Development and characterization of poly ethyl metha acrylate–iron oxide(III) based hydrophobic liquid nanocomposite films

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Abstract

Select applications of hydrophobic nanocomposites include preparation of robust self-cleaning surfaces, water-repellent glass surfaces, and waterproofing textiles. Various nanocomposites have been reported in the literature; however, the relationship between the nanocomposite surface morphology and its hydrophobicity needs to be understood better. In the present work Fe₂O₃ nanoparticles and poly ethyl metha acrylate (PEMA) were used in varying proportions to obtain a series of model hydrophobic surfaces (spin-coated on glass substrate). The hydrophobicity of these surfaces was measured by static contact angle; a maximum of ∼103° was obtained at highest loading of iron oxide nanoparticles. These surfaces were also characterized using AFM. The contact angle and characterization data were used to test some of the models which have been proposed in the recent literature on prediction of contact angle for composite surfaces. It is proposed that the hydrophobicity of the iron oxide–PEMA surface is due to the physical roughness causing air entrapment as well as the chemical heterogeneity. Based on the experimental studies and the simulations using the recent models on contact angle, some general features of relationship between a composite surface morphology and its hydrophobicity is proposed.

1. Introduction

Surface hydrophobicity is a phenomenon in which a surface behaves as water repelling. This property has always been of great importance for researchers in past to solve a variety of engineering problems viz. making textiles which are water proof, water-repellent glass windows for automobiles and self-cleaning surfaces [1,2]. This property of transparent hydrophobic coatings is also being used in anti-snow, anti-rust [3] and reduced frictional resistance for aerospace applications. The best example of a super-hydrophobic surface available in nature is the self-cleaning leaf of a lotus plant (Nelumbo nucifera) [4–6]. The water contact angle on lotus leaf is 160° due to which it repels water droplets falling on its surface through a rolling mechanism [7]. In this process the organic dirt or impurities sticking to the leaf surface roll away with the droplets and as a result the lotus leaf remains lush green and clean even in murky ponds. This phenomenon is termed as “lotus leaf effect”. Various research groups viz. Fadeev and McCarthy [8], Lacroix et al. [9] have attempted to mimic this unique property of lotus leaf by preparing superhydrophobic surfaces using techniques such as plasma etching, photolithography [10–11] and silylation [12]. These techniques involve high temperature conditions and expensive procedures which make them limited in desired industrial applications and bulk production. In the present work, the hydrophobic liquid nanocomposites were developed using magnetic iron oxide nanoparticles in combination with polymers such as poly ethyl metha acrylate (PEMA). Initially, static contact angle measurements were carried out for glass surface coated with Fe₂O₃ and PEMA individually, to get an idea about their hydrophobicity. Then, the PEMA concentration was fixed corresponding to that which gave the maximum contact angle and the loading of Fe₂O₃ nanoparticles was varied. Static contact angle was measured for all such composite surfaces. In parallel, the surfaces were characterized using atomic force microscopy (AFM). It was found that PEMA is of low hydrophobicity; the maximum static contact angle with increasing PEMA loading on glass surface being 73.6°. When iron oxide nanoparticles are spin-coated on the PEMA surface the contact angle increases with increasing nanoparticle concentration. The highest contact angle was found to be ∼103.5°, obtained with high loading of nanoparticles. Quantitative analysis of the results was done using the model due to Kulinich and Farzaneh[13], which provides a framework for the prediction of contact angle for chemically heterogeneous and rough surfaces. Such simulation results also show that the contact angle increases at high surface area fraction of the Fe₂O₃ nanoparticles (fₙ). This increase is primarily due to the air entrapment between adjacent nanoparticles.
2. Materials and methods

Magnetic iron oxide (Fe$_2$O$_3$) nanoparticles uniformly ranging in size of 3–15 nm, solid content of 0.8–1.4%, dispersed in n-heptane were purchased from Fluka, Sigma Aldrich Co. TiO$_2$ nanoparticles were prepared from reverse micellar technique in the size range of 5–20 nm. TiO$_2$ nanoparticles were uniformly dispersed in n-Butanol using sonication for 1 h. The solvent n-Butanol was purchased from Merck Ltd. PEMA particles having very high molecular weight were obtained from Thomas Baker Ltd. The solvent chloroform (CHCl$_3$), $M = 119.38$ g/mol and density = 1.48 kg/l for dissolving PEMA was purchased from Merck Ltd. The TiO$_2$ nanoparticles dispersed in n-butanol were spin-coated on the micro glass slide at 5000 rpm and allowed to dry at room temperature for one day. PEMA was spin-coated on glass surface from chloroform solution. Fe$_2$O$_3$ nanoparticles were dispersed in suitable solvent such as n-heptane and then spin-coated at different concentration on top of the PEMA coating. The water static contact angle on all surfaces was measured using contact angle goniometer (GBX Digidrop intelligent version, France); the water drop 5 μl in volume in all cases. The contact angle video images were captured through online microscopy using Windrop++ software. All measurements were done at 25 °C. Lastly, the roughness of such prepared surfaces was analyzed using Atomic Force Microscopy (Nanoscope IV, Digital instruments, VEECO Metrology group). Surface characterization of PEMA–Fe$_2$O$_3$ coated was also carried out using scanning electron microscopy (SEM) (S-3400N model, HITACHI Co.).

3. Results and discussion

Through our experiments the average value of water static contact angle value of the pure glass substrate was 23°, suggesting moderate hydrophilicity. As shown in Fig. 1, TiO$_2$ nanoparticles coating reduced the contact angle to a very low value. The static contact angle decreased gradually to about 5.1° in 2–3 s which shows superhydrophillicity of these particles (Fig. 1(b)). The contact angle images for intermediate times were reported elsewhere [14]. As noted above PEMA was dissolved in the chloroform and then spin-coated on the glass slide. The concentration of PEMA was varied from 0.2 g PEMA/100 ml of chloroform to 1 g PEMA/100 ml chloroform to see the effect of such concentration variation on static contact angle. This shows that TiO$_2$ nanoparticles based coatings are superhydrophilic in nature [1,15]. The high hydrophilic nature of TiO$_2$ nanoparticles is due to the fact that, these nanoparticles are photoactive. In presence of UV light, H$_2$O they produce hydrophilic hydroxyl radicals (OH$^-$). These (OH$^-$) radicals cause wetting of water on TiO$_2$ coated glass surface as soon as water comes into contact with these radicals.

Fig. 2 shows the actual variation in water static contact angle with change in concentration of PEMA. The water static contact angle was maximum (73.6°) at 0.2 g PEMA loading/100 ml chloroform (used for spin coating glass surface) and it decreased to 66.1° at 1 g PEMA loading/100 ml chloroform. The reason for this decrease in water contact angle is formation of smooth films on one above another due to spin coating at high concentration. Whereas, at lower concentration the surface is rough and hence the water contact angle is high. It may be noted that Chibowski et al. [16] have studied PMMA coatings on glass and observed similar range of water static contact angle values.

For the next round of experiments, the glass surface was first spin-coated with 0.2 g PEMA/100 ml of chloroform solution; and on top of it the Fe$_2$O$_3$ nanoparticles were spin-coated using iron oxide suspension. The suspension volume used varied from 2 drops to 60 drops, each drop contained about $1 \times 10^{12}$ particles. We used the maximum value of contact value of 73.6° for PEMA coated glass films at 0.2 g PEMA loading/100 ml chloroform in our experiments further with Fe$_2$O$_3$ nanoparticles.

Fig. 3 shows the actual variation in static contact angle with iron oxide nanoparticles weight. For PEMA–Fe$_2$O$_3$ nanoparticles system the static contact angle value was 78° at low loading (12 drops of Fe$_2$O$_3$ suspension) and a value of 103.5° obtained at high loading (60 drops Fe$_2$O$_3$ suspension). A single drop (volume = 5 μl) of nanoparticles in n-heptane contained $1 \times 10^{12}$ nanoparticles. As shown in Fig. 3 the water static contact angle increases with loading of nanoparticles on PEMA. Thus, both nanoparticles as well the nanoparticle + PEMA combination render the surface moderately hydrophobic. In general, with increase in nanoparticle loading,
the interparticle air entrapment increases, and this causes contact angle to increase continuously. We discuss this effect in detail below. Two well-known effects that account for the value of apparent contact angle on real surfaces are Wenzel effect and Cassie effect. The Wenzel effect for surface roughness is given by [17]:

\[
\cos \theta_w = \left( \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \right)^r
\]

(1)

where, \( r \) is the roughness factor [17] and \( \gamma_{SV}, \gamma_{SL}, \) and \( \gamma_{LV} \) are the interfacial free energies per unit area of the solid–liquid, solid–gas, and liquid–gas interfaces respectively. The Cassie equation [17–19] for chemically heterogeneous and smooth surfaces is given by:

\[
\cos \theta_C = f_1 \cos \theta_1 + f_2 \cos \theta_2
\]

(2)

where, \( \theta_C \) is the apparent contact angle for a surface that consists of \( f_1 \) fraction of type-1 material and \( f_2 \) fraction of type-2 material and \( \theta_1 \) and \( \theta_2 \) are the corresponding equilibrium contact angles for pure homogeneous material. The Cassie–Baxter effect [19] is a special case of Cassie effect. It is applicable for a composite surface when air enters in the substrate in place of material-2. The Cassie–Baxter expression can be written as,

\[
\cos \theta_{CB} = f \cos \theta + f - 1
\]

(3)

where, \( \theta_{CB} \) is the Cassie–Baxter contact angle for a composite surface and \( f \) is the area fraction of solid material in contact with water. While the Wenzel effect is due to the increase in surface area arising out of the surface roughness, the Cassie–Baxter effect is due to the non-homogeneous material surface where different fractions of surface area on the substrate have different equilibrium contact angles. Neither of these contact angle models is applicable for the Fe\(_2\)O\(_3\)–PEMA coating, as it is both rough as well as chemically heterogeneous. The contact angle model that better describes such a surface is the Kulinich and Farzaneh model [13], given by:

\[
\cos \theta^* = f_1 (f_{w1} (1 + \cos \theta_1) - 1) + (1 - f_1) f_{w2} (1 + \cos \theta_2) - 1
\]

(4)

where \( f_1 + f_2 = 1 \)

(5)

\[ f_{w1} + f_{w2} = 1 \]

(6)

and \( f_{w1} f_{w2} = 1 \)

(7)

where, \( \theta^* \) represents the contact angle when the surface is partially covered with air. Whereas, \( \theta_1 \) and \( \theta_2 \) represents the intrinsic equilibrium contact angles on phase-1 and phase-2, respectively. Here, \( f_1 \) represents the net area fraction of phase-1, \( f_{w1} \) represents the area fraction of water covered phase-1, \( f_{w2} \) represents the net area fraction of phase-2, and \( f_{w2} \) represents the area fraction of water covered phase-2. For Fe\(_2\)O\(_3\)–glass system, 1 refers to Fe\(_2\)O\(_3\) nanoparticles and 2 refers to glass. For Fe\(_2\)O\(_3\)–PEMA system, 1 refers to Fe\(_2\)O\(_3\) nanoparticles and 2 refer to PEMA. We show below that Eq. (4) reasonably well reproduces the contact angle variation seen for both Fe\(_2\)O\(_3\)–glass system and Fe\(_2\)O\(_3\)–PEMA systems. But before that we discuss the results of the SEM and AFM experiments for obtaining a view of the morphology that obtains due to nanoparticle deposition either on glass directly or on PEMA film.
As mentioned earlier the morphology of the surfaces was studied using SEM and AFM techniques. Fig. 4 shows the SEM micrographs for Fe$_2$O$_3$ nanoparticles on glass at medium loading. As may be seen, the nanoparticles seem to be forming a leafy, branched kind of structure. This is possibly due to the self-assembly of the nanoparticles.

Fig. 5(a) and (b) shows AFM micrographs for PEMA–Fe$_2$O$_3$ nanoparticle system at 10 drops (low loading) and 60 drops (high loading) of suspension of nanoparticles (related experimental details described in Section 2). The nanoparticles are clearly visible in these micrographs. Fig. 6(a)–(c) represents the corresponding 3D AFM micrographs; all were captured at a scan rate of 1.507 Hz and a data scale of 55 nm. It is clear from the Fig. 6(a) and (c) that in case of low loading of nanoparticles on PEMA film, the surface morphology is nearly same as in the case of iron oxide nanoparticles on glass surface at low loading. The surface looks rough because of voids present between the nanoparticles. Fig. 6(b) shows the AFM image for Fe$_2$O$_3$ on glass at high loading (60 drops of Fe$_2$O$_3$ suspension). At higher loading, the Fe$_2$O$_3$ nanoparticles are very close to each other and thus forming a nanorod like structure which imparts smoothness to the structure. Therefore, Fig. 6(b) appears to suggest a smoother surface.

![Fig. 6. AFM 3D-micrograph for: (a) Fe$_2$O$_3$ on glass at low loading (10 drops Fe$_2$O$_3$ suspension) (b) Fe$_2$O$_3$ on glass at high loading (60 drops Fe$_2$O$_3$ suspension) (c) Fe$_2$O$_3$ on PEMA at low loading (10 drops Fe$_2$O$_3$ suspension).](image)

Based on the above considerations in Fig. 7(a), we show a schematic geometry of the possible surface morphology at high loading of nanoparticles on glass. We propose that there is only point contact of water drop with the nanoparticle surface. The increase in air-entrapment inside the pore between two successive nanoparticles is a potential cause for increased hydrophobicity. As shown in Fig. 3, this possibly causes the water static contact angle to increase with nanoparticle loading from 78° (at 2.049 × 10$^{-4}$ g) to 103.5° (at 1.024 × 10$^{-3}$ g). The schematic surface geometry is likely to hold good for a PEMA surface as well, which is proposed in Fig. 7(b). Based on these schematics we now show the results of simulation of contact angle using the Kulinich and Farzaneh [13] model for surfaces which are both rough and chemically heterogeneous, which is the case in our system.

3.1. Fe$_2$O$_3$–glass system

The effect of variation in the area fractions on apparent contact angle was studied employing the Kulinich and Farzaneh relation as shown in Eq. (4). Fig. 8 shows the plots of $\theta^o$ (apparent contact angle) versus $f_w$ (fraction of Fe$_2$O$_3$ on glass) for various values of $f_{Fe2O3}^G$ (area fraction of glass wetted by water). For example, Fig. 8(a) is plotted

![Fig. 7. Schematic of surface morphology of (a) glass surface with Fe$_2$O$_3$ nanoparticles (b) of PEMA (on glass) with Fe$_2$O$_3$ nanoparticles.](image)
for \( f_w^W = 0.2 \) and so on. For each \( f_w^W \) a set of curves is plotted with \( f_n \) (area fraction of nanoparticles wetted by water) as a second parameter. Its value ranges from 0 to 1.0. This variation means the area fraction of Fe\(_2\)O\(_3\) in direct contact with water is increasing from very low value to very high value. Similarly, the simulations were carried out for \( f_w^W = 0.5, f_w^W = 0.8, f_w^W = 0.99 \). The case \( f_w^W = 0.99 \) represents the condition when the fraction of water-wetted glass is very high, in comparison with the fraction of water-wetted nanoparticles. In this plot the zero point value (\( f_n = 0 \)) comes out to be 23° which is the average value of water static contact angle for glass surface only. Our experimental observation is that the apparent contact angle increases with nanoparticle loading whether on both glass and PEMA surface (Fig. 3). From the AFM pictures (Fig. 6) it would be apparent that the area fraction of nanoparticles \( (f_n) \) for the entire range of concentration (i.e., total mass of nanoparticles used for coating glass) is likely to be high. Unfortunately, it is not possible to recover the exact area fraction quantitatively from SEM or AFM images. At relatively higher values of \( f_n \) the situation would correspond to the proposed schematic in Fig. 7. Under this condition the actual area fraction of contact between the nanoparticles and the water drop is likely to be intermediate. The water static contact angle for Fe\(_2\)O\(_3\) nanoparticles is 84° at 10 drops of Fe\(_2\)O\(_3\) on glass which is not very high and hence favors the hydrophilicity. The water static contact angle at 60 drops of iron oxide nanoparticles on glass is 101° which is only a marginal increase as the loading is increased. Therefore, the water would wet the nanoparticle surfaces and also penetrate the gap between them to wet the glass surface. Under such a condition the fraction \( f_w^W \) is expected to be high. Graphically, the situation may lie between plots shown in Fig. 8(c) and (d). As is evident under such conditions if the value of \( f_n \) is increased (i.e. increase in loading of nanoparticles on glass), the water contact angle would show a monotonic increase. This is indeed what is also observed in our experiments (Fig. 3). This suggests that as the fraction \( f_n \) of Fe\(_2\)O\(_3\) coated is high, the surface morphology is such that the air-entrapment is high inside the spacings between the two adjacent nanoparticles and their contact with water is, as argued above, is intermediate. But the value of \( f_w^W \) is high since iron oxide nanoparticles are somewhat hydrophilic in nature and hence they allow water to come into contact with glass surface below nanoparticles. If we assume that \( f_w^W \) is high (say above 0.8) and \( f_w^W \) is intermediate, the curves corresponding to \( f_w^W = 0.5 \), in either Fig. 8(c) or (d) seems to approximately reproduce the experimental measurement on contact angle for Fe\(_2\)O\(_3\) nanoparticle coated glass surface where the water static contact angle ranges from 84° to 101° (see Fig. 3).

### 3.2. Fe\(_2\)O\(_3\)–PEMA system

We have also used the Kulinich and Farzaneh equation to simulate the experimental conditions in case of the Fe\(_2\)O\(_3\)–PEMA system. As in the case of Fe\(_2\)O\(_3\)–glass system discussed above, the area fractions were varied and their effect on apparent contact angle analyzed. Fig. 9 shows the plots of \( \theta' \) versus \( f_n \) (fraction of Fe\(_2\)O\(_3\) on PEMA coated glass surface) for various values of \( f_w^W \). The curves were likewise plotted for \( f_n^W \) (area fraction of nanoparticles in contact with water) as a parameter, its value ranging from 0 to 1.0. As noted earlier for all Fe\(_2\)O\(_3\)–PEMA surfaces we have used PEMA coating corresponding to the highest contact angle (i.e., a coating obtained form 0.2 g of PEMA/100 ml chloroform), as shown in Fig. 2. The case \( f_w^W = 0.99 \) represents the condition when the fraction of water-wetted glass is very high, in comparison with the fraction of water-wetted nanoparticles. In this plot the zero point value (\( f_n = 0 \)) corresponds to 66.1° which is the value of highest water static contact angle for PEMA-coated glass surface only. Similar water contact angle values reported elsewhere [14] for glass surface coated using 1 gm PEMA in 100 ml chloroform and for pure acrylic sheet suggest that the surface of glass covered at high concentration of PEMA is similar to that of pure PEMA (i.e., very little of the glass surface, if
any, is left uncoated by PEMA). This is supported by the fact that for pure acrylic sheet, the water static contact angle is close to 65.8°. Therefore, in analogy with the earlier case of Fe₂O₃–glass system, in the Fe₂O₃–PEMA system, the glass surface may be assumed to be replaced with a PEMA surface. Consequently, the mechanism for enhancement of contact angle on such a surface with increase of nanoparticle loading is likely to be the same as in the case of Fe₂O₃–glass system. The expected surface morphology in such a system is proposed in Fig. 7(b), particularly at relatively higher values of $f_w$, which is possibly the situation as concluded in the last section using the SEM and AFM data. As with the case of Fe₂O₃–glass system, in this case where glass is replaced with PEMA, the actual experimental situation possibly corresponds to the cases simulated in Fig. 9(c) and (d), or intermediate to these two. The hydrophilicity of Fe₂O₃ nanoparticles would allow water to wet their surface and also allow water penetrate the gap between them to wet the glass surface. Consequently, the fraction $f_w$ is expected to be high, and as shown in Fig. 9(c) and (d) the water contact angle is expected to increase with nanoparticle concentration on the surface. As is evident from Fig. 3 experimentally the contact angle ranges from 78° to 103.5°, from the lowest to highest nanoparticle loading. In terms of simulated contact angle curves if, as in the case of we assume that $f_w$ is high (say above 0.8) and $f_n$ intermediate (as assumed for Fe₂O₃–glass system), the curves corresponding to $f_w$ = 0.5, in either Fig. 9(c) or (d) seems to approximately reproduce the experimental measurement.

In summary, from the discussions on the contact angle behaviour for Fe₂O₃–glass and Fe₂O₃–PEMA systems the main generalized conclusion could be that it is the combination of surface roughness and chemical heterogeneity which is responsible for the enhanced hydrophobicity of the composite surfaces.

4. Summary

The present work presents a fairly simple procedure for preparing hydrophilic or hydrophobic coatings using nanocomposites. In contrast, TiO₂ nanoparticles can be used where wetting of glass is desirable. Further, an attempt was made to mimic the superhydrophobic lotus leaf effect by imparting physical roughness and heterogeneity to a surface, which are also the features of lotus leaf surface. For the experimental composite systems used, Fe₂O₃–glass and Fe₂O₃–PEMA, at higher loading of nanoparticles, the contact angle increases to a maximum of 103.5° (for Fe₂O₃–PEMA surface), which is representative of a moderate hydrophobicity. However, this may constitute a substantial enhancement given the fact that the original glass surface upon which the composite has been formed is hydrophilic (contact angle = 23°). It is shown that high loading of nanoparticles gives rise to a complex physically rough surface structure which causes air-entrapment inside the pores of adjacent Fe₂O₃ nanoparticles. This principally leads to enhanced hydrophobicity of the surface. If PEMA is used in place of glass as the subsurface the resultant hydrophobicity is marginally higher (Fig. 5). This suggests that chemical heterogeneity of the surface may also potentially contribute to enhanced hydrophobicity. PEMA, however, is not hydrophobic as such as its contact angle is less than 90° (actually around 66.1°, under the experimental conditions used in the present work. It follows that if one replaces PEMA with a strongly hydrophobic material as the subsurface under Fe₂O₃ nanoparticles, one may, in principle, be able to obtain a surface with superhydrophobic character. In conclusion, the results of the present work suggest that a judicious combination of nanoparticles and polymeric substance is the key to achieve surfaces with ultrahydrophobic character. The best results are expected if both
themselves hydrophobic. This would provide a combination of roughness and heterogeneity of the surface, which are key factors for creating hydrophobic surfaces or even ultrahydrophobic surfaces.

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References


Glossary

Contact angle ($\theta$): the angle between the tangent to the liquid–vapor interface and the tangent to the solid surface at the contact line between three phases

Ultrahydrophobicity: the phenomena in which the contact angle of a water droplet on a given substrate is 150° or above

Lotus leaf effect: the name of the effect given to the high value of contact angle of water droplet on the surface of the physically rough and chemically hydrophobic lotus leaf