

1                   **Controlling the Wettability of Plastic by Thermally**  
2                   **Embedding Coated Aluminium Oxide Nanoparticles into the**  
3                   **Surface**  
4

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11   **Keywords:** *superhydrophobic surfaces, nanoparticles, durable, branched carboxylic acid, Al<sub>2</sub>O<sub>3</sub>,*  
12   *thermal embedding.*

13   **Abstract**

14   ***Hypothesis***

15   Nanoparticle embedding into the surface of plastics provides an effective anchor that improves the  
16   durability of coatings formed from functionalized nanoparticles. Coatings formed from thermally  
17   embedded particles show superior wear resistance relative to coatings formed from non-embedded  
18   particles. As a consequence of this, embedded nanoparticles functionalized with hydrophilic and  
19   hydrophobic carboxylates are better suited for controlling the wettability of plastics than when the  
20   nanoparticles are deposited onto the plastic under ambient conditions.

21   ***Experiments***

22 Carboxylate-functionalized Al<sub>2</sub>O<sub>3</sub> nanoparticles were embedded into ethylene vinyl acetate through  
23 spray coating the particles onto the substrate during heating. Sonication was used to remove excess  
24 particles that did not become embedded into the material. Coatings formed from the embedded  
25 particles were characterized through scanning electron microscopy (SEM), atomic force microscopy  
26 (AFM), energy dispersive x-ray spectroscopy (EDX), and x-ray photoelectron spectroscopy (XPS).  
27 The wettability of the coatings was characterized using static and dynamic contact angle (CA)  
28 measurements to measure the apparent water contact angles, and sliding angle measurements, whilst  
29 the durability of the coatings was studied using scratch testing, tape peel tests, and abrasion tests.  
30 The build-up of fog on the substrates was also studied through exposing the surfaces to water vapour.

### 31 *Findings*

32 Thermal embedding of the particles into the surface of the plastic was observed to occur when the  
33 material was heated to temperatures around its melting temperature. AFM and SEM showed that  
34 plastic embedded with the nanoparticles possessed a morphology that was substantially rougher than  
35 the untreated plastic. CA measurements showed that plastic embedded with hydrophobic isostearate  
36 functionalized nanoparticles was highly hydrophobic and displayed a CA of approximately 152°.  
37 Dynamic CA measurements and sliding angle measurements revealed that plastic embedded with  
38 the isostearate functionalized nanoparticles showed petal-like wetting behavior. Furthermore, it was  
39 observed that the CA of the plastic could be varied from highly hydrophobic to highly hydrophilic  
40 through embedding varying amounts of isostearate and hydrophilic 2-[2-(2-  
41 methoxyethoxy)ethoxy]acetate functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles into the surface of the material.  
42 Scratch testing showed that thermally embedding the nanoparticles into the plastic substantially  
43 improved their abrasion resistance, relative to when the nanoparticles are deposited onto the non-  
44 heated material. This methodology indicates that embedding nanoparticles into plastics creates

45 durable coatings that can display variable wettability. Consequently, this methodology could be  
46 useful in applications where it is desirable to keep plastics dry, such as for food packaging or medical  
47 devices.

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## 49 **1. Introduction**

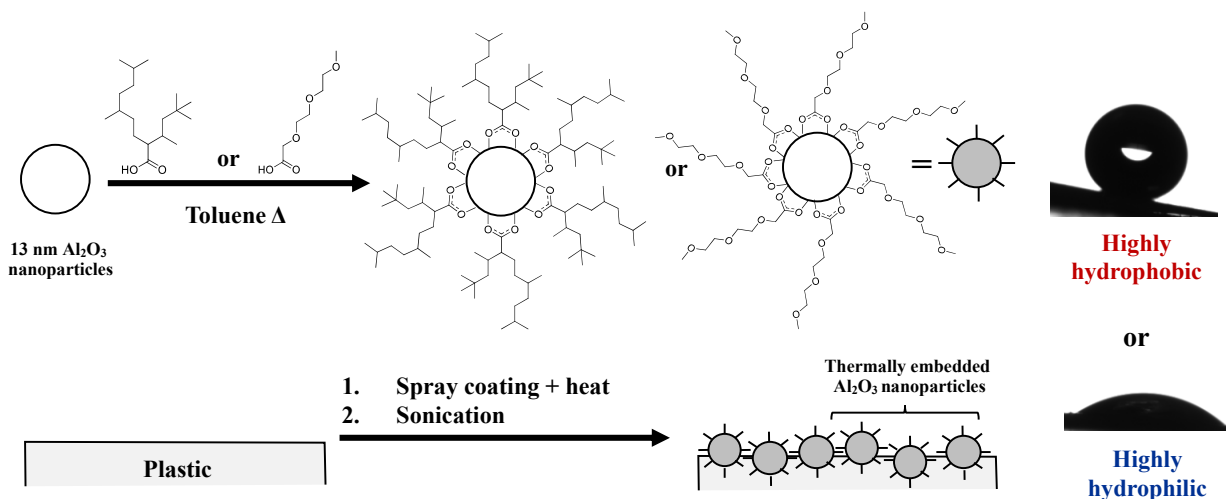
50 Improving the durability of superhydrophobic coatings still remains a major challenge within the  
51 research community. Coatings created using functionalised nanoparticles have been studied due to  
52 their low wettability and ease at which they can be applied onto different surfaces.<sup>1-6</sup> However,  
53 despite their potential utility, these coatings show poor abrasion resistance, which limits their use in  
54 practical applications. To overcome this, composite coatings have been developed that improve the  
55 coatings' durability through embedding the nanoparticles in polymer films<sup>7-9</sup> and mixing them with  
56 resins.<sup>10-13</sup> These materials can either be pre-cast onto the substrate using techniques such as spin<sup>9</sup>  
57 or spray<sup>10</sup> coating or can be added directly to suspensions containing the nanoparticles.<sup>11,13</sup> For  
58 example, Si et al. prepared robust water-repellent surfaces using suspensions containing  
59 functionalised MgO and TiO<sub>2</sub> nanoparticles and epoxy resin.<sup>11</sup> These coatings showed remarkable  
60 durability when subjected to knife-scratch and sandpaper abrasion tests, and were resistant to some  
61 forms of chemical damage.<sup>11</sup>

62 Despite their effectiveness, these techniques increase the number of materials and steps  
63 required during the fabrication processes. Furthermore, the monomers that are used to produce  
64 commercially available adhesives like epoxy resin are often harmful to the population and  
65 environment,<sup>14</sup> and it is desirable to avoid their release if possible. As a consequence of these factors  
66 it is necessary to investigate other approaches that can improve the adhesion of nanoparticles onto  
67 substrates. Thermally embedding nanoparticles into surfaces has been reported for materials such as

68 glass,<sup>15</sup> graphene,<sup>16</sup> and plastics.<sup>17-19</sup> During this process the materials are heated to temperatures  
69 greater than or approaching their glass transition temperatures, which affects softening of the  
70 materials so that they are in liquid-like state. In this state particles on the surface can penetrate into  
71 the material and become embedded in the surface layers.<sup>17</sup> For example, Teichroeb and Forrest  
72 showed that it was possible to embed Au nanoparticles into polystyrene through heating the polymer  
73 to temperatures close to its bulk transition temperature.<sup>19</sup> AFM indicated that the nanoparticles were  
74 partially embedded into the polymer, with a large proportion of the total particle diameter protruding  
75 outside the material.<sup>19</sup>

76         Embedding nanoparticles into polymers has been used for a variety of purposes, such as to  
77 affect changes in the optical properties,<sup>21,21</sup> as a probe to study glass transition temperatures,<sup>19,22</sup> or  
78 in sensing applications.<sup>24,25</sup> However, to our knowledge, this methodology has not yet been used to  
79 control the wettability of surfaces. Furthermore, investigations into the durability of thermally  
80 embedded nanoparticles have not yet been undertaken. Herein, we investigate the embedding of  
81 isostearate and 2-2-2-methoxyethoxyethoxy acetate functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles into plastic  
82 as route to control its apparent water contact angle (CA). Functionalisation is achieved through  
83 refluxing the particles with the desired carboxylic acid in toluene. Embedding the particles into the  
84 plastic was then carried out through spray coating and subsequent sonication (Scheme 1). Sonication  
85 was used to remove non-embedded particles from the plastic. The wear resistance of the plastic  
86 embedded with the isostearate functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles, relative to the analogous non-  
87 heated nanoparticle coating is also reported in this study.

88



89

90 **Scheme 1.** Diagram showing the methods used to synthesise the nanoparticles and embed the

91 particles into the plastic substrate.

## 92 2. Experimental methods

93 **Materials and reagents** Al<sub>2</sub>O<sub>3</sub> nanoparticles (d = 13 nm) and 2-2-2-methoxyethoxyethoxy acetic

94 acid were purchased from Sigma-Aldrich. Isostearic acid was purchased from Nissan Chemical

95 Industries and was used without further purification. Toluene and isopropanol were supplied by

96 VWR Chemicals. Plastic film (75 μm thickness), composed of 5-ply ethylene vinyl acetate/ ethylene

97 vinyl acetate/ poly-vinylidene dichloride/ ethylene vinyl acetate/ ethylene vinyl acetate was selected

98 as the substrate in this study.

99 **Synthesis of the carboxylate functionalized Al<sub>2</sub>O<sub>3</sub> nanoparticles** The isostearate and 2-2-2-

100 methoxyethoxyethoxy acetate functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles were synthesized using a similar

101 method to what we have previously reported<sup>4, 5</sup>. In a typical experiment, Al<sub>2</sub>O<sub>3</sub> nanoparticles (1.0

102 mol equiv.) were refluxed with isostearic or 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (1.4 mol

103 equiv.) in toluene for twenty-four hours. The volume of toluene was controlled such that 350 mL

104 was added per 15.0 g of Al<sub>2</sub>O<sub>3</sub>. Purification of the nanoparticles was achieved through centrifuging  
105 the reaction suspension at 5000 rpm for one hour. Following this, the supernatant was removed and  
106 the nanoparticles were suspended in isopropanol. This suspension was mixed using a spatula and  
107 then centrifuged at 5000 rpm for one hour. The supernatant from this suspension was then discarded.  
108 This procedure was repeated two further times using isopropanol, and then once using ethanol. When  
109 this had been completed the nanoparticle slurries were dried at 100 °C for at least four hours.

110 **Preparation of the spray coating suspensions** Isopropanolic suspensions containing 2 %wt  
111 Al<sub>2</sub>O<sub>3</sub> nanoparticles were prepared that contained different amounts of isostearate and 2-[2-(2-  
112 methoxyethoxy)ethoxy] acetate functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles. Despite varying the relative  
113 amounts of these two particles in the suspensions the total concentration of the particles was  
114 maintained at 2 %wt. Samples were prepared containing 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, and  
115 100% isostearate functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles. 2-[2-(2-methoxyethoxy)ethoxy] acetate  
116 functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles made up the balance for each suspension. These suspensions  
117 were used to embed particles into the plastic during the thermal embedding experiments.

118 **Thermal embedding of the nanoparticles into the plastic film** Plastic film was first attached to  
119 the back of a glass petri dish. The film was then heated on a hot plate until it had reached its melting  
120 temperature (80-90 °C), whereupon the material was observed to plastically deform. Following this,  
121 functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles were sprayed onto the heated plastic from the 2 %wt  
122 isopropanolic suspensions using a hand-held spray gun. Five layers of nanoparticles were sprayed  
123 onto the plastic before the samples were sonicated in isopropanol. Samples were continually heated  
124 throughout the entire number of passes of spray coating. Following each pass of spray coating,  
125 pressure was exerted onto the coated plastic through rolling a glass rod across the surface of the  
126 samples using the middle and index fingers. The pressure was controlled so that the rolling action

127 did not damage the substrate. The pressure was not measured during the process, although it has  
128 been observed that middle and index fingers typically exert forces ranging between 35-50 N<sup>26</sup>. This  
129 was carried out when isopropanol was no longer observed on the surfaces and was carried out in  
130 order to promote embedding of the nanoparticles into the plastic. Once the spray coating had been  
131 completed, samples were sonicated in isopropanol for ten minutes in order to remove loose particles  
132 that had not been embedded into the plastic, and then dried using a gentle stream of nitrogen.

133 **Characterisation** Apparent water contact angles (CAs) were measured using a Krüss DSA25  
134 Drop Shape Analyser and the sessile drop method. Measurements were made using 4  $\mu\text{L}$  droplets of  
135 deionised water under ambient conditions. The CAs quoted in this study are the average of three  
136 measurements performed at different locations on the surfaces; uncertainties are the associated  
137 standard deviations. Advancing and receding CA measurements were made by dosing a 5.0  $\mu\text{L}$   
138 droplet with H<sub>2</sub>O at a rate of 0.5  $\mu\text{Ls}^{-1}$  until its final volume reached 35.0  $\mu\text{L}$ . Water was then  
139 removed from the droplet at a rate of 0.5  $\mu\text{Ls}^{-1}$  until its volume returned to 5.0  $\mu\text{L}$ . During the sliding  
140 angle measurements samples were tilted from 0-90° at a rate of 60°min<sup>-1</sup>. Atomic force microscopy  
141 (AFM) was carried out using a JPK Nanowizard AFM in tapping mode. The root-mean-squared  
142 roughness measurements that are discussed in the surface characterisation section were performed  
143 on the 5 × 5  $\mu\text{m}^2$  areas displayed in figure 1. Scanning electron microscopy (SEM) was carried out  
144 using a Hitachi S4800 scanning electron microscope equipped with a Silicon Drift X-Max EDX  
145 detector. Samples that were used to study the cross section of the coated material were prepared  
146 through mechanically cutting the coated material at positions towards the centre of samples.  
147 Typically, the sample size used during the preparation of these specimens was less than 5 cm × 5  
148 cm. Cross-sectional imaging was performed on the newly created edges. EDX spectra were analysed  
149 using Inca EDX software (Oxford Instr.). X-ray photoelectron spectroscopy was performed using an

150 Axis Supra XPS using a monochromated Al  $K_{\alpha}$  source and large area slot mode detector (ca.  $300 \times$   
151  $800 \mu\text{m}^2$ ) analysis area. Spectra were recorded using a charge neutralizer to limit differential  
152 charging and binding energies were calibrated to the main hydrocarbon peak (BE 284.8 eV). XPS  
153 spectra were analysed using CASA software. Scratch testing was carried out in accordance to ISO  
154 1518-1:2019. During testing, a 1 mm tungsten carbide tip was moved laterally across the substrates  
155 over a distance of 10 cm. The load was kept constant during sliding. Different weights (2, 5, 10, 20  
156 and 50 g) were used during the tests to investigate the durability of the nanoparticle films. Anti-  
157 fogging experiments were performed through attaching samples to a lid of a sealed box that  
158 contained a vessel of boiling water. Samples were kept within the box for ten minutes to allow water  
159 vapour to condense onto the surface of the samples. SEM, AFM, and XPS were carried out on the  
160 as received plastic substrate, and the heated and non-heated isostearate functionalised nanoparticle  
161 films, before and after sonication in isopropanol. CA measurements were carried out on these  
162 surfaces and also plastic that had been embedded with both isostearate and the 2-[2-(2-  
163 methoxyethoxy)ethoxy]acetate functionalised nanoparticles. The durability tests were performed on  
164 films formed from the isostearate functionalised nanoparticles that had been deposited onto the non-  
165 heated plastic, and the plastic following thermal embedding of the isostearate functionalised  
166 nanoparticles.

### 167 **3. Results and discussion**

#### 168 **Surface characterization**

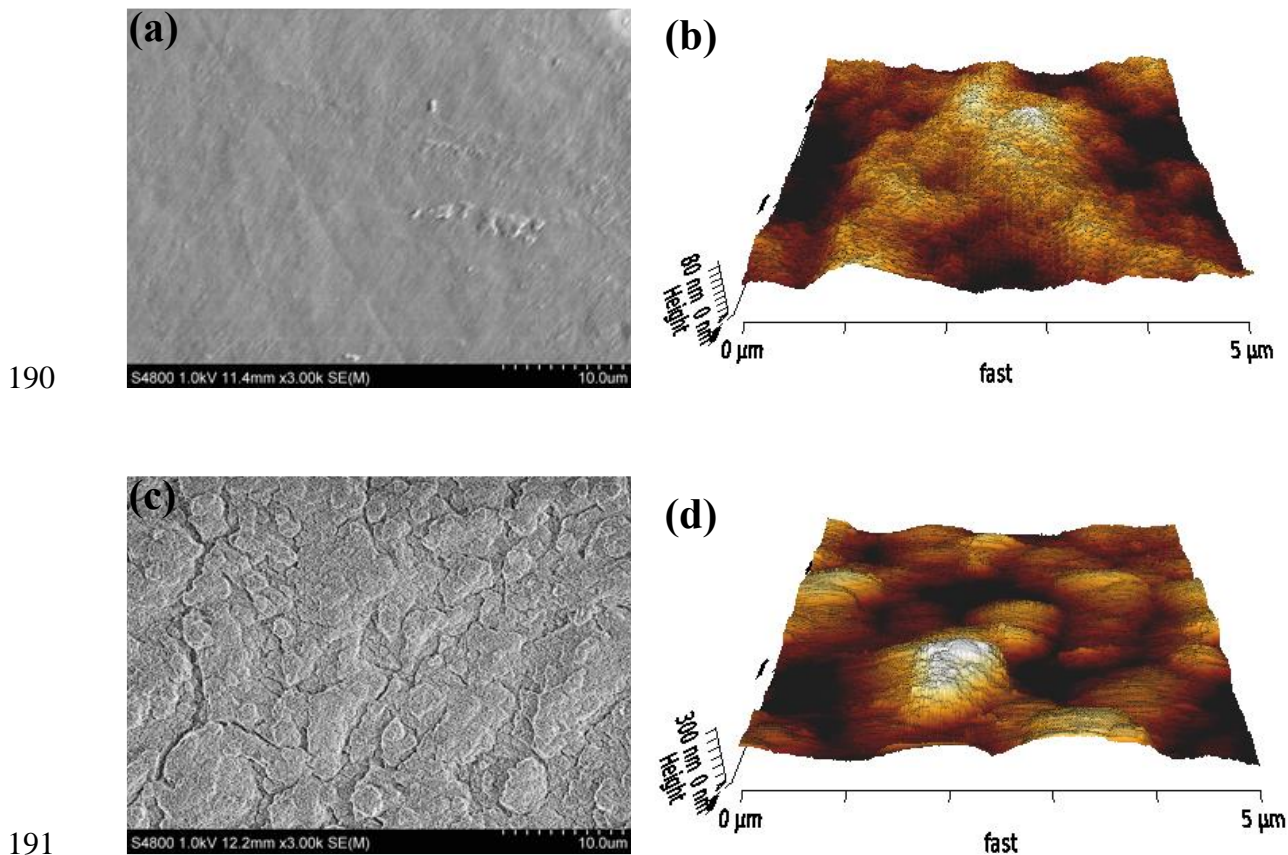
169 SEM, AFM and XPS were used to study the surface morphology and elemental composition of  
170 the heated plastic following thermal embedding of the isostearate functionalised  $\text{Al}_2\text{O}_3$  nanoparticles.  
171 SEM of the plastic after spray coating showed that large amounts of non-embedded nanoparticles



172 were deposited onto the material during spraying (Fig. S1, see ESI). Removal of non-embedded  
173 nanoparticles was readily achieved through sonication of the heat-treated substrates in isopropanol.  
174 Following sonication, SEM revealed that agglomerates of nanoparticles had become embedded  
175 within the surface of the plastic (Fig. 1c). By comparison, the morphology of sonicated specimens  
176 that had not been heated was similar to that of the uncoated plastic (Fig. 1a and Fig. S2a, see ESI).  
177 This indicates that the particles do not become embedded into the plastic when the spray coating is  
178 performed under ambient conditions. Visually, it was also possible to gain an understanding of the  
179 success of the embedding experiments from the appearance of the samples. Samples embedded with  
180 the nanoparticles remained white after sonication, unlike the non-heated specimens (Fig. S3, see  
181 ESI).

182 AFM showed that the topography of the plastic that had been embedded with the  
183 nanoparticles was substantially rougher than the as received plastic (Fig. 1d and b). The root-mean  
184 squared roughness of the plastic after nanoparticle embedding was observed to be 43.92 nm, whereas  
185 the uncoated plastic displayed a root-mean squared roughness of 13.86 nm. Residual nanoparticles  
186 were also observed on the surface of the non-heated plastic after sonication (Fig. S2b), indicating  
187 that the treatment was not completely effective at removing non-embedded particles from the  
188 substrate.

189



**Fig 1.** SEM and AFM images of the as received plastic (a) and (b), and the isostearate functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles embedded into the plastic film (c) and (d).

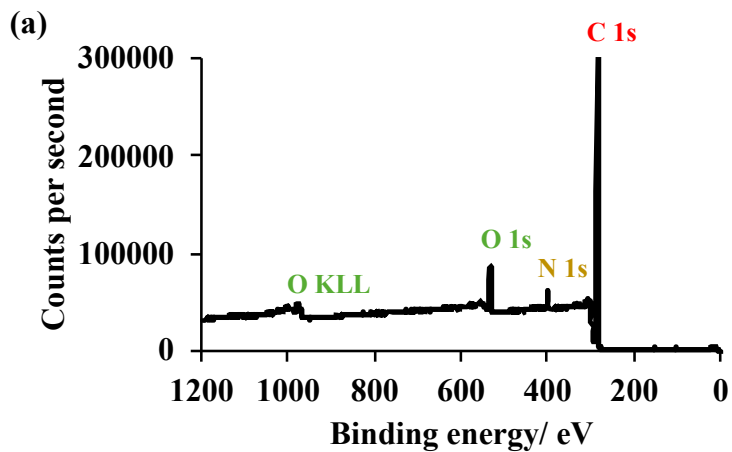
XPS analysis was carried out on the uncoated plastic and photoelectron peaks ascribed to C, O, and N were observed in the spectrum, as shown in Fig. 2a.<sup>27</sup> In addition, a low intensity Al photoelectron peak was also observed. This could be attributed to the presence of residual methylaluminoxane, which is used as a co-catalyst in the olefin polymerisation process<sup>28</sup>, however, the atomic percentage of Al was only observed to be 0.6 %, indicating that a relatively small amount of this compound was present in the surface layers. Larger amounts of Al were detected on plastic films that were spray coated with the functionalised nanoparticles and then sonicated in isopropanol (Table 1). For the heat-treated film this is ascribed to the embedded nanoparticles, whereas for the

202 non-heated film it is ascribed to the residual particles that were observed using AFM. XPS survey  
203 spectra of these surfaces are displayed in Fig. 2b and c.

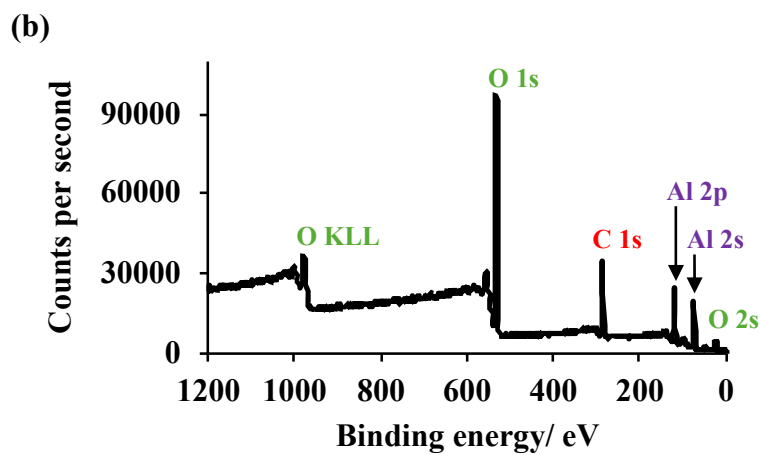
204 The atomic percentage of Al observed in the heat-treated film was substantially larger than  
205 what was detected on the non-heated film (Table 1). This indicates that many more particles were  
206 present within the uppermost surface layers (0-10 nm)<sup>29</sup> of the plastic, confirming that the  
207 morphological changes observed using AFM and SEM were due to the thermal embedding of the  
208 nanoparticles. Analysis of the atomic percentages of O and Al showed that the Al:O ratio for the  
209 heat-treated film was approximately 1.0:1.6 (Table 1). This is similar to 1.0:1.5, the stoichiometric  
210 ratio of Al:O in Al<sub>2</sub>O<sub>3</sub>, which shows that the O that is detected is largely credited to the nanoparticles  
211 and not the substrate. This suggests that the embedded nanoparticles form at least the majority of the  
212 surface. By comparison, the Al:O ratio observed in the non-heated film was about 1.0:2.7, indicating  
213 that far more of the O detected is from the ethylene vinyl acetate. This is in line with the SEM data,  
214 which shows that the residual particles do not completely cover the surface of the plastic (SI Fig.  
215 S2a).

216 Further SEM was performed to investigate how deep the nanoparticles became embedded into the  
217 plastic during heating. Based on the magnification and EDX maps for Al and O (Figure 3 (d) and  
218 (e) respectively), it can be observed that some of the nanoparticles penetrate into the bulk of the  
219 material. This indicates that the particles embed deeper into the plastic than the depth that is sampled  
220 using XPS (0-10 nm)<sup>29</sup>. However, the data also show that substantially more particles remain  
221 embedded in the surface of the plastic rather than penetrating into the bulk of the plastic. The Al that  
222 is detected on the non-coated side of the material could potentially arise from the transfer of  
223 nanoparticles from the coated to non-coated side when the specimen was cut to prepare the cross  
224 section. Given that the diameter of the Al<sub>2</sub>O<sub>3</sub> nanoparticles used in this study was 13 nm, this data

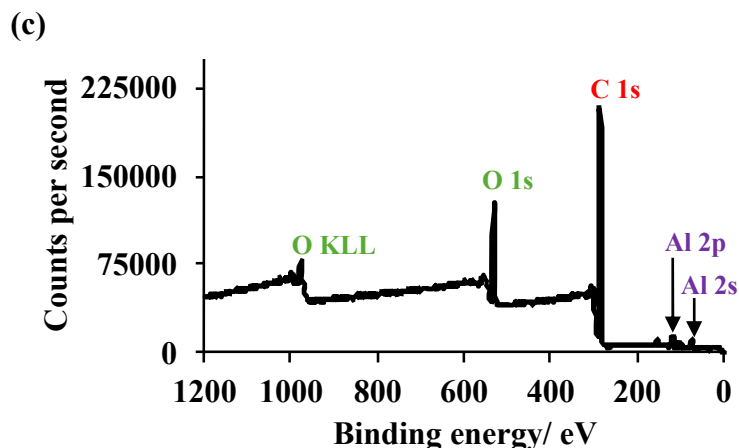
225 suggests that the depth of thermal embedding of the particles into the plastic is of the order of  
226 hundreds of times the particle diameter.



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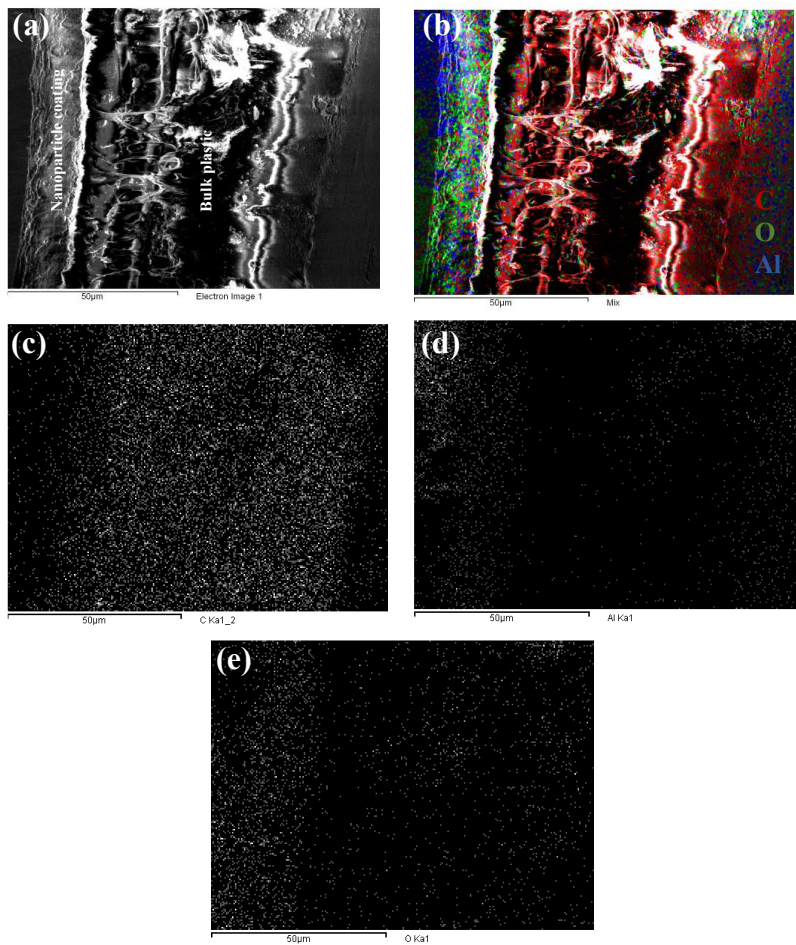


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230 **Fig 2.** XPS survey spectra of the as received plastic (a), and isostearate functionalised Al<sub>2</sub>O<sub>3</sub>  
 231 nanoparticles deposited onto (b) the heat-treated plastic and (c) the non-heated plastic. Spectra of  
 232 the coated plastic were recorded after the surfaces had been sonicated in isopropanol.

233 **Table 1.** Atomic percentages of elements that were observed on the as received plastic, plastic  
 234 after (1) spray coating with the isostearate functionalised nanoparticles and (2) sonication in  
 235 isopropanol, and plastic embedded with the isostearate functionalised nanoparticles. Small amounts  
 236 of Si were also observed on these surfaces which complete the balances. This is ascribed to  
 237 compounds found on the surface of laboratory gloves<sup>30</sup>.

Element	Plastic	Non-heated film	Heat-treated film
C	88.1 ± 0.8	76.7 ± 5.2	33.2 ± 1.9
O	8.0 ± 0.6	15.3 ± 2.9	40.9 ± 1.3
N	2.8 ± 0.4	Not detected	Not detected
Al	0.6 ± 0.5	5.7 ± 1.9	26.0 ± 0.7



239

240 **Fig 3.** 5.0 kV SEM image (a) and EDX map (b) of the cross section of the plastic substrate

241 embedded with the isostearate functionalised nanoparticles. EDX maps of the individual elements

242 C, Al, and O, are shown in (c), (d), and (e) respectively. The orientation of the sample in the images

243 is such that the surface embedded with the particles is perpendicular to the scale bars of the images.

244 EDX spectra were acquired using a 5.0 kV accelerating voltage.

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246

247

## 248 **Wetting behaviour**

249           The CA of the as received plastic was observed to be approximately  $88 \pm 2^\circ$ . Thermally  
250 embedding the isostearate functionalised nanoparticles into the plastic was observed to make it  
251 substantially more hydrophobic and display a CA of about  $152 \pm 3^\circ$ . This behaviour is due to both  
252 low surface energy, which is ascribed to the chemical functionality found on the surface of the  
253 particles, and roughness that is created when the particles become embedded into the plastic<sup>31</sup>.  
254 Embedding 2-[2-(2-methoxyethoxy)ethoxy] acetate functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles into plastic  
255 was also investigated in order to further study the scope of this methodology. It was observed that  
256 the CA of the plastic embedded with these nanoparticles was about  $37.2 \pm 7.2^\circ$ , which is ascribed to  
257 the hydrophilicity of the ether functional groups of the carboxylate chains. Interestingly, this coating  
258 was not superhydrophilic as observed in our previous publication<sup>5</sup>. This indicates that the plastic  
259 surrounding the nanoparticles also has a bearing on the wettability of the surface.

260           Dynamic contact angle measurements were employed to probe the surface heterogeneity<sup>32, 33</sup> of  
261 plastic samples embedded with the isostearate-functionalised nanoparticles. It was observed that the  
262 receding CA of plastic embedded with the nanoparticles was substantially lower than when the  
263 particles were spray-coated onto the material under ambient conditions (Table 2). As a consequence  
264 of this, plastic embedded with the particles showed a much larger contact angle hysteresis, relative  
265 to the non-heated nanoparticle film. In line with the high contact angle hysteresis, nanoparticle  
266 embedded plastic also showed a larger sliding angle compared to the non-heated nanoparticle film  
267 (Table 2). This indicates that plastic embedded with nanoparticles shows less effective self-cleaning  
268 behaviour relative to nanoparticle films spray-coated onto the plastic at ambient conditions.

269 Surfaces where water droplets adhere strongly and show CAs greater than 150° are often observed  
 270 in nature<sup>34,35</sup>. Petals are examples of such surfaces<sup>34</sup>. In these systems it has been postulated that the  
 271 high adhesive force that droplets experience on these surfaces is due liquid penetrating into larger  
 272 grooves that are formed between microstructures, and is thus indicative of surface heterogeneity<sup>34</sup>.  
 273 Consideration of the dynamic wetting and sliding angle data for the embedded nanoparticle film  
 274 suggests that this surface exhibits petal-like wetting behaviour where the high adhesion is caused by  
 275 water penetrating into grooves formed between the microstructures<sup>34</sup>. AFM imaging showed that the  
 276 embedded nanoparticles displayed a root mean squared roughness similar to when the particles are  
 277 deposited onto the plastic at room temperature<sup>36</sup> (222 nm versus 210 nm), which suggests that  
 278 topographic variations that could affect this behaviour do not exist on the nanoscale. The AFM image  
 279 of the embedded particles from which this measurement was performed is displayed in Fig. S4. This  
 280 is compared to our previously published data relating to nanoparticle films deposited onto the same  
 281 plastic substrate (Table 1 and Fig. S6 (b) in reference 36).

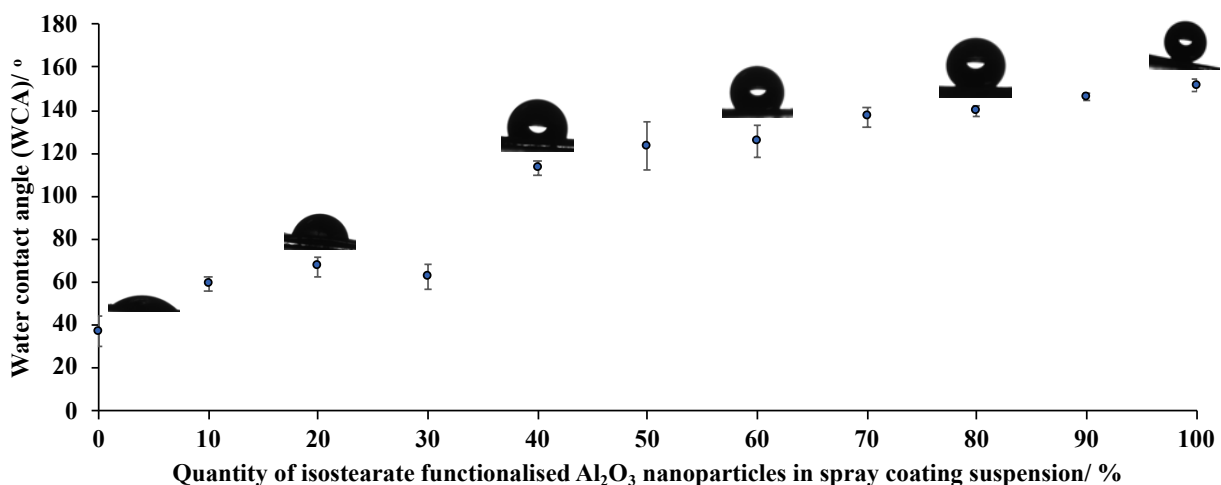
282 **Table 2.** Dynamic CAs and tilt angles of the as received plastic, and the plastic after deposition of  
 283 isostearate functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticle films. Values of the advancing and receding CAs for  
 284 the as received plastic and the non-embedded particles are taken from our previous publication<sup>36</sup>.

Surface	Advancing CA (°)	Receding CA (°)	Hysteresis (°)	Sliding angle (°)
Plastic	110 ± 1	84 ± 2	26	56 ± 17
Non-heated film	160 ± 4	147 ± 5	13	7 ± 2
Embedded film	155 ± 3	106 ± 3	49	21 ± 11

285



286 Further work was carried out to investigate whether thermally embedding different mass  
287 fractions of these nanoparticles could be used to control the wettability of the plastic. It was observed  
288 that the CA could be steadily lowered from about 150° to 115°, with reasonable control, by reducing  
289 the amount of the hydrophobic nanoparticles in the coating (Fig. 4). However, a larger drop in the  
290 CA was observed when the mass of the hydrophobic nanoparticles was reduced below forty percent.  
291 Here the CA was observed to be reduced from 115° to approximately 60-65°. This could indicate  
292 that there exists a ratio of hydrophobic to hydrophilic moieties on the nanoparticles above which it  
293 becomes substantially more favourable for water droplets to spread on the surface.



294  
295 **Fig 4.** CAs of the plastic substrate embedded with different amounts of isostearate and 2-2-2-  
296 methoxyethoxyethoxy acetate functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles. For each coating, the balance is  
297 made up by the 2-2-methoxyethoxyethoxy acetate functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles.

### 298 **Durability and anti-fogging behaviour**

299 The durability of the plastic embedded with the isostearate functionalised nanoparticles was  
300 further studied to evaluate the potential utility of these coatings. In addition to being sonication

301 resistant, the embedded nanoparticles were observed to be resistant to finger-wiping and tape peel  
302 tests using M4 Scotch tape. CAs between 145-150° were observed after subjecting the coating to  
303 abrasion using fingers and one single tape peel test, indicating at least the majority of nanoparticles  
304 remained embedded in the plastic (Fig. S5 (a) and (b)). SEM showed that these samples possessed  
305 similar surface morphologies to the surface before the durability tests, in support of this assertion  
306 (Fig. S6 (a)-(c)). Similar durability has also been reported for silica nanoparticles embedded in  
307 poly(methyl methacrylate)<sup>37</sup>. However, water droplets were more adherent onto the surfaces  
308 following these treatments and would not roll off during sliding angle measurements. This could  
309 suggest that some nanomaterial was removed during the tests, despite the samples showing similar  
310 surface morphologies. The CAs of the nanoparticles embedded in the plastic was observed to be  
311 slightly reduced to about 139° after five tape peel tests (Fig. S5 (c)), indicating the loss of some  
312 nanoparticles from the substrate. This was confirmed using SEM, which showed that discrete areas  
313 of the plastic existed that appeared smoother as is shown in Fig. S6 (d).

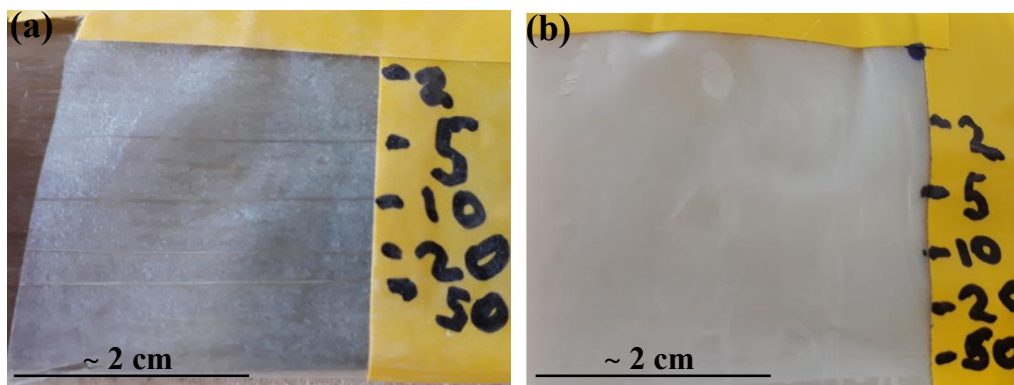
314 By comparison, particles could be readily removed from isostearate functionalised nanoparticle  
315 films deposited on the non-heated plastic through finger-wiping or through sonication. This  
316 generated surfaces that displayed CAs of about 102 and 90° respectively (Fig. S7 (b) and (c)). This  
317 indicated that at least the majority of particles had been removed from the surfaces, which was  
318 confirmed using SEM (Fig. S8 (a) and (b) and Fig. S2 (a)). The non-heated films retained their  
319 superhydrophobicity after one tape peel test, but showed a CA of about 104° after five tape peel  
320 tests, indicating particle removal. This was once again confirmed by SEM (Fig. S8 (c)).

321 Scratch testing was also carried out to further investigate the durability of the plastic  
322 embedded with the isostearate functionalised nanoparticles. Optically visible scratches were  
323 observed right across nanoparticle films spray coated onto the non-heated plastic, for all loads greater

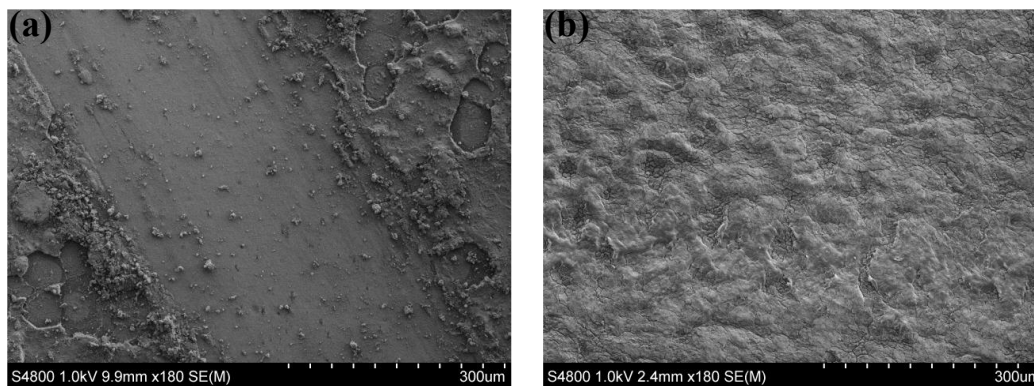
324 than 2 g (Fig. 5a). By comparison, scratches into the plastic embedded with the nanoparticles were  
325 only faintly optically visible when the substrate was subjected to higher loads (20 or 50 g) (Fig. 5b).  
326 SEM analysis showed that large amounts of nanoparticles had been removed and/ or displaced when  
327 the non-heated substrate was scratched under a 5 g load (Fig. 6a). By comparison, it was difficult to  
328 identify the wear scars on plastic specimens that had been thermally embedded with the  
329 nanoparticles, even after subjecting the surface to a 50 g load during scratch testing (Fig. 6b). This  
330 indicates that embedding the particles into the plastic greatly improves their abrasion resistance and  
331 greatly enhances the durability of nanoparticle films.

332 Despite the absence of surface wear observed using SEM, CAs of the scratched areas of the  
333 nanoparticle-embedded plastic varied between 135-145°. Furthermore, water droplets showed  
334 greater adhesion to these areas and did not slide off the surfaces, even after tilting to 90°. This data  
335 suggests that some damage to the surface was occurring, despite the apparent lack of wear observed  
336 on the surface. The CA of the surfaces was not observed to be affected by the magnitude of the  
337 applied load. For example, the CAs of areas subjected to 20 and 50 g loads were both about 139°  
338 (Fig. S9 (a) and (b)).

339 CA measurements were also performed on areas of the non-heated nanoparticle films that were  
340 scratched using the 50 g load. These areas showed a CA of about 150° but they displayed sliding  
341 angles between 11 and 66°. Four microlitre water droplets were used in these experiments, which  
342 have a diameter larger than that of the tip used during the tests (~ 2 mm versus ~ 1 mm). Furthermore,  
343 loose particles were also observed on the worn areas, as observed in Fig. 6a. It is plausible that both  
344 of these factors could contribute to the high hydrophobicity observed in these areas.



345  
346 **Fig 5.** Images of (a) an isostearate functionalised nanoparticle film on the non-heated  
347 plastic after scratch testing, and (b) thermally embedded isostearate functionalised  
348 nanoparticles in the plastic following scratch testing. The numbers correspond to the loads  
349 in g that the surfaces were subjected to during testing.



350  
351 **Fig 6.** SEM images of (a) an isostearate functionalised nanoparticle film on the non-  
352 heated plastic after scratch testing (load = 5 g), and (b) thermally embedded isostearate  
353 functionalised nanoparticles in the plastic following scratch testing (load = 50 g).

354 It was also found that the embedded nanoparticle films showed anti-fogging behaviour. Fog  
355 is observed on surfaces when the diameter of water droplets exceeds half the shortest wavelength of  
356 visible light (190 nm)<sup>38</sup>. Visible light is scattered from droplets that are greater than this size resulting

357 in surfaces appearing “foggy”. Uncoated plastic, and plastic samples coated with the embedded and  
358 non-embedded isostearate functionalised nanoparticles were exposed to vapour from boiling water  
359 inside a sealed container. It was observed that water droplets of a range of different sizes were  
360 formed on the uncoated plastic (Fig. S10 (b)). By comparison, smaller water droplets were observed  
361 on the nanoparticle coated surfaces (Fig. S10 (b)), which could suggest that the larger droplets may  
362 have rolled off the surfaces during fog formation. No substantial differences between the levels of  
363 fog build-up were observed on the nanoparticle coated surfaces. This could suggest that embedding  
364 the nanoparticles into the plastic may not play a major role in affecting the potential use of this  
365 methodology to create surfaces that show fog resistance, despite the increased adhesion of water  
366 droplets onto the surface. In addition, it was also observed that the coated samples became dry  
367 substantially faster than the uncoated plastic. This could suggest that more spherical droplets show  
368 a higher evaporation rate, relative to those with lower contact angles.

#### 369 **4. Conclusions**

370 In this study we report thermal embedding of nanoparticles into plastic for wettability and durability  
371 studies. Nanoparticles are functionalised with non-toxic hydrocarbons to achieve highly  
372 hydrophobic/hydrophilic surfaces. We have shown that it is possible to greatly improve the abrasion  
373 resistance of nanoparticle coatings through thermally embedding the particles into the surface of  
374 plastic. Embedding functionalized  $\text{Al}_2\text{O}_3$  nanoparticles into the surface layers of plastic was  
375 observed to substantially improve their wear resistance, as observed through scratch and sonication  
376 tests. By comparison, coatings formed from the non-embedded nanoparticles were readily removed  
377 under these conditions. Previous work investigating improving the durability of nanoparticle  
378 coatings has involved utilising binders<sup>7-9</sup>, or mixing the particles with commercially available  
379 adhesives<sup>10-13</sup>. The work reported herein advances this area of research since it shows that the

380 mechanical durability of nanoparticle coatings can be improved through embedding the particles  
381 into the substrate material itself, rather than through combining the particles with additives. The  
382 technique of thermal embedding of nanoparticles into plastic has never been used to control the  
383 wettability of surfaces, as well as for improving the durability of surface coatings.

384 Using this methodology, we have shown that surface wettability of plastic can be tailored from  
385 highly hydrophobic to highly hydrophilic depending on the chemical functionality of the  
386 nanoparticles. Embedding different mass fractions of these particles allowed this wettability control  
387 with CAs ranging from around 150 to 40°. This could mean that nanoparticle embedded plastic could  
388 be used for applications that include both waterproofing and water collection. Interestingly, plastic  
389 embedded with the hydrophobic isostearate functionalised nanoparticles was observed to show  
390 petal-like wetting behaviour<sup>34,35</sup>, despite showing a CA greater than 150°. As a consequence of this,  
391 our future work will investigate whether it is possible to embed particles into plastic so that it shows  
392 lotus-like wetting behaviour.

### 393 **Associated content**

394 The following file is available free of charge:

395  
396 SEM image of the isostearate functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles deposited onto the heated plastic  
397 before sonication in isopropanol, SEM and AFM images of the plastic substrate following (1) spray  
398 coating with the isostearate functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles, and (2) sonication in isopropanol,  
399 and photograph of the as received plastic and plastic after embedding with the isostearate  
400 functionalised Al<sub>2</sub>O<sub>3</sub> nanoparticles. SEM images and water CA images on plastic embedded and  
401 non-embedded with the isostearate functionalized nanoparticles after finger wiping, tape peel and  
402 mechanical test.

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406 Notes

407 The authors declare that there are no conflicts of interest.

408

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417 **References**

- 418 1. X. M. Bao, J. F. Cui, H. X. Sun, W. D. Liang, Z. Q. Zhu, J. An, B. P. Yang, P. Q. La, and A. Li,  
419 Facile preparation of superhydrophobic surfaces based on metal oxide nanoparticles, *Appl. Surf. Sci.*  
420 303 (2014) 473–480.
- 421 2. N. Agrawal, S. Munjal, M. Z. Ansari, and N. Khare, Superhydrophobic palmitic acid modified  
422 ZnO nanoparticles, *Ceram. Int.* 43 (2017) 14271–14276.

- 423 3. Z. T. Li, B. Lin, L. W. Jiang, E. C. Lin, J. Chen, S. J. Zhang, Y. W. Tang, F. A. He, and D. H. Li,  
424 Effective preparation of magnetic superhydrophobic Fe<sub>3</sub>O<sub>4</sub>/PU sponge for oil-water separation,  
425 *Appl. Surf. Sci.* 427 (2018) 56–64.
- 426 4. S. Alexander, J. Eastoe, A. M. Lord, F. Guittard, and A. R. Barron, Branched Hydrocarbon Low  
427 Surface Energy Materials for Superhydrophobic Nanoparticle Derived Surfaces, *ACS Appl. Mater.*  
428 *Interfaces* 8 (2016) 660-666.
- 429 5. W. A. Shatty, A. M. Lord, S. Alexander, and A. R. Barron, Tunable Surface Properties of  
430 Aluminum Oxide Nanoparticles from Highly Hydrophobic to Highly Hydrophilic, *ACS Omega* 2  
431 (2017), 2507-2514.
- 432 6. D. Hill, H. Attia, A. R. Barron, and S. Alexander, Size and morphology dependent surface wetting  
433 based on hydrocarbon functionalized nanoparticles, *J. Colloid Interface Sci.* 543 (2019) 328-334.
- 434 7. I. S. Bayer, A. J. Davis, and A. Biswas, Robust superhydrophobic surfaces from small diffusion  
435 flame treatment of hydrophobic polymers. *RSC Adv.* 4 (2014), 264-268.
- 436 8. I. S. Bayer, K. G. Krishnan, R. Robison, E. Loth, D. H. Berry, T. E. Farrell, and J. D. Crouch,  
437 Thermal Alternating Polymer Nanocomposite (TAPNC) Coating Designed to Prevent Aerodynamic  
438 Insect Fouling, *Sci. Rep.* 6 (2016) 38459-38472.
- 439 9. M. Manca, A. Cannavale, L. De Marco, A. S. Arico, R. Cingolani, and G. Gigli, Durable  
440 Superhydrophobic and Antireflective Surfaces by Trimethylsilanized Silica Nanoparticles-Based  
441 Sol-Gel Processing, *Langmuir* 25 (2009) 6357-6362.
- 442 10. B. Chen, J. Qiu, E. Sakai, N. Kanazawa, R. Liang, and H. Feng, Robust and Superhydrophobic  
443 Surface Modification by a “Paint + Adhesive” Method: Applications in Self-Cleaning after Oil  
444 Contamination and Oil–Water Separation, *ACS Appl. Mater. Interfaces* 8 (2016), 17659-17667.



- 445 11. Y. Si, F. Yang, and Z. Guo, Bio-inspired one-pot route to prepare robust and repairable micro-  
446 nanoscale superhydrophobic coatings, *J. Colloid Interface Sci.* 498 (2017) 182-193.
- 447 12. Y. Lu, S. Sathasivam, J. Song, C. R. Crick, C. J. Carmalt, and I. P. Parkin, Robust self-cleaning  
448 surfaces that function when exposed to either air or oil, *Science* 347 (2015), 1132-1135.
- 449 13. D. Ebert, and B. Bhushan, Transparent, Superhydrophobic, and Wear-Resistant Coatings on  
450 Glass and Polymer Substrates Using SiO<sub>2</sub>, ZnO, and ITO Nanoparticles, *Langmuir* 28 (2012) 11391-  
451 11399.
- 452 14. D. Lithner, Å. Larsson, and G. Dave, Environmental and health hazard ranking and assessment  
453 of plastic polymers based on chemical composition, *Sci. Total Environ.* 409 (2011), 3309-3324.
- 454 15. T. Karakouz, B. M. Maoz, G. Lando, A. Vaskevich, and I. Rubinstein, Stabilization of Gold  
455 Nanoparticle Films on Glass by Thermal Embedding, *ACS Appl. Mater. Interfaces*, 3 (2011), 978-  
456 987.
- 457 16. Q. Xi, X. Chen, D. G. Evans, and W. Yang, Gold Nanoparticle-Embedded Porous Graphene  
458 Thin Films Fabricated via Layer-by-Layer Self-Assembly and Subsequent Thermal Annealing for  
459 Electrochemical Sensing. *Langmuir* 28 (2012) 9885-9892.
- 460 17. J. Prakash, J. C. Pivin, and H. C. Swart, Noble metal nanoparticles embedding into polymeric  
461 materials: From fundamentals to applications. *Adv. Colloid Interface Sci.* 226 (2015) 187-202.
- 462 18. V. Zaporozhchenko, T. Strunskus, J. Erichsen, and F. Faupel, Embedding of noble metal  
463 nanoclusters into polymers as a potential probe of the surface glass transition, *Macromolecules* 34  
464 (2001) 1125-1127.
- 465 19. J. H. Teichroeb, and J. A. Forrest, Direct Imaging of Nanoparticle Embedding to Probe  
466 Viscoelasticity of Polymer Surfaces, *Phys. Rev. Lett.* 91 (2003) 016104.

- 467 20. A. L. Stepanov, Synthesis of Silver Nanoparticles in Dielectric Matrix by Ion Implantation: A  
468 Review. *Rev. Adv. Mater. Sci.* 26 (2010) 1-29.
- 469 21. D. K. Avasthi, Y. K. Mishra, D. Kabiraj, N. P. Lalla, and J. C. Pivin, Synthesis of metal–polymer  
470 nanocomposite for optical applications. *Nanotechnology*, 18 (2007) 125604-125608.
- 471 22. Sharp, J. S.; Teichroeb, J. H.; Forrest, J. A. The properties of free polymer surfaces and their  
472 influence on the glass transition temperature of thin polystyrene films. *Eur. Phys. J. E: Soft Matter*  
473 *Biol. Phys.*, **2004**, 15, 473-487.
- 474 23. Weber, R.; Grotkopp, I.; Stettner, J.; Tolan, M.; Press, W. Embedding of Gold Nanoclusters on  
475 Polystyrene Surfaces: Influence of the Surface Modification on the Glass Transition.  
476 *Macromolecules*, **2003**, 36, 9100-9106.
- 477 24. S. Prakash, T. Chakrabarty, A. K. Singh, and V. K. Shahi, Polymer thin films embedded with  
478 metal nanoparticles for electrochemical biosensors applications. *Biosens. Bioelectron.* 41 (2013) 43-  
479 53.
- 480 25. C. Hanisch, A. Kulkarni, V. Zaporozhchenko, and F. Faupel, Polymer-metal nanocomposites with  
481 2- dimensional Au nanoparticle arrays for sensoric applications. *J. Phys.: Conf. Ser.* 100 (2008)  
482 052043.
- 483 26. K. J., Bretz, Á. Jobbágy, and K. Bretz, Force measurement of hand and fingers. *Biomechanica*  
484 *Hungarica* 3.1 (2010).
- 485 27. J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben in Handbook of X-ray Photoelectron  
486 Spectroscopy, *Perkin-Elmer Corporation* 1992, Appendix H, pp. 256.
- 487 28. D. W. Sauter, M. Taoufik, and C. Boisson, Polyolefins, a Success Story, *Polymers* 9 (2017) 185-  
488 198.

- 489 29. M. P. Seah and W. A. Dench, Quantitative electron spectroscopy of surfaces: A standard database  
490 for electron inelastic mean free paths in solids. *Surf. Interface Anal.* 1 (1979), 2-11.
- 491 30. A. Plasencia, J. D. Piasecki, and B. R. Strohmeier, XPS Surface Characterization of Disposable  
492 Laboratory Gloves and the Transfer of Glove Components to Other Surfaces, *Spectroscopy* 27  
493 (2012) 36-47.
- 494 31. M. Miwa, A. Nakajima, A. Fujishima, K. Hashimoto, and T. Watanabe, Effects of the Surface  
495 Roughness on Sliding Angles of Water Droplets on Superhydrophobic Surfaces, *Langmuir*, 16  
496 (2000) 5754-5760.
- 497 32. J. Drelich, and J. D. Miller, The Effect of Solid Surface Heterogeneity and Roughness on the  
498 Contact Angle/Drop (Bubble) Size Relationship, *J. Colloid Interf. Sci.* 164 (1994) 252–259.
- 499 33. J. Drelich, J. D. Miller, and R. J. Good, The Effect of Drop (Bubble) Size on Advancing and  
500 Receding Contact Angles for Heterogeneous and Rough Solid Surfaces as Observed with Sessile-  
501 Drop and Captive-Bubble Techniques, *J. Colloid Interf. Sci.* 179 (1996) 37-50.
- 502 34. L. Feng, Y. Zhang, J. Xi, Y. Zhu, N. Wang, F. Xia, and L. Jiang, Petal effect: a superhydrophobic  
503 state with high adhesive force, *Langmuir* 24 (2008) 4114-4119.
- 504 35. Z. Cheng, M. Du, H. Lai, N. Zhangab, and Kening Sun, From petal effect to lotus effect: a facile  
505 solution immersion process for the fabrication of super-hydrophobic surfaces with controlled  
506 adhesion, *Nanoscale* 5 (2013) 2776-2783.
- 507 36. D. Hill, Andrew R. Barron, and S. Alexander, Comparison of hydrophobicity and durability of  
508 functionalized aluminium oxide nanoparticle coatings with magnetite nanoparticles—links between  
509 morphology and wettability, *J. Colloid Interf. Sci.* 555 (2019) 323-330.

510 37. N. Mizoshita and H. Tanaka, Versatile Antireflection Coating for Plastics: Partial Embedding of  
511 Mesoporous Silica Nanoparticles onto Substrate Surface, *ACS Appl. Mater. Interfaces* 8 (2016)  
512 31330-31338.

513 38. Z. Sun, T. Liao, K. Liu, L. Jiang, J. H. Kim, and S. X. Dou, Fly-Eye Inspired Superhydrophobic,  
514 Anti-Fogging Inorganic Nanostructures, *Small* 10 (2014) 3001-3006.

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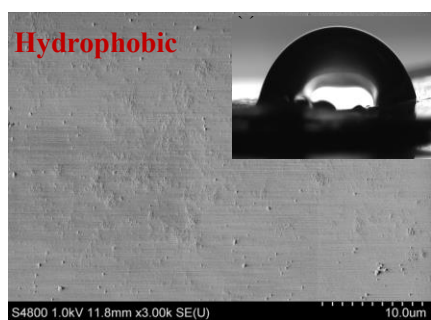
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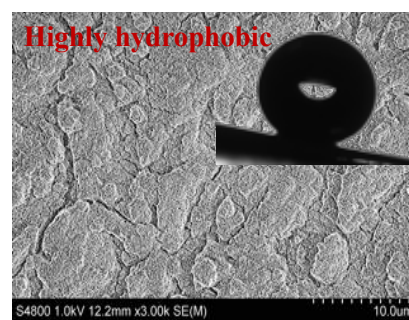
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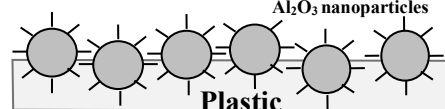
520 TOC



1) Spray coating + heat  
2) Sonication



Thermally embedded  
Al<sub>2</sub>O<sub>3</sub> nanoparticles



521