1 Article

# Functionalization Effect on Polymer Nanocomposites Coatings based on TiO<sub>2</sub>-SiO<sub>2</sub> Nanoparticles with

**4** Superhydrophilic Properties

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12 Abstract: In this study, a novel binary nanocomposite system based on TiO2-SiO2 was functionalized 13 with trimethylolpropane triacrylate (TMPTA) and characterized by XPS and XRD. Results revealed 14 that TiO<sub>2</sub>-SiO<sub>2</sub> nanoparticles were covalently functionalized. Functionalized nanoparticles at low 15 concentrations (0.1 wt% and 0.5 wt%) were dispersed in acrylic acid acting as a polymer matrix. 16 Nanocomposite coatings analysis demonstrate to achieve superhydrophilic properties as well as 17 very good optical characteristics. Water contact angle characterization showed the functionalization 18 effect by achieving a superhydrophilic behavior with a contact angle less than 5°. UV-Vis 19 measurements demonstrated high optical transmittance above 95% for the coatings. Based on the 20 obtained results a mechanism describing the chemical interactions of the constituents responsible 21 for the synergy in the nanocomposite as well as the morphological play role in the behavior are 22 presented.

- 23 Keywords: TiO<sub>2</sub>-SiO<sub>2</sub> functionalization, superhydrophilic coating, nanocomposite coating.
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#### 26 1. Introduction

27 New materials with novel properties are always required in order to overcome the increasing 28 technological demands. Some of these materials are based on polymer nanocomposites, in which 29 dispersed nanoparticles are incorporated into a matrix. In order to improve the affinity of these 30 phases and avoid agglomeration, surface modification is required on the nanoparticles, this process 31 is known as functionalization.

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It is known that functionalization of nanoparticles has interesting advantages, the functional groups at the nanoparticle acts as anchor point to other groups or molecules in the matrix, it is possible to increase affinity with the receptor compound, for example a polymeric matrix [1, 2]. Through nanoparticles functionalization is possible to obtain materials with functional features.

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Nowadays, the formulation of polymer-inorganic nanocomposite materials has been widely researched due to their interesting properties, because it combines the features of organic and inorganic materials, generating a new material for different potential applications. These materials acquire the synergy of the flexibility and the processability of the polymers with the optical and hydrophilic properties of the inorganic component, generating a compatible compound with both features [3].

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Recently, oxide nanoparticles have been studied as reinforcement of polymer nanocomposites
for many applications. For example, in the development of functional coatings with special
properties, like protective or self-cleaning features [4, 5]. A variety of inorganic nanoparticles have
been used for the development of self-cleaning coatings, mainly metal oxides as TiO<sub>2</sub> and SiO<sub>2</sub>.

49 Nanoparticles of TiO<sub>2</sub> and SiO<sub>2</sub> show interesting properties, like optical, superhydrophilic and
50 photocatalytic features, so these oxides can be considered as suitable materials for the development
51 of self-cleaning and anti-reflective coatings [6-8].

There exist several studies related to TiO<sub>2</sub>/SiO<sub>2</sub> as films, where the effect of TiO<sub>2</sub> addition to SiO<sub>2</sub> on the optical, mechanical, wettability and the photocatalytic activity has been investigated [9-13]. Other studies have been carried out on TiO<sub>2</sub>-SiO<sub>2</sub> mixing by sol-gel method, where in some cases optical properties, particularly antireflection has been compromised [14]. However, the preparation of polymer nanocomposites coatings based on TiO<sub>2</sub>-SiO<sub>2</sub> have not been reported yet.

In order to achieve a polymer nanocomposite, surface modification of nanoparticle is required, typical functionalization agents include: silanes [15], amines [16] and thiols [17], but modification conditions require low humidity and inert atmosphere. Polyacrylic polymer exhibits good transparency, is hydrophilic and can be a good candidate for coatings where transparency is required. Trimethylolpropane triacrylate (TMPTA) is a molecule with a high content of oxygen functionalities, which could be used as crosslinking or functionalizing agent of metal oxide nanoparticles. Although, there is work related, it is scarce [18, 19] and without explanation of the chemical interaction.

As mentioned before, the goal of a nanocomposite is to achieve the synergy of the properties from polymer and the dispersed nanoparticles. One of the main effects for the nanoparticle functionalization, is to increase the affinity with its matrix without altering the property of the nanoparticle. In order to achieve functional nanocomposite coatings such as self-cleaning, a critical step is to understand and control the interactions of functionalized nanoparticles in a polymeric matrix.

Here, a study of the functionalization effect on nanocomposites coatings with hydrophilic and
 superhydrophilic properties is presented, obtained through surface modification of TiO<sub>2</sub>-SiO<sub>2</sub>
 nanoparticles with trimethylolpropane triacrylate.

- 73 2. Materials and Methods
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- 75 2.1 Materials
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TiO<sub>2</sub> nanoparticles (TiO<sub>2</sub> P90) with a particle size of about 25 nm, density of 120 g/L, specific surface 90  $\pm$  20 m<sup>2</sup>/g and SiO<sub>2</sub> (Aerosil 200) with an average nanoparticle size of 12 nm, density of 50 g/L and specific surface of 200  $\pm$  25 m<sup>2</sup>/g were provided from Evonik. Trimethylolpropane triacrylate (TMPTA) chemical grade inhibited with 600 ppm of monomethyl ether hydroquinone and acrylic acid (AA) monomer (99%, inhibited with 200 ppm MEHQ) were purchased by Sigma Aldrich and ethanol was purchased from Fermont. Reagents were used as received.

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#### 84 2.2 Functionalization of TiO<sub>2</sub>-SiO<sub>2</sub> nanoparticles

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Functionalization was carried out in a TiO<sub>2</sub>-SiO<sub>2</sub> system with a 1:1 (wt/wt) ratio. Nanoparticles
ratio was determinated trough previous experiments. First, nanoparticles were dispersed in 10 mL
ethanol with the aid of ultrasonication for 30 min using 100% of amplitude, supplying 59400 J of
energy. Next, TMPTA was added to the previous nanoparticle dispersion in a 1:5 (wt/wt) ratio, the
solution was stirred vigorously for 4 h. Thereafter, it was sonicated for 2 h, the resultant solution was
filtered through a PTFE membrane filter with a pore size of about 0.2 µm and dried at 65°C for 24 h.
In Table 1, the nomenclature of modified nanoparticles is shown.

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94 2.3 Preparation of TiO<sub>2</sub>-SiO<sub>2</sub> embedded nanocomposite coatings

- 96 Solutions of non-functionalized and functionalized nanoparticles at 0.1 and 0.5 wt% in ethanol 97 and acrylic acid as monomer were sonicated for 30 min supplying 594 kJ/g of energy and 100% 98 amplitude. The obtained nanocomposites were used for film fabrication by spin coating, a wet 99 rotational speed of 2000 rpm and a holding time of 9 s, then a drying rotational speed of 2500 rpm 100 and a holding time of 20 s were used. Glass slides  $(6.25 \text{ cm}^2)$  used as substrates were washed by 101 sonication in cyclohexanone, chloroform, acetone, isopropanol and deionized water for 15 min each, 102 respectively. The obtained coating was air dried at 60°C for 30 min. Later coatings were cured in the 103 UV oven for 15 min. The nanocomposite coatings obtained presented a thickness of ~70 nm. The pure 104 acrylic acid was used as a control to elucidate the effect of nanoparticles addition. Samples were 105 labeled as shown in Table 1.
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Table 1. Nomenclature for nanocomposite coatings.

Nanocomposite	Nanoparticles	wt%	Nomenclature
	Non-functionalized	0.1	0.1 wt% TiO2-SiO2/PAA
1102-5102/PAA		0.5	0.5 wt% TiO2-SiO2/PAA
	Functionalized	0.1	0.1 wt% f-TiO2-SiO2/PAA
1-1102-5102/PAA		0.5	0.5 wt% f-TiO <sub>2</sub> -SiO <sub>2</sub> /PAA

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**110** *2.4 Characterization* 

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112 In order to evaluate the nanoparticles surface modification, the chemical state analysis was 113 carried out by X-ray Photoelectron Spectroscopy (XPS) measurements using a Thermo Scientific 114 Escalab 250 Xi instrument. The base pressure during the analysis was 10<sup>-10</sup> mbar and photoelectrons 115 were generated by an Alk $\alpha$  (1486.68 eV) X-ray source equipped with a monochromator and with a 116 spot-size of 650 µ m. The x-ray voltage and power were 14 kV and 350 W, respectively. Acquisition 117 conditions for low-resolution analysis for the survey were: pass energy of 46.95 eV at a take-off angle 118 of 45° and 1 eV/step. And for the high-resolution spectra within the selected regions were as follow: 119 20 eV pass energy, 45° take-off angle, and 0.1 eV/step. Selected region spectra were recorded covering 120 the Ti2p<sub>3/2</sub>, Ti2p<sub>1/2</sub>, Si2p<sub>3/2</sub>, Si2p<sub>1/2</sub>, as well as C1s and O1s photoelectron peaks. The experimental error 121 of the binding energy shift was smaller than this value. The recorded photoelectron peaks were 122 finally fitted using the Avantage software V 5.41. 123

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125 X-ray diffraction (XRD) was used to identify the structure of the nanoparticles powder before 126 and after functionalization. XRD pattern was recorded using a X'Pert X-ray diffractometer of 127 Panalytical in  $2\theta$  range of 5-100° with a step size of 0.0170° and scan rate of 1°min<sup>-1</sup> using CuK $\alpha$ 128 radiation. The water contact angles were measured with an OCA 15 plus, dataphysics model, at room 129 temperature in air following the ASTM5725-99 standard, the SCA20 software was used for the 130 analysis. Transmission spectra of the nanocomposites coatings under normally incident light were 131 recorder on a Cary 5000 UV-Vis-NIR spectrophotometer of Agilent Technologies. Morphologies of 132 nanocomposite coatings were analyzed by atomic force microscopy (AFM), model MFP3D-SA of 133 Asylum Research, using a rectangular cantilever with a resonant frequency of 70KHz and a nominal 134 force constant of 2 N/m, the topography images (1  $\mu$ m x 1  $\mu$ m) were taken in contact mode for each 135 surface. Roughness calculations and the 3D images were obtained using Argyle light analysis 136 software. Scanning electron microscopy (SEM) images were recorded using a FEI NovaNano SEM 137 2000 without gold coating with a Helix detector in immersion mode.

#### 138 3. Results

#### **139** *3.1. Functionalization of TiO*<sub>2</sub>*-SiO*<sub>2</sub> *nanoparticles*

140 To understand the functionalization effect and the interaction between TiO<sub>2</sub> and SiO<sub>2</sub> 141 nanoparticles with TMPTA, the systems were analized by means of XPS. As shown in Figure 1, the 142 Ti2p spectra (Figure 1A) of TiO<sub>2</sub> shows the Ti2p<sub>3/2</sub> signal with a binding energy at 458.5 eV, and a 143  $Ti2p_{3/2}$  –  $Ti2p_{1/2}$  separation of 5.74 eV, this espectra is in agreement of that for TiO<sub>2</sub> pristine 144 nanoparticles [20]. The Ti2p spectra for f-TiO<sub>2</sub>-SiO<sub>2</sub> decrease in intensity and becomes broader, where 145 the Ti2p<sub>3/2</sub> FWHM increase from 1 to 1.23 eV and the peak shape change for the functionalization 146 effect. The mathematical analysis of the signal corresponding to O1s of the f-TiO<sub>2</sub>-SiO<sub>2</sub> sample, can 147 be adjusted with two different signals (Fig. 1A inset), the first one at 529.8 eV and the second one at 148 533.5 eV. The signal at 529.8 eV corresponding to O1s of TiO<sup>2</sup> nanoparticles and the signal at 533.5 eV 149 is attributed to oxygen to SiO<sub>2</sub> nanoparticles. Furthermore, the Si2p spectra (Figure 1B), shows a 150 signal at a binding energy of 103.6 eV, as well as, the Si2p spectra of nanoparticles obtained after 151 functionalization where a broadenning of the signal was observed, changing the FWHM from 1.93 to 152 2.14 eV, as well as the peak position and shape. The peak can be analyzed using three doublet signals 153 (Figure 1B inset), one at 102.3 eV and 102.7 of Si-Ti bonding, other at 102.9 eV and 103.4 eV of Si-C 154 bonding and other at 103.6 eV and 104.1 eV that was attributed to Si-O [21]. From here, we can suggest 155 that functionalization took place on nanoparticle surface.

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O1s XPS spectra; **(B)** Si2p XPS spectra of the pristine and functionalized nanoparticles.

To determinate that nanoparticle structure remains after the functionalization process, X-ray diffraction analysis was carried out. Figure 2 shows the X-ray diffractograms of the nonfunctionalized (Figure 2A) and functionalized nanoparticles (Figure 2B). The X-ray diffractions patterns of TiO<sub>2</sub>-SiO<sub>2</sub> and f-TiO<sub>2</sub>-SiO<sub>2</sub> samples demonstrate the presence of anatase phase originated by TiO<sub>2</sub> [22] and a weak signal at 23° which is assigned to the amorphous SiO<sub>2</sub> [23, 24]. These results suggest that nanoparticles have not changed its crystalline arrangement due to functionalization process, so is possible to establish that functionalization only modified the nanoparticles surface.

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Figure 2. X-ray diffractograms of: (A) TiO<sub>2</sub>-SiO<sub>2</sub> nanoparticles, (B) f-TiO<sub>2</sub>-SiO<sub>2</sub> nanoparticles.

174 XPS analysis confirms that TMPTA effectively modifies the surface of TiO<sub>2</sub> and SiO<sub>2</sub>
 175 nanoparticles. Also, XRD diffractograms show that no structural modifications were suffered during
 176 functionalization.

#### **177** *3.2. Surface wettability of nanocomposite coatings*

178 Surface wettability is critical for self-cleanning applications. Figure 3 shows the wettability 179 behaviour of all evaluated coatings. The water contact angle on glass substrate (Figure 3A) and 180 polyacrylic coating (Figure 3B) are 24° and 39°, respectively. The incorporation of TiO<sub>2</sub>-SiO<sub>2</sub> 181 nanoparticles decreases the water contact angle, as it can be seen in Figures 3C-43. The results indicate 182 that nanocomposites based on functionalized nanoparticles present lower contact angle. At a 183 nanoparticle concentration of 0.5wt% (Figure 3F) water contact angle is even lower than the coating 184 with 0.1 wt% (Figure 3E). Apparently, nanoparticles concentration is an important factor in the 185 development of surfaces with hydrophilic properties, obtaining a superhydrophilic behaviour with 186 less than 5° water contact angle, been the case for the 0.5wt% f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA sample. In the other 187 hand, the non-functionalized nanoparticles coatings (Figure 3C, 3D) shows water contact angles of 188 32° and 17°, respectively. It has been seen that nanopaticle concentration and roughness (as shown 189 below) are not the only factors that influence the wettability of nanocomposites; it is thought that 190 wettability is determinated for the interaction between the arrangement of functionalized 191 nanoparticles and the polymer matrix. It can be remarked, that the incorporation of modified 192 nanoparticles to polymer matrix produce nanocomposites with different features, low water contact 193 angle and superhydrophilic properties. These properties are strongly related to the chemical 194 interaction between all the constituents in the nanocomposite.

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## Figure 3. Images of water contact angle of (A) glass substrate, (B) acrylic coating, (C) 0.1wt% TiO<sub>2</sub>-SiO<sub>2</sub>/PAA (D) 0.5wt% TiO<sub>2</sub>-SiO<sub>2</sub>/PAA, (E) 0.1wt% f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA, (F) 0.5wt% f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA.

- **199** *3.3 Transparency of nanocomposite coatings*
- Figure 4 depicts the captions of the nanocomposites coatings. As it can be appreciated in the
- 201 image, all coatings are highly transparent and homogeneous, lacking the presence of agglomerates
- 202 on the surface.



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**204** Figure 4. Images of nanocomposite coating on glass substrate of: (A) 0.1wt% TiO<sub>2</sub>-SiO<sub>2</sub>/PAA,

(B) 0.5wt%TiO2-SiO2/PAA, (C) 0.1wt% f-TiO2-SiO2/PAA and (D) 0.5wt% f-TiO2-SiO2/PAA.

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206 Transmission spectra of the nanocomposite coatings are shown in Figure 5. For comparison, the 207 transmission spectra of a glass substrate and polyacrylic acid on glass are also shown. The glass 208 substrate transmittance in the wavelength range between 370 -700 nm is about 97.5%. Considering 209 the maximal transmittance for all the coatings at 395 nm (inset in Figure 5, see dashed line), when 210 glass is coated with polyacrylic acid, the transmittance slightly decreases to 96.8%. In the case of 211 functionalized based coatings, 0.1 wt% f-TiO2-SiO2/PAA and 0.5wt% f-TiO2-SiO2/PAA, maximal 212 transmittance decreases to 96.4% and 95.8%, respectively. Coatings with non-functionalized 213 nanoparticles show the lowest maximal transmittance of 95.4% for 0.1wt%TiO<sub>2</sub>-SiO<sub>2</sub>/PAA and 94.5% 214 for 0.1wt%f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA. This behavior can be attributed to the presence of SiO<sub>2</sub> nanoparticles, it 215 has been reported that SiO<sub>2</sub> nanoparticles increase the %T in binary film systems of TiO<sub>2</sub>/SiO<sub>2</sub> [7] due 216 to its low refractive index. Therefore, the SiO<sub>2</sub> nanoparticles can act as an effective antireflection 217 material. By looking at the inset in Figure 5, it can be distinguished that nanocomposite coatings show 218 less than 2.5% loss in transmittance. Furthermore, there is no shifting in the position of maximal 219 transmittance to longer wavelengths, as a clear signal of an even thickness and insignificant scattering 220 effect caused by the nanoparticles. Based on these results, the nanocomposites coatings obtained does 221 not reduce considerable the transmittance of the glass, this is an interesting property for optical 222 applications where high transmittance is usually required.



Figure 5. Transmission spectra of the prepared nanocomposite coatings at a wavelength ranging
 from 250 to 700 nm.

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#### **228** 3.4 Morphology and roughness analysis of f-TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite coatings

229 Figure 7 shows the top view images of all samples by SEM. In the micrographs is observed that 230 nanocomposite coatings 0.1wt%f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA (Figure 6C) and 0.5wt%f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA (Figure 231 6D) show a better dispersion than the 0.1wt%TiO2-SiO2/PAA (Figure 6A) and 0.5wt% TiO2-SiO2/PAA 232 (Figure 6B) samples. Coatings with functionalized nanoparticles are uniform and small 233 agglomerations of TiO<sub>2</sub>-SiO<sub>2</sub> particles distribute randomly on the surface. Figures 6A-D also indicates 234 that an increase in TiO<sub>2</sub>-SiO<sub>2</sub> concentration increases the coverage of nanoparticles on the surface. 235 This grade of dispersion creates roughness on the top surface; such characteristic is more evident for 236 coatings with functionalized nanoparticles.



Contact mode AFM images of 2µm x 2µm for all the nanocomposite coatings are shown in Figure
7. The nanocomposite coating of 0.5 wt% f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA (Figure 7D) shows agglomerates, where
apparently SiO<sub>2</sub> nanoparticles surround TiO<sub>2</sub> nanoparticles, this behavior is also observed in the
nanocomposite coating for 0.1wt%f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA.

The change on surface roughness is confirmed by AFM measurements. The root mean squared
 roughness (R<sub>rms</sub>) revealed that the nanocomposites coatings of 0.1wt%TiO<sub>2</sub>-SiO<sub>2</sub>/PAA (Figure 8A),

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0.5wt%TiO2-SiO2/PAA (Figure 8B), 0.1wt% f-TiO2-SiO2/PAA (Figure 8C), 0.5wt% f-TiO2-SiO2/PAA 246 (Figure 8D) present roughness of 37.50nm, 54.88nm, 18.01nm and 25.69nm, respectively. When the 247 248 roughness data and water contact angle are correlated, it can be observed that, roughness for 249 0.1wt%TiO2-SiO2/PAA, 0.5wt%TiO2-SiO2/PAA and 0.1wt%f-TiO2-SiO2/PAA produce hydrophilic 250 coatings with contact angles of 32°, 17° and 13°, respectively; while for the one of 0.5wt%f-TiO<sub>2</sub>-251 SiO<sub>2</sub>/PAA results in a superhydrophilic coating with contact angles < 5°. Therefore, the decrease of 252 water contact angle can be attributed to the surface roughness in agreement with the model discussed 253 later.

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Figure 7. AFM images of nanocomposites coatings: (A) 0.1wt% TiO<sub>2</sub>-SiO<sub>2</sub>/PAA, (B) 0.5wt% TiO<sub>2</sub>-SiO<sub>2</sub> /PAA,
(C) 0.1wt% f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA, (D) 0.5wt% f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA.

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0.1wt% f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA 258

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Figure 8. 3D AFM images of nanocomposite coatings: (A) 0.1wt% TiO2-SiO2/PAA, (B) 0.5wt% TiO2-SiO2/PAA, (C) 0.1wt% f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA, (D) 0.5wt% f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA.

0.5wt% f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA

#### 261 4. Discussion

262 Based on the previous results, it can be seen that nanoparticle functionalization plays an important 263 role in the properties and performance of the nanocomposites as functional coatings. In order to 264 understand the interaction of the constituents in the present system, that gives as result functional 265 properties, further discussion is needed.

266 In general, the wettability of a solid surface with a liquid is governed both by its chemical 267 composition and by its microstructure (or surface roughness). It is well known that the Wenzel [25] 268 and Cassie-Baxter [26] models are two wetting models, which commonly used to correlate the contact 269 angle with surface roughness. To explain our results, the Wenzel model has been considered.

270 According to Wenzel model, the apparent contact angle on a rough surface,  $\theta_{W}$  is expressed as:

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$$\cos \theta_W = r(\cos \theta)$$
 Equation (1)

272 where  $\theta$  is the contact angle on the flat surface and *r* is the roughness factor, defined as the ratio 273 of the true area of the solid surface to its projection area. Since *r* is always larger than 1, from Equation 274 (1),  $\theta_{\text{W}}$  is lower than  $\theta_{\text{W}}$  if the surface is originally hydrophilic ( $\theta < 90^{\circ}$ ).

275 This means, that the hydrophilic properties are enhanced when the roughness of the hydrophilic 276 surface is increased.

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From Figures 7 and 8, it can be seen that the surface is quite rough, which partially explains the wettability of the coating. But, to reach such roughness, the state on nanoparticle dispersion is an important issue. This is where functionalization of the TiO<sub>2</sub>-SiO<sub>2</sub> nanoparticles makes a contribution to the superhydrophilicity and it comes into consideration. To explain the functionalization, we consider the role of sonication and XPS spectra (c.f. Figure 1)

As mentioned in the methodology, ultrasonic was an approach for nanoparticle functionalization, as an energy of 594 kJ/g was used with the purpose to achieve functionalization and assist dispersion. Due to their extremely large surface-area/particle-size ratio, nanoparticles tend to strongly agglomerate, hence reducing the resultant expected properties on the nanocomposite.

The interactions that normally occur in ultrasonic cavitation with compounds are complex [27], usually alone having energy for organic compound degradation [28], or for catalysis of more complex reactions called sonocatalysis [29]; where normally reactions do not proceed without sonication, sonication enables other paths for the reaction. Along with the system, there is the presence of metallic oxide nanoparticles, which usually contain, depending on their synthesis or further treatment surface hydroxyl groups, which are often energetically, difficult to remove [30, 31].

292 It is known that reactivity of a substance increases with smaller particles. In this study,  $SiO_2$  has 293 a specific surface area of  $200 \pm 25$  m<sup>2</sup>/g while TiO<sub>2</sub> 90 ± 20 m<sup>2</sup>/g, (according to the supplier) meaning 294 that SiO<sub>2</sub> will have better affinity with the adsorption and reaction in the system. It is also known that 295 SiO<sub>2</sub> can react with trialkoxyalkyl molecules at high temperatures to form an ester between silanol 296 groups and ester groups [32]. The sonication process provides the required energy for the reaction to 297 proceed as shown in figure 9A. Thus, one product between SiO<sub>2</sub> and TMPTA is an acrylic surface 298 moietie (mode I) as seen in figure 9B; and the other pathway produces a SiO<sub>2</sub> functionalized via vinyl 299 group (mode II) as shown in figure 9C. This is in accordance with XPS Si2p spectra, were evidence of 300 a Si-C bonding is present. The proposed reaction of this process appears in Figure 9.



**Figure 9.** Proposed reaction mechanism for SiO<sup>2</sup> nanoparticles functionalized with TMPTA, under sonication condition.

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305 For the TiO<sub>2</sub> nanoparticles, it is known that titanium can bind to acrylic systems via dentate 306 ligands [33]. This could explain the slight decrease in carbonyl groups in the TMPTA, suggesting a 307 more complex interaction in the cavitation process in order to get reduced. It is known that excited 308 TiO<sub>2</sub> generates electrons in the conduction band, that can be transferred to organic compounds [34]. 309 Also, there is evidence that TiO<sub>2</sub> can undergo the same phenomena in ultrasonication conditions [35, 310 36] so reduction of carbonyl group could also be suggested. The reaction between TiO<sub>2</sub> and TMPTA 311 to functionalize TiO<sub>2</sub> appears in Figure 10. It occurs in a similar manner as in the case of SiO<sub>2</sub> 312 nanoparticles, where sonication process turns the particles more reactive as shown in figure 10A. 313 Then, it follows two suggested routes, one in which the carbonyl group could get reduced by 314 sonication process and TiO2 interacts as seen in figure 10B obtaining the functionalized TiO2 (mode 315 I). The second way where TiO<sub>2</sub> would get bonded by vinyl interactions in TMPTA (mode II) as seen 316 in figure 10C.



Figure 10. Proposed reaction mechanism for functionalized TiO<sub>2</sub> nanoparticles with TMPTA, under sonication
 conditions.

320 For the functionalization of the binary system, it can be concluded that it should consist on a 321 combination of both phenomena. For the binary (TiO2-SiO2) system, both metallic oxides are 322 functionalized at the same time, meaning that in parallel with the cavitations, enough energy is 323 exerted for nanoparticles to collide during the functionalization. As a function of concentration, 324 higher concentrations represent higher collision frequency, as studied by Pradhan [37]. Also, TiO2 325 and SiO<sub>2</sub> have different sizes, meaning a difference in surface energy, the system nature is to decrease 326 this excess surface energy, so the particles tend to form controlled agglomerates between them. Thus, 327 the particles are functionalized in this condition.

Additionally, the superhydrophilicity of the present system could be attributed to the synergy between f-TiO<sub>2</sub>-SiO<sub>2</sub> nanoparticles and acrylic matrix. TMPTA functionalization of nanoparticle surface shows intact acryloyl group, meaning that its property to propagate through photoinitiation and polymerize via crosslinking remains as shown in Figure 11. The proposed mechanism shows the

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way that both modes (I and II) of functionalized  $TiO_2$  and  $SiO_2$  nanoparticles can interact in the

333 polymerization under UV conditions (figure 11A-D).

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Figure 11. Proposed reaction mechanism under UV crosslinking conditions of acrylic acid in presence of: (A)
 functionalized TiO<sub>2</sub> nanoparticles (mode I), (B) functionalized TiO<sub>2</sub> nanoparticles (mode II) (C)
 functionalized SiO<sub>2</sub> nanoparticles mode (I), (D) functionalized SiO<sub>2</sub> nanoparticles mode (II).

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From the crosslinking and polymerization of both functionalized nanoparticles in Figure 11, it can be concluded that the binary system should be a mixture of both reactions, as represented in

341 Figure 12, where the polymerization between vinyl groups in the surface of the nanoparticles can also

342 takes place. For clarity purpose, a schematic representation of the final nanocomposite appears in

**343** figure 13.



**Figure 12.** Proposal for the polymerization of moieties between functionalized TiO<sub>2</sub>-SiO<sub>2</sub> nanoparticles.

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Figure 13. Schematic representation of f-TiO<sub>2</sub>-SiO<sub>2</sub>/PAA nanocomposite where both modes of functionalized
 TiO<sub>2</sub> and functionalized SiO<sub>2</sub> are polymerized with acrylic acid monomer, and also entanglement between
 functionalized nanoparticles.

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#### 353 5. Conclusions

A facile method for surface functionalization of TiO<sub>2</sub>-SiO<sub>2</sub> binary system was achieved using TMPTA with the aid of ultrasonic. Covalently functionalized TiO<sub>2</sub>-SiO<sub>2</sub> nanoparticles were dispersed in an acrylic matrix resulting in the formation of nanocomposite coatings with hydrophilic and superhydrophilic behavior. These properties were enhanced without sacrificing visible light transmission. Superhydrophilic coatings with water contact angles below 5° have many important applications, as self-cleaning coatings. These results provide valuable guidance for the design and manufacture of self-cleaning coatings.

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### 362 6. Patents

This study generated a patent request number MX/a/2016/014953 at the Mexican Institute ofIndustrial Property.

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