Quantitative test method for evaluation of anti-fingerprint property of coated surfaces

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Abstract

An artificial fingerprint liquid is formulated from artificial sweat, hydroxyl-terminated polydimethylsiloxane and a solvent for direct determination of anti-fingerprint property of a coated surface. A range of smooth and rough surfaces with different anti-fingerprint (AF) properties were fabricated by sol–gel technology, on which the AF liquid contact angles, artificial fingerprint and real human fingerprints (HF) were verified and correlated. It is proved that a surface with AF contact angle above 87° is fingerprint free. This provides an objective and quantitative test method to determine anti-fingerprint property of coated surfaces. It is also concluded that AF property can be achieved on smooth and optically clear surfaces. Deep porous structures are more favorable than bumpy structure for oleophobic and AF properties.

Keywords: Anti-fingerprint; Contact angle; Oleophobicity; Hydrophobicity; Coating

1. Introduction

With the arising usages of electronic devices with integrated touch screen panels, the demand for anti-fingerprint materials is expected to greatly increase in the next few years [1]. Such devices are routinely subjected to touch and thus commonly stained with undesirable fingerprint, skin oil, sweat and cosmetics when used. These motivate the increasing demand of anti-fingerprint coating by today's discerning consumer. The anti-fingerprint property provides material surfaces with self-cleaning, or easy-to-clean features that improve aesthetic appearance and save maintaining cost. Much research has been done to construct anti-fingerprint coating on different material surfaces [2–4]. Despite these achievements, the quantification of human fingerprint mark on surfaces has not been fully investigated. The direct fingerprint test is qualitative and subjective due to the large variation of human finger marks under different environmental condition and different skin conditions. The common characterization methods for anti-fingerprint determination are the hydrophobicity and oleophobicity tests, in which the contact angles against water and n-hexadecane are measured respectively. However, the correlation between the contact angles and actual visibility and adhering property of human finger mark has not been established. An artificial fingerprint liquid was used to perform an evaluation of anti-staining, fingerprint adhering or removing property on an optical disk surface [5,6], however, the mentioned liquid was mixed with inorganic and organic particles to simulate the finger mark, which is a direct simulation of finger mark, and still lacks of quantitative criteria to determine the anti-fingerprint property of a surface.

In this paper, we report a newly formulated artificial fingerprint liquid, which can be prepared easily and used as the test liquid for contact angle measurement on a surface, from which, the anti-fingerprint property is directly determined. A surface with contact angle close to or higher than 90° against this liquid is fingerprint free. With addition of inorganic nano-particles in this liquid, direct simulation of human fingerprint was obtained. All these properties were proved by testing on smooth and rough surfaces coated by specially formulated sol–gel materials with different levels of anti-fingerprint properties. Both contact angles and artificial finger marks are correlated to human finger marks (about 20 people provided their finger marks on different surfaces). These provided a complete solution for simulation and quantitative evaluation of anti-fingerprint property of a coated surface, and correlated and confirmed by the actual human finger marks, therefore, could be used as a standard test method for developing anti-fingerprint materials and quantitative evaluation of the anti-fingerprint property of such materials and surfaces.

2. Experimental details

2.1. Preparation of fingerprint liquid

An artificial fingerprint liquid was formulated by mixing an artificial sweat with hydroxyl-terminated polydimethylsiloxane (PDMS, $M_n \sim 550$, viscosity~ 25 cSt) and 1-methoxy-2-propanol (MP) in different ratios. The artificial sweat (AS) was formulated by mixing the following substances: lactic acid 3 ml/l, acetic acid 5 ml/l, sodium chloride 10 g/l, sodium hydrogen phosphate 10 g/l, and DI water. The artificial fingerprint liquid is then prepared by dissolving an equal amount of 1-methoxy-2-propanol and hydroxyl terminated PDMS, and then adding into the artificial sweat. The solution was stirred for at least 4 h at room temperature before being used. The PDMS content was varied by 5 wt%, 10 wt%, 20 wt% of total solution. Using a rubber stamp with fine line patterns as a tool, artificial fingerprint was deposited on smooth plastic and glass surfaces using the liquids and dried. Meantime, human fingerprint was also deposited on the same substrate.

2.2. Preparation of sol-gel coating solution

To prepare sol–gel coatings, firstly a mixture of TEOS (Tetraethyl orthosilicate), MEMO (3-Methacryloxypropyltrimethoxysilane) and EtOH (ethanol) was made under vigorous stirring. After the mixture was stirred until homogeneous, water and hydrochloric acid (HCl) catalyst were added for the hydrolysis of the precursors to take place. The optimum molar ratio of TEOS:MEMO:EtOH:H_2O= 1:0.25:6:2.4. HCl was added in trace amount to obtain pH 3 of the solution. The reaction time was set to be 24 h in order to ensure completed hydrolysis reaction. Then acidified AS40 colloidal silica (pH 3, average diameter of the silica particles was 20 nm) was added into the sol–gel solution for mechanical property enhancing purpose. When the mixture solution was homogeneous, F8815 (a fluoroalkylfunctional waterborne oligosiloxane supplied by Evonik Degussa) in amount of 10 wt% was added as hydrophobic additive and then followed by curing agent, Darocur 1173 of Ciba. All the mentioned processes were carried out under vigorous stirring of the mixture solution. This formed the clear fingerprint solution. To further simulate the human fingerprint, micro- and nano-sized particles were added into the selected liquid (S3), which was made of PDMS, MP and artificial sweat in weight ratio of 1:1:3. Silica and alumina particles in micro- and nano-sizes (Aerosil 300 nano-silica, Alu300 nano-alumina from Evonik Degussa, and 40 OS micro-alumina from Sasol) were dispersed in the S3 liquid in different weight percentages, and artificial finger marks were deposited on non-coated PMMA plates by a rubber stamp to obtain similar finger marks as the human fingerprint (HF).

2.3. Coating and curing processes

PMMA plate in size of 100 × 50 × 3 (mm × mm × mm) was used as the substrate. The substrate was first washed by isopropanol (IPA), and dried by blowing nitrogen gas. To obtain smooth coatings, the substrate was coated using a dip coater with constant withdrawal speed of 10mm/s. To obtain nanostructured surfaces, a LVMP (low volume medium pressure) spray technique was used to deposit coatings on cleaned PMMA substrate. By controlling the spraying pressure, feed rate and spray strokes, different surface roughness and morphology structures were obtained, which provided a range of surface structures for different anti-fingerprint properties. After dip coating or spray coating, the specimen was dried in a furnace at 80°C for 10 min, and then cured by UV source with intensity of 2.507 J/cm^2.

2.4. Coating characterization

A VCA Optima (VCA-2500XE AST products, Inc) contact angle machine was used to measure static contact angle, advancing and receding contact angles using water, and the formulated artificial fingerprint liquids. To prevent cross-contamination, new syringe needle was used for each liquid. A drop of 0.5 μl liquid was used for static contact angle, and an addition or reduction of 0.2 μl of liquid was sued for measurement of advancing and receding angles. The difference between these two angles is the contact angle hysteresis. The surface tension of each liquid was measured using the Pendant drop method by the VCA optima machine. The surface roughness (Ra) of all the samples were measured by a Tayler–Hobson Stylus Profilometer. Surface structures were observed under field-emission scanning electron microscopy (FESEM, JEOL JSM-6340F)). Coating's light transmittance was measured by UV–vis spectrophotometer (SHIMADZU UV-3101PC UV–vis-NIR scanning spectrophotometer). The image of the liquid drop was taken by a digital carema.

3. Result and discussions

3.1. Wetting behavior of clear fingerprint liquids

In the artificial fingerprint liquid, the artificial sweat worked as the perspiration of human fingertip, PDMS served as oil based component in human finger mark, while 1-methoxy-2-propanol (MP) as the common solvent for good mixing of the substances. By varying the ratios of the three components, different surface tensions of the liquids ranging from 23 to 33 mJ/m^2 were obtained. This is in the same surface tension range of human fingerprint of 20–50 mJ/m^2 as reported [6]. Using a rubber stamp with fine line patterns as a tool, artificial fingerprint was deposited on smooth plastic surfaces using the liquids and dried. Meantime, human fingerprint was deposited on the same substrate. Then water contact angles in terms of static, advancing, and receding angles were measured directly on the marks, and the values were compared as shown in Table 1. It was found that the optimum composition of artificial fingerprint liquid (S4) consisted of PDMS, MP and artificial sweat in weight ratio of 3:3:4, which created the same water contact angles as the human fingerprint. This indicates our formulated fingerprint liquid has similar surface tension value as the human finger liquid.

3.2. Surface wetting behavior of simulated fingerprints

To further simulate the human fingerprint, micro- and nano-sized particles were added into the S3 liquid, which was made of PDMS, MP and artificial sweat in weight ratio of 1:1:3. This liquid generated the closest contact angles as human fingerprint after adding solid particles. Table 2 shows the water contact angles measured on the artificial fingerprints with different micro- and nano-particles contents compared to the results on human fingerprint. It is seen that very similar static, advancing and receding contact angles to HF mark can be achieved by using silica or alumina fillers. The combination of micro- and nano-sized particles could provide lower contact angles, but white particles and some bubbles were observed. Using only nano-particles, uniform artificial marks (sample AF Al6 with 2.5 wt% Alu300 filler) were achieved with the same contact angles as the HF mark. Fig. 1 shows the images of HF mark (a), AF Al6 mark (b) and AF Si3 mark (c) on uncoated PMMA. Both HF mark and AF Al6 mark are uniform, while AF Si3 mark contains visible particles and some bubbles as highlighted by the red circles. From the above study, we can conclude that the formulated artificial fingerprint liquid (S3) possesses very similar performance as the human fingerprint, therefore, could be used as a test liquid to evaluate the anti-fingerprint properties of coated surfaces.

3.3. Tuning anti-fingerprint property by FAS and roughness

To vary the anti-fingerprint property of surface, coating samples were made using sol–gel materials with solid fillers and additives containing fluorinated alkoxysilane (FAS), in combination with the low volume medium pressure air spray process [7]. FAS was reported to be able to exhibit very good hydrophobic and oleophobic characteristics [8,9]. In addition, Nakagawa and Soga [10] reported that a water repellent silica film with high thermal stability can be prepared in a TEOS sol containing (2-perfluorooctyl)-ethyltrimethoxysilane (a type of FAS). The F8815 additive used in this study contains FAS in solvent. Colloidal silica (particle size 20 nm) was added into the solution for enhancing mechanical property of the coating without influencing the optical transmittance [11]. By varying the spray parameters and solid contents in the coating recipe, a range of samples with different surface roughness values and structures were obtained. Fig. 2 shows the contact angles measured by S3 artificial fingerprint liquid on the samples versus their surface roughness Ra values. It is seen that there is no direct correlation between anti-fingerprint contact angle and roughness Ra value. AF contact angles above 85° were achieved on surfaces with Ra values from 0.5 μm to 1.5 μm. The human fingerprint tests showed that when AF contact angle is close to 90° (e.g. 87–88°), no finger mark was deposited on the surfaces.

3.4. Prediction of anti-fingerprint property by model equation

In order to find a trend between surface roughness factor and AF contact angle, traditional theories [12,13] describing correlations between water contact angle and surface roughness factor were investigated. However, because AF liquid is used instead of water in our contact angle measurement, and the AF contact angle shows positive trend with increasing Ra, a new roughness factor (R_f) is needed for theoretical prediction of AF contact angles. For the surfaces exhibit Ra > 1 μm, when using Ra/Rv as the roughness factor in Cassie–Baxter model [14], the experimental AFCosθ value showed linear correlation with Ra/Rv value as plotted in Fig. 3. Ra is the arithmetic mean roughness of the surface and Rv is defined as the valley depth of the roughness profile below mean line. Cassie–Baxter model postulates that the microscopic pockets of air trapped below the liquid droplet would lead to a composite interface resulting in superhydrophobic nature. According to the regression equation in Fig. 3, AFCosθ = 0.6591(Ra/Rv) − 0.2515, to obtain AF θ ≥ 90°, the Ra/Rv value should be ≤0.3816. This means that the surface overall roughness (Ra) should be small, and relatively deeper valleys (higher Rv) in the roughness profile will promote repellence of fingerprint. The deeper valleys would enhance air trapping under the liquid droplet, therefore, promote oleophobic or hydrophobic performance.

For the surfaces exhibit Ra≤1 μm, the experimental AFCosO value showed a linear correlation with Ra/Rv in a different gradient as shown in Fig. 4. According to the regression equation, AFCosθ = 0.3313(Ra/Rv) − 0.0812, to obtain AF θ ≥90°, Ra/Rv value should be ≤ 0.2451. This implies that a lower surface average roughness (Ra <1 μm) with relatively deeper valleys (higher Rv) would be beneficial for anti-fingerprint property. The required ratio of Ra/Rv is lower than the ratio for rougher surfaces (Ra > 1 μm), which means for smoother surfaces, even deeper valleys are required to impart oleophobic or anti-fingerprint property. Fig. 5 shows tow typical surface morphologies of the samples with Ra < 1 μm and Ra > 1 μm respectively. It is seen that both surfaces are porous, and the rougher surface contains some bumps. Both surfaces are anti-fingerprint, but with different water contact angles (116° and 120° respectively). This implies that water contact angle is more sensitive to the bumpy structures, like the lotus leaf effect

[15,16], while oleophobic property is less dependent on the bumpy structure. Deep porous structures are more favorable. Both samples are optically clear. From the above findings, it is clear that anti-fingerprint property is not necessarily to be on rough surfaces, smooth surfaces with suitable Ra/Rv ratios could lead to anti-fingerprint property. This finding is important for fabricating anti-fingerprint surfaces without the need of high roughness, which would affect the appearance and optical transmittance. The deeper valleys could favor air trapping beneath the liquid drop, therefore, promote anti-fingerprint property. This provides design guidelines for surface texturing for anti-fingerprint property, such as nano-porous or mesoporous coatings [17,18].

From the above analyses, an overall equation for prediction of the anti-fingerprint contact angle can be derived as:

where *a* and *b* are constants related to the roughness range (Ra larger or smaller than 1 μm), which can be obtained by plotting any two points in each range, and R_f is a roughness factor (=Ra/Rv) related to the profile of the surface roughness, which can be measured using a stylus Profilometer. The suitable roughness (Ra) range for the above equation is below 2 μm. It has been proven by actual human fingerprint tests that as long as the AF contact angle is above 87°–88°, the surface is fingerprint free. Therefore, this method and equation can be used as a standard and objective test method for evaluation of the oleophobic or anti-fingerprint property of a coated surface. Fig. 6 shows the images of artificial fingerprint by rubber stamp (a) and drops of AF liquid (b) on the coated surface (AFCA 88°). No human finger mark was observed on this surface. The samples also showed excellent optical transmittance due to low surface roughness, therefore, are suitable for display applications.

4. Conclusion

An artificial fingerprint liquid consisting PDMS, MP and artificial sweat in weight ratio of 3:3:4 has been formulated as the standard test liquid for direct determination (contact angle >87°) of anti-fingerprint property of a coated surface. This has been confirmed by real human fingerprint on different samples with different anti-fingerprint properties. An equation is proposed to predict the anti-fingerprint property of the surface by measuring the roughness profile and calculating the Ra/Rv value. This method can be used as a standard and objective test method for the evaluation of anti-fingerprint property of a coated surface. Smooth surfaces with deep valleys (nano-porous or mesoporous structure) would promote oleophobic property. This provides a design guideline for fabricating anti-fingerprint surfaces.

Acknowledgement

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Sample	Weight ratio PDMS:MP:AS	Static θ_{H_2O} (°)	Advancing θ_{H_2O} (°)	Receding θ_{H_2O} (°)	θ_{H_2O} hysteresis (°)	Surface tension (mJ/m^2)
AF S1	1:1:18	80.8	79.3	77.9	1.4	32.3
AF S2	1:1:8	78.3	77.5	76.9	0.6	29.8
AF S3	1:1:3	72.6	71.5	70.8	0.7	26.4
AF S4	3:3:4	70.9	70.6	68.2	2.4	23.2
HFmark[a]	–	70.3	68.1	65.5	2.7	20–50

Standard deviations of all contact angle data are below 10%.

[a] Human finger mark.

Table 1

Sample	Weight ratio Micro:Nano	Static θ_{H_2O} (°)	Advancing θ_{H_2O} (°)	Receding θ_{H_2O} (°)	θ_{H_2O} hysteresis (°)	Observation
AF Si3	3:0.5	72.8	71.1	70.6	0.55	Visible particle
AF Si4	4:0.5	41.0	62.2	51.7	9.7	Visible particle and bubble
AF Al3	4:0.5	67.5	66.7	65.5	1.2	White particles
AF Al5	0:1	77.4	74.3	72.9	1.4	Uniform mark
AF Al6	0:2.5	70.4	66.9	64.5	2.4	Uniform mark
HFmark[a]	–	70.3	68.1	65.5	2.7	Uniform mark

Standard deviations of all contact angle data are below 10%. Si_3 and Si_4: with silica filler, Al_3, Al_5 and Al_6: with alumina filler.

[a] Human finger mark.

Table 2

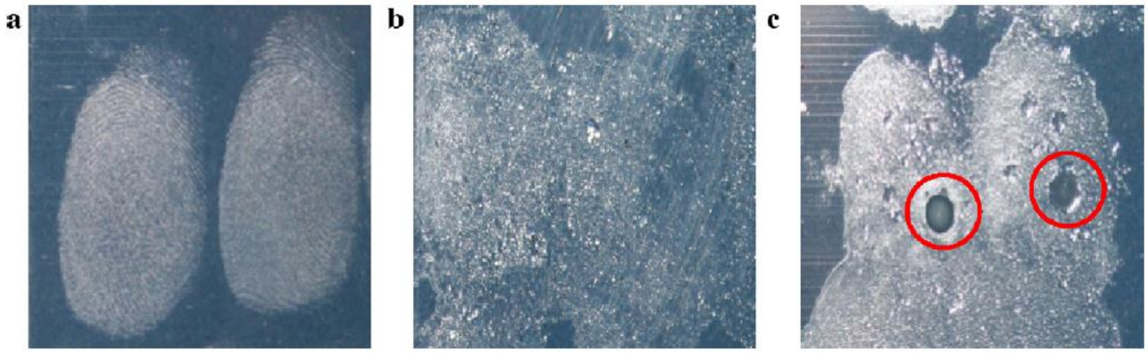


Fig. 1

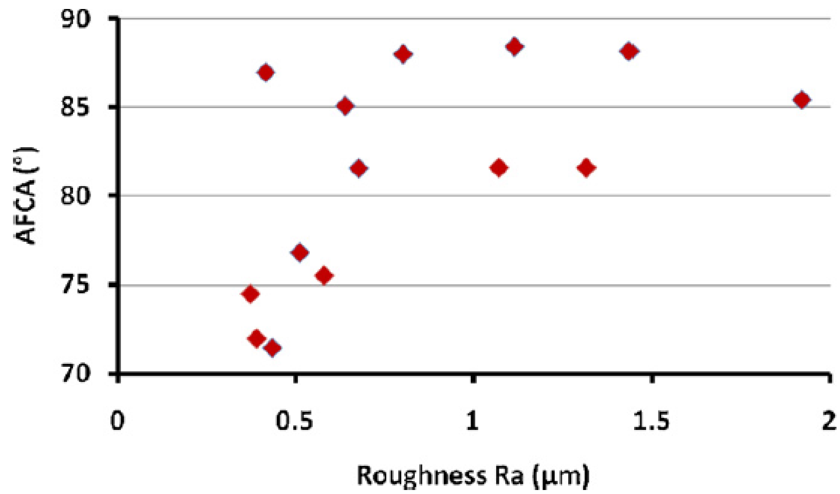
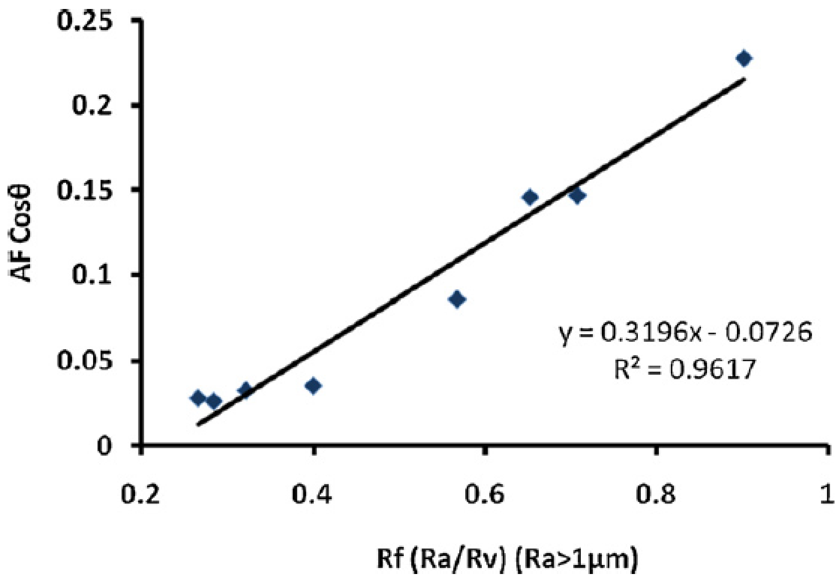


Fig. 2



0.25
0.2
0.15
0.1
0.05
0
AF Cosθ
y = 0.3196x - 0.0726
R² = 0.9617
0.2
0.4
0.6
0.8
1
Rf (Ra/Rv) (Ra>1μm)

Fig. 3

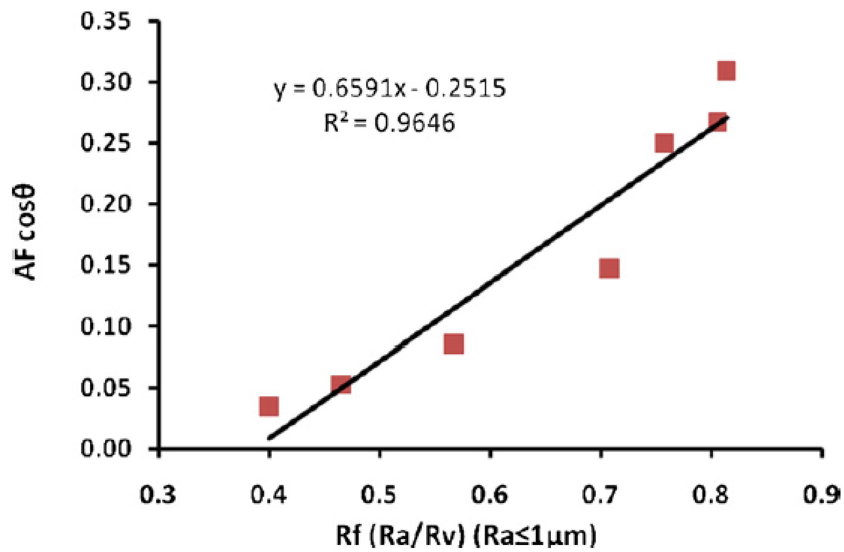

y = 0.6591x - 0.2515
R² = 0.9646
AF cosθ
Rf (Ra/Rv) (Ra≤1μm)
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.3
0.4
0.5
0.6
0.7
0.8
0.9

Fig. 4

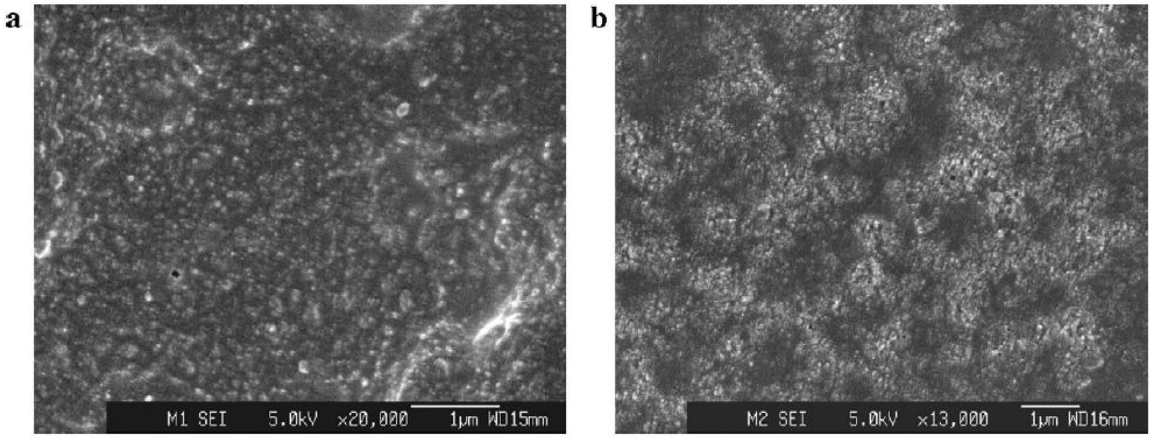


Fig. 5. SEM images of coated surfaces (a) Ra < 1 μm (WCA 116°, AFCA 88°), (b) Ra > 1 μm (WCA 120°, AFCA 86°).

Fig. 5

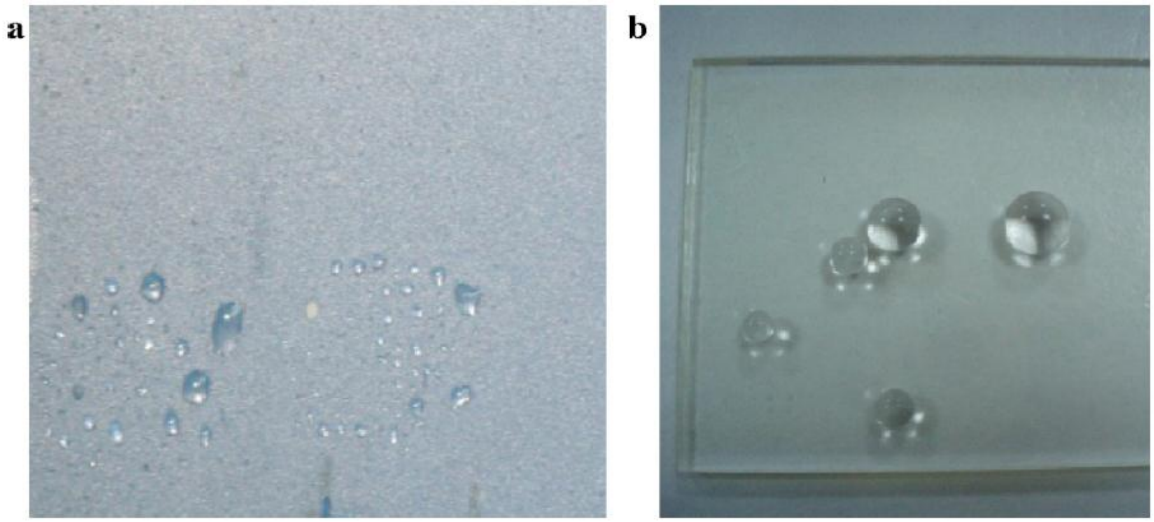


Fig. 6