimized wettability.

Figure 1. Changes in contact angle of de-ionized water droplets vs. TiO₂/SR concentration in SiO₂ solution before and after UV irradiation.

Figure 2. (a) The annealing effect on the hydrophobicity of sample prepared by equal concentration of TiO₂ and SiO₂ NPs. (b) TGA and differential thermal analysis experiment from the prepared superhydrophobic sample.

In this article, the wettability of rubber-modified TiO₂/SiO₂ nanocomposite as a coating layer is investigated. The coating layer was prepared with different concentrations of TiO₂ and SiO₂ NPs. Wettability of the as-prepared coating was examined by contact angle measurement of water droplets on the prepared coating surface. Also, UV and annealing effects were studied separately for the most hydrophobic surface.

2. Materials and methods

SiO₂ NPs were used with an average size of 20 nm from Kimia Gostar Poyesh Company and anatase TiO₂ NPs with an average size of 30 nm from US-Nano Company. Commercial silicon rubber (SelSil 100% silicone polymer) was prepared from SEL DIS Turkey and other materials including n-hexane (95%), acetone (99%), 1-methyl-2-pyrrolidinone (99%), ethylene glycol (99%) and glycerol (99%) were purchased from Merck.

To provide the composite, two solutions were prepared with TiO₂ and SiO₂ NPs, respectively. For the first solution, 5 mg of silicon rubber (SR) was added to 20 ml of n-hexane and then solved it by stirring for 60 min with an angular speed of 1200 RPM. Afterwards, the prepared solution was exposed in an ultrasonic bath for 10 min with a power of 400 W. In the next step, 10 mg of TiO₂ NPs were added to it and stirred for 30 min. To prepare the second solution, 10 mg of SiO₂ NPs were dissolved in 20 ml of n-hexane by stirring at a rate of 1200 RPM for 30 min and sonicating in an ultrasonic bath for 10 min.

Finally, TiO₂/SR solution and SiO₂ solution were mixed with 20, 40, 50, 60 and 100 wt%. The composite was deposited on a glass substrate by the drop-casting method and then dried at 65°C. The contact angle of deionized water droplets was measured for all samples before and after UV irradiation under a circulating fan for 30 min. A UV-C lamp was used as the UV source with a power of 1.40 mW cm⁻² and a peak emission of 254 nm. In addition,

Table 1. Surface tension and contact angle of the test liquids, which were used in this study. The surface tension was taken from ref. [4].

Liquid	γ_l (mJ m ⁻²)	Contact angle
1-Methyl-2-pyrrolidinone	40.79	30.6°
<i>n</i> -Hexane	18.43	0°
Ethylene glycol	47.99	101.7°
Water	72.80	151.1°
Glycerol	64.00	130.2°
Acetone	25.20	9.1°

Figure 3. Fitted curve for calculation of the surface free energy by Neumann method.

Figure 4. The FTIR spectrum of the as-prepared, UV irradiated and annealed coating at 300°C sample.

the prepared samples were annealed for 30 min at temperatures of 100, 150, 200, 250 and 300°C, and then the contact angle of water droplets was measured. The surface energy of the coatings was calculated from the contact angle of various droplets (at least 5 different points on 3 samples), including *n*-hexane, acetone, 1-methyl-2-pyrrolidinone and ethylene glycol. Scanning electron microscopy (SEM) was performed by an LEO 1455-VP SEM and optical

microscopy was performed by Motic BA210E Microscope. In the SEM experiment, the samples were coated with a thin layer of silver (around 10 nm). Fourier transform infrared (FTIR) spectroscopy was conducted by a Perkin-Elmer 580B spectrophotometer using the KBr disk technique. Atomic force microscopy (AFM) was performed by a Multi-Mode AFM from Ara-Research Company. The samples were prepared for AFM analysis by drop-casting method on a glass substrate and then dried at 65°C. Thermogravimetric analysis (TGA) was performed by NETZSCH STA 409 PC/PG instrument.

3. Results and discussion

Figure 1 shows the contact angle of prepared samples before and after UV exposure in various TiO₂/SR concentrations in the SiO₂ solution. As shown in figure, the prepared sample with the same ratio of TiO₂ and SiO₂ NPs is the best hydrophobic with a contact angle value of 129.5°. However, the contact angle of water droplets increases for all samples after UV irradiation, and the maximum contact angle becomes 151.1° for 50 wt% of TiO₂/SR solution in the SiO₂ solution. Wettens behaviour relates to the interaction of the fluid and the substrate, and when the liquid/vapour interfacial tension is stronger than the solid/liquid interfacial tension, the water drop on the surface can be spherical with the contact angle larger than 150° [4,5]. In addition, increasing the concentration of TiO₂ NPs in the composite increases the wettability of the surface. This can be due to SR wetting transparency, which transports the hydrophilic properties of TiO₂ NPs to the coating surface [11,23]. Wetting transparency is allowing the ‘transmission’ of the substrate wettability to above the surface coating [23]. When TiO₂ concentration is too high, the wettability increases due to the hydrophilicity of the NPs. The polymer layer is wetting transparent and does not disrupt the intrinsic wetting behaviour of the coating surfaces and therefore the surface wettability is modified according to the concentration of TiO₂ NPs.

Figure 2a shows the contact angle of water droplets for the coating surface with equal ratios of SiO₂ and TiO₂ NPs after annealing. Annealing temperatures were taken as 60, 100, 150, 200, 250 and 300°C for 30 min. Results show an increase in hydrophobicity, and the maximum contact angle (about 150°) was obtained for annealed samples at 300°C. As a matter of point, a critical annealing temperature can be obtained, which induce a wetting transition between two wetting modes; the Wenzel state and Cassie–Baxter state [24]. Cassie–Baxter and Wenzel regimes are two well-known models that explain the increase in contact angle due to the roughness of the surface and its structure [25–28]. The Cassie–Baxter regime is used when the liquid does not penetrate into the pores of the surface, and a layer of air lies between the surfaces and water droplets while in Wenzel model water droplet is in contact with all surfaces, and the

Figure 5. (a) Dynamics of water droplets on the prepared surface covered with hydrophobic coating, showing the water drop after collision and then raising due to the hydrophobicity. This continues many times until the drop leaves the surface without leaving any residue on the surface. (b) Advancing and receding a water droplet on the prepared surface, which shows superhydrophobicity of the surface.

whole surface is wetted [9,25–29]. The increase of the surface roughness can cause trapping the air pockets under the droplet. The Cassie–Baxter model can describe wetting of such a heterogeneous system, and the equilibrium conditions for a drop in this state are given by [27]:

$$\cos(\theta_{CB}) = f_s [R_F \cos(\theta_Y) + 1] - 1, \quad (1)$$

where θ_{CB} is the apparent contact angle in the Cassie–Baxter state, θ_Y is Young's contact angle for the smooth or simple surface, f_s is the area fractions of the solid and R_F the roughness ratio parameter, which is equal to the actual ratio of the solid–liquid surface area to the apparent solid–liquid surface area. Therefore, the value of R_F on a rough surface is higher than one. Neglecting the trapping air pockets and taking area fractions as 1, the equilibrium conditions for a drop can be taken as Wenzel state [26]:

$$\cos(\theta_W) = R_F \cos(\theta_Y), \quad (2)$$

where θ_W is the apparent contact angle. At low annealing temperatures, the contact angle was lower, suggesting that the wetting mode is in the Wenzel state, which describes intimate contact between the surface and water. In contrast, for higher annealing temperatures, the contact angle increases. The wetting mode is in the Cassie–Baxter state due to the good water-repellent property, and the interface tension between the surface and water is dramatically decreased due to the air trapping in the surface structures. Figure 2b shows the TGA and differential thermal analysis experiments from the prepared sample. As shown, 7.1% weight loss at the first stage and 25.57% at the second stage is observed for the most superhydrophobic composite. The first domain of weight loss is attributed to the solvent evaporation from the composite, while the second weight loss (25.57%) is attributed to the SR oxidation.

Figure 6. The contact angles of water droplets on the prepared coating after exposing in UV irradiation.

To calculate the surface free energy of the most hydrophobic coating, the Neumann equation is used [4]. For this purpose, the contact angle of several different liquids with different surface tensions was measured, as presented in table 1 and figure 3, by using the Neumann equation [30,31]:

$$\cos \theta = -1 + 2 \sqrt{\frac{\gamma_s}{\gamma_l}} e^{-\beta(\gamma_s - \gamma_l)^2} \quad (3)$$

where γ_l and γ_s represent the free energy of the liquid and the surface, respectively, θ is the contact angle related to the droplet on the surface and β is a constant, which is determined experimentally. The equation (1) can be rewritten as follows:

Figure 7. Photographs taken by optical microscopy for (a) as-prepared, (b) UV irradiated, (c) annealed at 150°C and (d) at 300°C samples. (e and f) AFM image of the surface for the as-prepared and annealed sample, respectively.

$$\ln \left[\gamma_1 \left(\frac{(1 + \cos \theta)^2}{2} \right) \right] = \ln(\gamma_s) - 2\beta(\gamma_s - \gamma_1)^2 \quad (4)$$

To obtain the surface free energy, the left side of the equation (4) has been plotted for the five liquids, including water, ethylene glycol, 1-methyl-2-pyrrolidinone, acetone and n-hexane, and then fit a second-order curve on them. The equation of the fitted curve, in figure 3, for the contact angle of the presented liquids in table 1 gives the surface free energy as 29.61 mJ m⁻².

FTIR spectroscopy was performed to investigate the difference between UV and annealing effect on the chemical composition of the prepared coating. Figure 4 shows the FTIR results for the as-prepared, UV irradiated and the annealed samples. As shown in this figure, the absorption peak around

the wavenumber of 3450 cm⁻¹ refers to the stretching vibrations of the Si-OH bond, and the peak at the wavenumber of 2930 cm⁻¹ is due to the asymmetric stretching vibrations of C-H [6]. In addition, absorption peaks corresponding to the Si-CH₃ and Si-O bonds are appearing at 1260 and 1090 cm⁻¹, respectively [32,33]. Absorption peaks in the range of 700–900 cm⁻¹ are due to Si-O symmetric stretching, Si-CH₃ bending, Si-C stretching and also Ti-O-Si stretching [34,35]. As shown in this figure, the relative intensity of C-H to the Si-O peak increases by UV irradiation, which can be due to photo-oxidation of the SR matrix in the presence of TiO₂ NPs. This process can increase the surface roughness by improving particle dispersion in the SR matrix, which is in agreement with the previously reported results [36]. In addition, three effects are observed in the annealed spectrum, in figure 4: broad water peaks at 3270 and 1630 cm⁻¹ decrease due to the evaporation of

Figure 8. Variation in roughness coefficient by annealing at temperatures up to 300°C.

water, the Si–OH peak decreases relative to Si–O–Si peaks showing that heat condenses the silica NPs, and some of the C–H peaks may have been lost due to oxidation.

Figure 5a shows the images of a water drop, which has thrown at a distance of 10 cm on the surface of the superhydrophobic coating. As shown, the water drop is distributed after a collision with the surface and then is raised due to the hydrophobicity of the surface and finally moves up. This continues many times until the drop leaves the surface without leaving any residue on the surface. This indicates an extremely high level of hydrophobicity without any hysteresis. Figure 5b shows the advancing and receding of a water droplet on the surface that confirms the previous results by exhibiting superhydrophobicity without hysteresis. To investigate the UV effect on the hydrophobicity of coating, we measured the contact angle of the treated coating for a few months. As shown in figure 6, the prepared composite shows acceptable stability in 120 days.

Figure 7a–d shows the microscopic photograph of the coating surface. As shown in this figure, the porosity of the surface increases after annealing and UV irradiation, which can increase the hydrophobicity of the surface, according to Cassie–Baxter regime [9,29]. Figure 7e and f also shows the

Figure 9. SEM images of (a) as-prepared, (b) UV irradiated and (c) annealed coating at 300°C samples. (d) Typical thickness of the coating layer.

AFM image from the prepared coating. The arithmetic average value of filtered roughness (R_a) was calculated from deviations about the centre surface within the AFM images. As shown, the R_a value increases from 128.2 to 287.4 nm by annealing the coating at 300°C. According to FTIR results, functional groups of the composite remain unchanged by annealing, and therefore increasing of hydrophobicity is mainly due to roughness enhancement, which is seen in figures 7 and 8.

Assuming a simple surface for the surface of as-prepared coating and a rough surface for the annealed samples at 300°C according to AFM data, we calculate minimum changes in R_F due to annealing according to equation (2). Figure 8 shows the minimum variation in roughness coefficient after annealing up to 73% of initial values. This is well illustrated by SEM analysis, as presented in figure 9. SEM images of the prepared surface for as-prepared, and UV irradiated and annealed samples at 300°C are presented in figure 9a–c. As shown, the prepared coating has a hierarchical structure with a rough surface, which is desirable for hydrophobic surfaces. In addition, the SEM image from the edge of the coated layer in figure 9d shows a thickness of 10–15 μm .

4. Conclusions

A superhydrophobic and low-hysteresis coating from rubber-modified $\text{TiO}_2/\text{SiO}_2$ nanocomposites were presented. The wettability of samples was studied by contact angle measurement of water droplets on the coating surface. UV and annealing effects were reported separately for the most hydrophobic surface, and results show that the roughness of surfaces increases by annealing and UV radiation as well as hydrophobicity of the samples. In addition, rapid imaging of water droplet dynamics shows no hysteresis for the surface wetting. FTIR spectroscopy shows that UV irradiation causes the formation of C–H functional groups on the surface, while annealing has no significant effect on the functional groups. The average contact angle of the deionized water droplet on the prepared coating was obtained at 151.1°, and its surface energy was measured as 29.61 mJ m^{-2} .

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