SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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FORMATION AND DURABILITY INVESTIGATION ON

GRAPHENE-BASED SUPERHYDROPHOBIC COATING

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Formation and Durability Investigation on Graphene-Based Superhydrophobic Coating**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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In the name of Allah, the Most Gracious, Most Merciful

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscope
FAS	Fluoroalkylsilane
FESEM	Field Effect Scanning Electron Microscope
FTIR	Fourier Transform Infrared
KOH	Potassium hydroxide
EPA	United State Environmental Protection Association
TMMS	Trimethylmethoxysilane
O	Oxygen
PDMS	Polydimethylsiloxane
pH	Potential of hydrogen
RMS	Root Mean Square
UV	Ultraviolet
WCA	Water contact angle
XRD	X-ray Diffraction
G	Graphene
GO	Graphene oxide
mGO	Modify Graphene Oxide
FGO	Fluorinated Graphene Oxide

LIST OF SYMBOLS

º	Degree
θ	Contact angle
γ_{SV}	Solid-vapor interface
γ_{SL}	Solid-liquid interface
γ_{LV}	Liquid-vapor interface
r	Roughness factor
f	Surface fraction
C	Celcius
rpm	Revolution per minute
%	Percentage
λ	Wavelength
kV	Kilovolt
Å	Angstrom
d.nm	Diameter in nanometer

PENYIASATAN KETAHANAN DAN PEMPBENTUKAN SALUTAN

SANGAT HIDROFOBIK BERASASKAN GRAFEN

ABSTRAK

Lapisan hidrofobik digunakan secara meluas dalam industri automotif, elektronik, perubatan, salutan cat, tekstil dan industri lain. Untuk memperluas aplikasi yang berpotensi, peralihan dari hidrofobik ke super hidrofobik yang menunjukkan sudut sentuhan air (WCA) dari 90º hingga lebih daripada 150º mesti dipertimbangkan oleh keperluannya. Fokus utama kerja ini adalah untuk meningkatkan hidrofobisiti dengan memasukkan nanopartikel ke dalam silane untuk memenuhi keperluan permukaan hidrofobik yang permukaan kasar dan tenaga permukaan yang rendah. Dalam karya ini, Graphene, Graphene Oxide dan nanopartikel graphene Oxide diubahsuai dengan gabungan Polydimethylsiloxane (PDMS) yang digunakan sebagai prekursor hidrofobik disebabkan oleh sifat-sifat bahan bukan fluorin dan juga mempunyai tenaga permukaan yang rendah. Zarah bersaiz nano didepositkan pada substrat kaca dengan kaedah penyemburan. Perbezaan zarah bersaiz nano dalam kekasaran dari analisis AFM dan kimia permukaan molekul dari analisis FTIR telah mempengaruhi kelakuan kebasahan; di mana kekasaran yang tinggi mengakibatkan sudut sentuh air (WCA) dan sudut gelangsar (SA) tinggi. G-PDMS dan mGO-PDMS mempunyai WCA sebanyak 159° dan 162°, sementara SA masing-masing adalah 30° dan 25°. GO-PDMS mempunyai WCA yang lebih rendah daripada 140° dan SA adalah 90°. Tahan ketahanan filem itu dibuktikan melalui ujian lekatan, penuaan UV dan kestabilan asid di pH 4 dan pH 10. Kertas ujian menunjukkan, G-PDMS mempunyai kestabilan yang lebih baik berbanding dengan PDMS-GO dan PDMS-mGO. Semua 3 filem mempunyai ketahanan yang lebih baik dalam persekitaran asas daripada persekitaran berasid. G-PDMS dan mGO-PDMS mempunyai ketahanan UV yang lebih baik daripada GO-PDMS.

FORMATION AND DURABILITY INVESTIGATION ON GRAPHENE-BASED SUPERHYDROPHOBIC COATING

ABSTRACT

Hydrophobic coatings are widely used in automotive, electronic, medical, paint coating, textiles and many other industries. In order to expand the potential application, transition from hydrophobic to super-hydrophobic which exhibit water contact angle (WCA) from 90º to more than 150º must be considered by its requirement. The main focus of this work is to improve hydrophobicity by incorporate nanoparticle into silane to satisfy both hydrophobic surface requirements which are rough surface and low surface energy. In this work, Graphene, Graphene Oxide and modified graphene Oxide nanoparticle was incorporate in Polydimethylsiloxane (PDMS) which used as the hydrophobic precursor due to its properties of non-fluorinated and low surface energy material. The nanoparticles were deposited on glass substrate by spraying method. The differences of nanoparticles in roughness from AFM analysis and molecular surface chemistry from FTIR analysis have influenced the wettability behaviour; whereby high roughness resulted in high water contact angle (WCA) and Sliding angle (SA). G-PDMS and mGO-PDMS has WCA of 159 º and 162º, while the SA is 30º and 25º, respectively. GO-PDMS has lower WCA of 140 º and SA is 90º. Durability of the film were eveluvated via peel off test, UV aging and acid-base stability at pH 4 and pH 10. Peel of test shows, G-PDMS has better stability compare to PDMS-GO and PDMS-mGO. All the 3 films has better durability in basic environment than acidic environment. G-PDMS and mGO-PDMS has better UV aging durability than GO-PDMS

CHAPTER 1

INTRODUCTION

1.1 Background

Hydrophobic have attracted the concern of researcher for both fundamental research and their practical applications. Hydrophobic surfaces can be fabricated by the combination of governing their topographic features and employed low surface energy material (Arkles, 2006a). Super water repellent surfaces emerge from a blend of inborn compound hydrophobicity and various leveled surface harshness. The superhydrophobic condition is characterized by high water contact angle, which is higher than 150°and relatively small sliding angle, which is lower than 5° . Coatings with high hydrophobic attributes offer ascent to natural self-cleaning, fabric protection and non-stick properties that have been applied on windows and mirrors (Simovich et al., 2015)

Hydrophobicity is the physical property that provides water repellence and non-wettability of a solid surface. Enlivened by lotus leaves, flower petals, water strides and different plants and bugs in nature (Liao et al., 2018). The surface structure of the leaves enables entrapment of air between water droplets and the surface (Ramaratnam et al., 2008). In the interim, low surface energy achieved from non-polar particles. This adds to less wetting and adherence between the water beads and the surface, therefore making a profoundly water repellent surface .

The appealing characteristic of hydrophobicity behaviour on strong surface plainly is vital and can be exploited in an assortment of application. Superhydrophobic surface coatings have become attracted because of their potential in business and

mechanical applications. Superhydrophobic coatings are portrayed by their distinctive nonadhesive and non-wetting attribute for different applications, for example, anti-icing, anti-corrosion, self-cleaning, ,low hydrodynamic rubbing, and also micro-electromechanical system (MEMS)(Golovin et al., 2017). Typically, fabricating hydrophobic textiles involve the treatment of the textile with selected low surface energy material which not affect the other properties of the textiles (Bhattcharyya, 2014).

Graphene coatings can be hydrophobic, conductive, and/or chemically resistant, and therefore have huge market potential, according to Elcora Resources Corporation, a partial owner of the Ragadera graphite mine in Sri Lanka that is working to increase the production of graphite and identify a suitable process for the commercial production of graphene. The company anticipates that hydrophobic graphene coatings will find applications where water-repellant surfaces are required, In recent years, due to the appealing hydrophobicity, graphene has been sequentially proposed to create superhydrophobic materials (Song et al., 2016).

1.2 Problem statement

Super-hydrophobic surfaces are mainly fabricated by manipulating the interface property via two ways creating a molecular-level variation of architecture to form a rough surface; terminally attaching various low surface-energy organic monolayers (ex: silane functionalizing agents) to the surface (Feng et al., 2002). These features allow water droplets to smoothly roll off from the surface (Erbil et al., 2003). The low sliding angle (SA) can be achieved by creating micro or nanostructured features, which can reduce the contact area between the surface and water droplet (Liu, 2016) . Application of ZnO (Kwak et al., 2009), TiO_2 (Jiang et al., 2015), SiO_2 (Zhang et al., 2017) , Al_2O_3 (Ioannis et al., 2012), $CaCO_3$ (Yuan et al., 2014) and SnO_2 (Manoudis and Karapanagiotis, 2014) nanoparticles could enhance the surface roughness, because aggregation of nanoparticles minimize the contact area, thus enhancing the super-hydrophobic behaviour. However, the use of graphene based materials are not well exploited although it has various superior properties such as exhibits many distinctive physicochemical properties such as high thermal conductivity, good thermal/chemical stability and exceptional mechanical modulus. Therefore the use of G, GO and mGO particles was explored in this work.

Another important aspect in fabrication of superhydrophobic surface, is the use of low surface energy materials (Liao et al., 2018). The high WCA can also be attained by lowering the surface free energy using silane functionalizing agents. The surface free energy of functional groups is in the order of $-CF3 < -CF2 < -CH3 < -CH2$, indicating fluorinated compounds are beneficial for super-hydrophobicity (de Givenchy et al., 2009) . However, the long chain fluoro silanes are expensive and toxic (Prevedouros et al., 2006) which bring potential risk to human health and environment (Xue et al.,

2014). Therefore, long chain non-fluoro silanes such as polydimethylsiloxane (PDMS) (He et al., 2012), hexadecyltrimethoxysilane (HDTMS) (Xu et al., 2015) , octadecyltrichlorosilane (ODTCS) (Li and Yoon, 2013), methyltriethoxysilane (MTES) (Latthe et al., 2010), trimethylethoxysilane (TMES) (Mohamed et al., 2015) and methoxytrimethylsilane (MTMS) (Mohamed et al., 2015) are preferred to improve the hydrophobicity. Matin et al successfully prepared a transparent and durable super-hydrophobic coating by dropping ODTCS on glass with the help of a disposable dropper. Even though WCA was attained in the range of 150° with SA< 10°, the coating method is not feasible for industrial applications (Matin et al., 2016). Similarly, Latthe et al. developed a hydrophobic coating via a two-step process using methyltriethoxysilane (MTES) and trimethylethoxysilane (TMES). WCA of 120° was achieved witha SA of 9°, however 14 h was required to complete silanization process (Latthe et al., 2010). Mahadik et al. (Mahadik et al., 2010) and Karapanagiotis et al. (Karapanagiotis et al., 2014) reported a WCA of ~170° after 24 h of deposition time using MTMS. The prolonged deposition time is economically not feasible for industrial applications. Polydimetlylsiloxane (PDMS) – SiO2 (Bravo et al., 2007) (He et al., 2012) mixture was also used to fabricate the super-hydrophobic surfaces with WCA of 140°–160° for catheters (Rosato, 1983) and microvalveswhere (Allen, 2011) self-cleaning properties are important to avoid fouling. PDMS has low toxicity, high chemical stability, mechanical elasticity, long-term endurance and attractive transparency for outdoor applications (Allen, 2011). Therefore, in this work PDMS was selected as surface functionalizing agent.

Many useful methods have been employed to fabricate super-hydrophobic surfaces on fabric such as chemical process include sol-gel (Cai et al., 2014) , aggregation or

assembly of colloids, chemical bath deposition, chemical vapour deposition, plasma treatment and electrospinning, and hydrothermal synthesis (Mahadik et al., 2013). This techniques are the most reported methods in fabricating hydrophobic surfaces However, this method is complicated and sophiscated. So, the fabrication process of superhydrophobic coating with facile spraying method is investigated. Spraying is thought to be one effective technique to create artificial superhydrophobic surfaces due to its simplicity, low-cost and low-temperature method.

The durability is one of the concerns in hydrophobic coating fabrication. There is only a few research discussed on the removal of hydrophobic coating and many research show that the durability is non-promising. Since the application of this hydrophobic is to made a superhydrophobic glass coating that have a good durability, the suitable method to remove the hydrophobic coating is required to be easily adapted.

1.3 Objectives

The main objectives of this project

1. To synthesize and analyse surface chemistry of GO prepared by Hummer method and mGO modified with TMMS versus G.
2. To fabricate G-PDMS, GO-PDMS and mGO-PDMS and investigate the roughness and wettability of the hydrophobic coating.
3. To study the durability of G-PDMS, GO-PDMS and mGO-PDMS via peel off test, UV aging and acid-base stability at pH 4 and pH 10.

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1.4 Scope of work

This project is conducted to produce graphene in different form to serve as a superhydrophobic coating. In order to achieve the desired wettability behaviour, commercial graphene is converted graphene oxide via Hummer method to break the molecular structure of graphene and let the hydroxyl group to bind with the graphene structure to become graphene oxide. After that, Graphene oxide will undergoes modification with addition of Trimethylmethoxysilane (TMMS) that have been through silanization process so that Si-OH bond will form and then will form hydrogen bonding with graphene oxide. This process resulted in modified graphene oxide. The functional group and the size of the particles were analysed via FTIR and Malvern Nanosizer. The particles were then incorporated into polydimethysiloxane (PDMS) to form superhydrophobic coating on glass substrate via spray coating. The surface morphology and roughness were analyse with FESEM and AFM while the WCA and SA were evaluated using goniometer. The durability of the film were tested via peel off test for 25 times, UV aging upto 60 hours and acid-base stability at pH 4 and pH 10 for duration of 20 Days.

1.5 Thesis Overview

This thesis is organized with five chapters consequently. Chapter 1 describes a brief introduction, problem statement, objectives, scope of worh and thesis overview. In Chapter 2 a fundamental concepts of hydrophobicity and super-hydrophobicity, surface wetting capability, Wenzel State and Cassie–Baxter state, natural and artificial super-hydrophobic surfaces, review on superhydrophobic surface fabrication by various other authors are eloborated. Chapter 3 details the experiment procedures that are used in this study. This includes the raw materials and functions, experimental procedure, and characterization techniques. This covers a brief explanation on the characterization equipment, their operation principles and sample preparation. Chapter 4 presents the experimental results and comprehensive discussion on the wettability and durability of G-PDMS, GO-PDMS and mGO-PDMS superhydrophobic film on glass substrate. Finally, Chapter 5 is devoted to the conclusions of this research work and suggestions for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This section depicts the essential idea of hydrophobic surfaces and the key in wetting properties that are important to understand non-wetting impact. This impact could provide profit headway in the engineering technology and other industry applications. This review starts with a concise discussion of the essentials of hydrophobicity, their durability and then followed by fabrication method. Material used to form superhydrophobic surface by various research is discussed.

2.2 Definition of hydrophobic and super-hydrophobicity

The concepts of hydrophobicity and superhydrophobicity are of vital importance both for fundamental purpose as well as in industrial application. Many current research about this concept have been done today. Hydrophobic and hydrophilic are frequently used descriptors of surfaces. A surface is hydrophobic if it tends not to adsorb water or be wetted by water. A surface is hydrophilic if it tends to adsorb water or be wetted by water. More particularly, the terms explained about the interaction of the boundary layer of a solid phase with liquid or vapor water (Arkles, 2006b). These different behaviours can be correlated to the surface energies of both water and solid material. The simplest explanation of hydrophilic shows robust affinity towards water, hydrophobicity is a surface having static water contact angle higher than 90º, while a super-hydrophobic surface is a surgace when a drop of water forms an almost perfect sphere and even a very slight tilting is sufficient to cause the water drop to roll off. In addition to high water contact angle and low slid- ing angle, the ability of a surface to bounce off water

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droplets constitutes the third property of a superhydrophobic surface that is important for both biological and technical applications (Subhash Latthe et al., 2012). The surface is theoretical to exhibit a contact angle higher than 150º as shown in Figure 2.1 (Nuraje et al., 2013). A hydrophopic literally fear to water or in chemistry it can be said as water repellent. It is because polar and nonpolar molecules concept . The Advantages may include decreased dirt retention, self-cleanability, improved moisture and corrosion resistance, as well as extended life expectancy of the coating and substrate (Law, 2014)
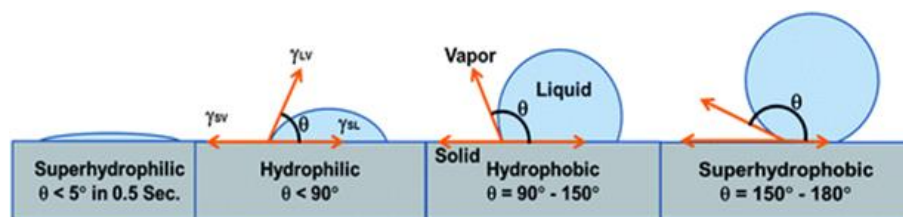
Figure 2.1: Schematic illustration showing a macroscopic contact angle of water droplet on a hydrophilic, hydrophobic and super-hydrophobic surface (Nuraje et al., 2013)

2.3 Surface wetting capability

Wettability and repellence are important properties of solid surfaces from both fundamental and practical aspects. The wettability of a solid surface is a properties of materials that dependant on both chemical composition and morphology of the surfaces. Wetting is the ability of a liquid to wet the surface, which resulted from intermolecular interactions when the two are brought together (Quéré, 2008). liquid-solid interface will show that if the liquid-solid molecular interaction is weaker than the liquid-liquid one, the cohesive forces are stronger than the adhesive forces, leading to the tendency of surface non-wetting. In contrast, if the adhesive force is stronger than cohesive force, lead to surface wetting.

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One approach to evaluate a liquid wetting ability is to measure the contact angle of a liquid droplet on an object surface (Shibuichi et al., 1996). The contact angle (CA, θ) can be defined as parameter that show the wettability of the surface base on the interaction between the solid and liquid as the angle at which the liquid-vapor interface meets the solid-liquid interface, and formed by the solid-liquid interface and the liquid-vapor interface measured from the liquid side as seen in Figure 2.1. The contact angle is determined by the resultant between adhesive and cohesive forces (Cassie and Baxter, 1944). As the tendency of a drop to spread out over a flat, solid surface increases, the contact angle decreases. Thus, the contact angle provides an inverse measure of wettability.

Table 2.1 shows the liquid contact angles and the corresponding surface wettability. The strength of interaction can be seen from the wettability. Contact angle less than 90° generally means that the surface is wettable, and the liquid can spread out over the surface. Contact angle greater than 90° (high contact angle) usually suggests

that the surface is non-wettable and the liquid minimizes its contact area with the surface to form a liquid droplet. For water, a wettable surface is alternatively described as hydrophilic surface as water is polar molecules, while a non-wettable surface usually has a nonpolar properties, which can be described as hydrophobic surface.

Table 2.1: Contact angle and the surface wettability

Contact angle (º)	Degree of wetting	Strength of		
		solid/liquid interactions	liquid/liquid interactions	Sliding angle (º)
$\theta = 0$	Perfect wetting	Stronger	Weaker	180°
$0 < \theta < 90º$	High wettability	Stronger	Stronger	> 5°
		Weaker	Weaker	
$90º \leq \theta \leq 180º$	Low wettability	Weaker	Stronger	< 5 °
$\theta = 180º$	Perfect non wetting	Weaker	Stronger	0°

2.3.1 Basic wetting on smooth surface

Further increase of the hydrophobicity requires manipulation of the surface topography. The fact that roughness can strongly affect the wetting of a surface was already discussed by Wenzel in 1936 and then by Cassie and Baxter in 1944. Figure 2.2 displays wetting behaviour for smooth surface and homogeneous surface, the features of liquid contact angle is given by Young Equation (Equation 2.1) :

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$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \qquad \text{... Equation 2.1}$$
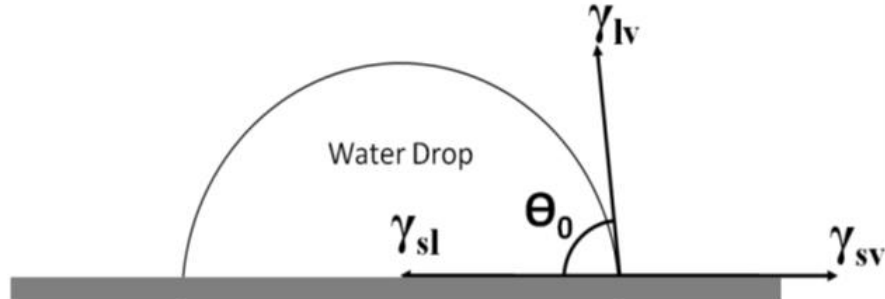
Figure 2.2: Wetting behaviour of smooth

surface

where, γ_{SV}, γ_{SL}, γ_{LV} are the interfacial tensions of the solid vapor, solid liquid and liquid vapor interfaces, respectively. There is a limitation in the application of the Young equation in that it is strictly valid only for surfaces that are atomically smooth, chemically homogeneous, and do not transform by possible interactions with the probing liquid.

According to Young Equation, the highest contact angle will be achieved by decreasing the surface free energy of the solid-air interface, γ_{SV} (Bhushan and Jung, 2011).

2.3.2 Wetting on rough surfaces - Wenzel State and Cassie–Baxter

In the Wenzel state, the drop deposited on a surface and the bottom of the drop penetrates into the asperities (Figure 2.3), the increase of the surface roughness (due to the existence of the texture) amplifies the natural hydrophobicity or hydrophilicity of the material. Thus the key parameter governing the contact angle on the same material is the solid roughness. The apparent contact angle on such rough surface can be described by the Wenzel equation:

$$\cos\theta_w = r\cos\theta \qquad \text{... Equation 2.2}$$

where the apparent contact angle, θ_w can be observe by eye or an optical microscope; and r defined as the ratio between the true surface area over the projected area, the roughness factor is always larger than 1 for a rough solid surface; is the contact angle of the corresponding smooth surface obtained by the Young's equation.
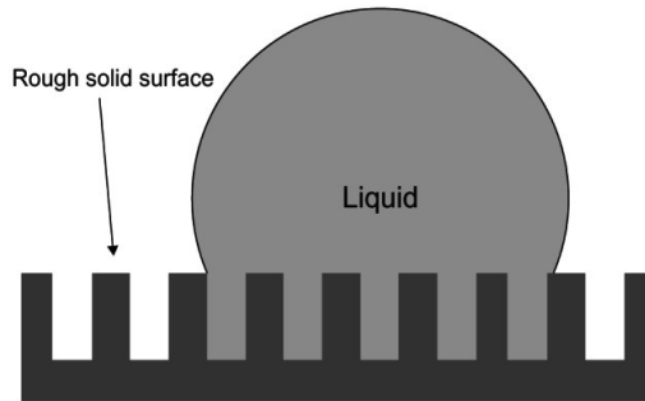
Figure 2.3: illustration of water droplet on solid surface (Wenzel model)

For a given hydrophilic surface ($< 90°$), liquid drop has lower contact angle on rough surface compared with corresponding smooth one. If the surface essentially is hydrophobic ($> 90°$), liquid drop has higher contact angle on rough surface compared with corresponding smooth one.

However, in a research reported by Papadopoulos et.al.,(2013) has found that the contact angle in Wenzel state is not always the same, if the substrate has regular periodic array. So the pillar distance is different at main axis and diagonal axis. Different of curvature at the bottom of the water drop will be inducing as the water contact line pinning at the pillars. When the drop shape asymmetry factor is decreasing, the distance from the substrate will be increase (Papadopoulos et. al., 2013). The differences in terms of WCA and TA is the higher the WCA, the lower drop shape asymmetry factoer, automatically the lower the tilted angle. The higher CAH between

the water droplet and the substrate, the higher the tilted angle as the water droplet stick to the coating surface. It can be seen at figure 2.4 below.
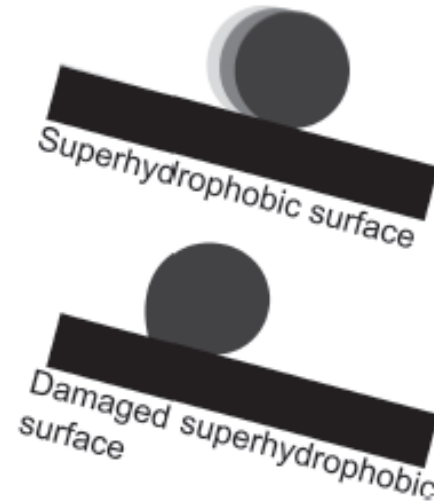
Figure 2.4 : Due to the high contact angle and low hysteresis, water droplets easily roll off superhydrophobic surfaces. However, damage to the surface often leads to an increased contact angle hysteresis and, consequently, droplets stick to the coating surface (Verho et al., 2011)

Another model that considers a roughened surface was suggested by Cassie and Baxter in 1944 (Cassie & Baxter, 1944) As the surface roughness or the surface hydrophobicity increases, it becomes unlikely for water to completely follow the surface topography of a hydrophobic substrate. The system is in a high energy state if water has a complete contact with the solid surface. Instead, Cassie-Baxter model incorporates air may be trapped between water and the surface texture (Figure 2.5).
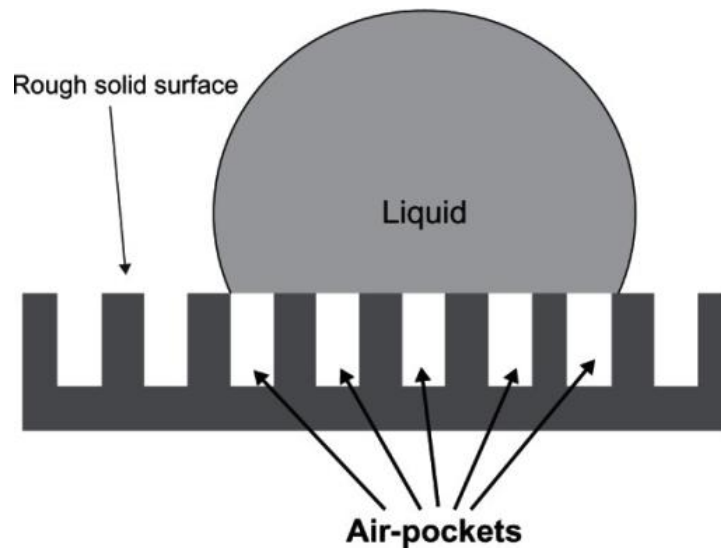
Figure 2.5 : A water drop suspended on a rough surface, with air

trapped between asperities (Cassie-Baxter model)

The apparent contact angle for this vapour-liquid-solid composite interface is the sum from all contributions of the different phase fractions as in Equation 2.3. The minimum interfacial energy, together with Young's relation applied to each solid surface, result to Cassie-Baxter relation (Equation 2.3):

$$\cos\theta_c = f_1\cos\theta_1 + f_2\cos\theta_2 \quad \dots \textbf{Equation 2.3}$$

where θ_c is the apparent contact angle, θ_1 & θ_2 and are the contact angles on two different kinds of materials; f_1 & f_2 are the surface fraction of materials 1 and 2, respectively. If the liquid would fully rest on air and close to this extreme situation, the WCA would be higher.

In summary, the Wenzel's model points that water droplet and the rough surface are contacted completely at any contact point of coverage without air trapped between the asparities, In Wenzel's model, the contact area is larger between the water droplet and the rough surface, it is difficult for a water droplet to move across the surface, so a Wenzel's surface is "sticky" which higher adhesive force. It is also challenging for a

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water droplet rolling across the rough surface. However, in Cassie-Baxter's model indicate that the water droplet and the rough surface are not contact completely, the air pockets trapped underneath, and the surface is made "slippery" which has low adhesive force. Therefore, both Wenzel and Cassie-Baxter approaches cannot be applied on a rough surface simultaneously. Transition between those two wetting states is possible, and it has been the subject of many studies, the roll-off angle and the CA on rough surfaces are different with the changes of the surface dimensions feature such as the protrusion size, height, shape and distribution. Some researchers noted that Cassie-Baxter's state is metastable, and it tends to transfer into the Wenzel's model thermodynamically. A small pressure on the water droplet is applied for the transition from the Cassie to the Wenzel approaches. Decreasing the droplet volume can induced the transition (Kavousanakis et al., 2015).

A transition between Wenzel and Cassie is the intermediate situations which we can call it as Revised model. In reality, surfaces often exhibit wetting behaviour of Revised models with partial liquid penetration on the rough structure. Studies also have shown how transitions between the two states clearly defined are possible, for example, simply shifting the method with which the droplet is added to the surface or by increasing the amount of ethanol in a water/ethanol mixture. Revised model happened caused by the decrease of surface tension of water droplet under high temperature (Li et al., 2013). Another method is to put physical pressure on the droplet while it rests on the surface. Clearly, the activation energy for transition between the states is low enough for this to occur (Bussonniè et al., 2017). The water droplet shape model have been show below in the figure 2.6

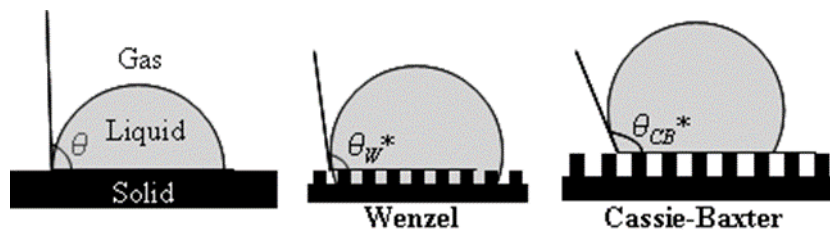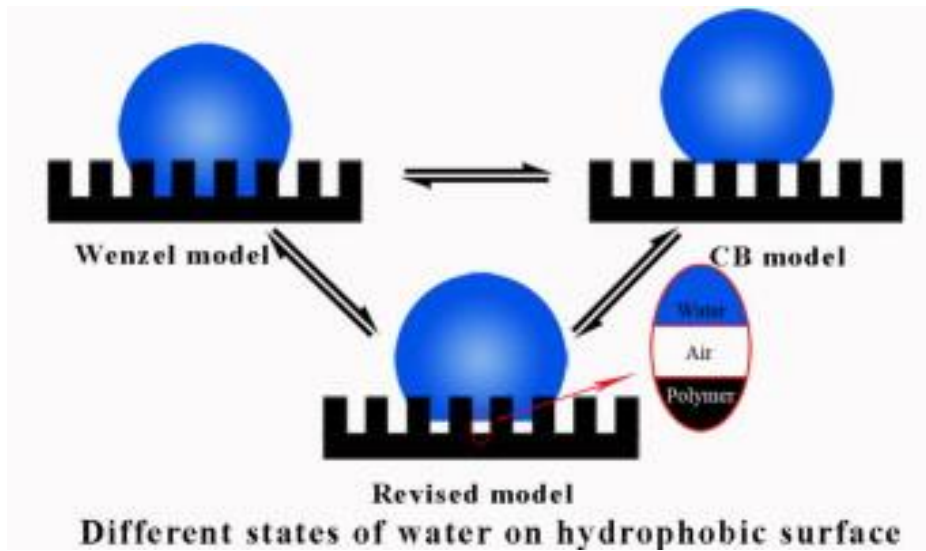Figure 2.6 : Four different wetting cases. 1) Young's model, 2) Wenzel model,

3) Revised model and 4) Cassie-Baxter model.

Table 2.2 : The model of the water droplet shape, their WCA and TA

Model	TA	WCA
Young	$> 5°$	$\theta = 0$
Wenzel	$> 5°$	$0 < \theta < 90°$
Cassie-baxter	$< 5°$	$90° \leq \theta \leq 180°$
Revised	$> 10°$	$90° \leq \theta \leq 150°$

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2.4 Natural and artificial superhydrophobic surfaces

2.4.1 Natural superhydrophobic surfaces

The nature of super-hydrophobic surfaces is originally drawn from the inspiration of lotus leaves in nature. Therefore, the very robust water repellence (super-hydrophobicity) and the self-cleaning properties exhibited by the lotus leaves that have been referred as "lotus effect". This interesting phenomenon has triggerd comprehensive research to make artificial super-hydrophobic surfaces for many application.

Natural superhydrophobicity has recently gained much attention and inspired mimetic attempts. In many plants, notably the Lotus flower. It is a species which usually grows in shallow waters and swamps in eastern Asia. It is noticed that the leaf surface is very rough with 5-10μm protrusions and valleys, which are covered by around 100 nm nano-meter sized particles of a hydrophobic material. It leaves utilize superhydrophobicity as the basis of a self-cleaning mechanism: water drops completely roll off the leaf, carrying undesirable particulates. Possible man-made applications range from nanochips to self-cleaning windows. To turn a hydrophobic surface into a superhydrophobic one, its surface must be made rough in a way that is just beginning to unravel.

The water CA and sliding angle of Lotus leaf are around 164° and 3° respectively (Koch et al., 2008). The super-hydrophobicity of Lotus leaf is based on the epicuticula wax secreted by leaf itself. The CA of the epicuticula wax is about 110°, which provides a low surface free energy. It has been found that both epicuticula wax

and surface roughness contribute to the super-hydrophobicity of Lotus leaf. Figure 2.7 show SEM images of Lotus leaf with hierarchical structures.
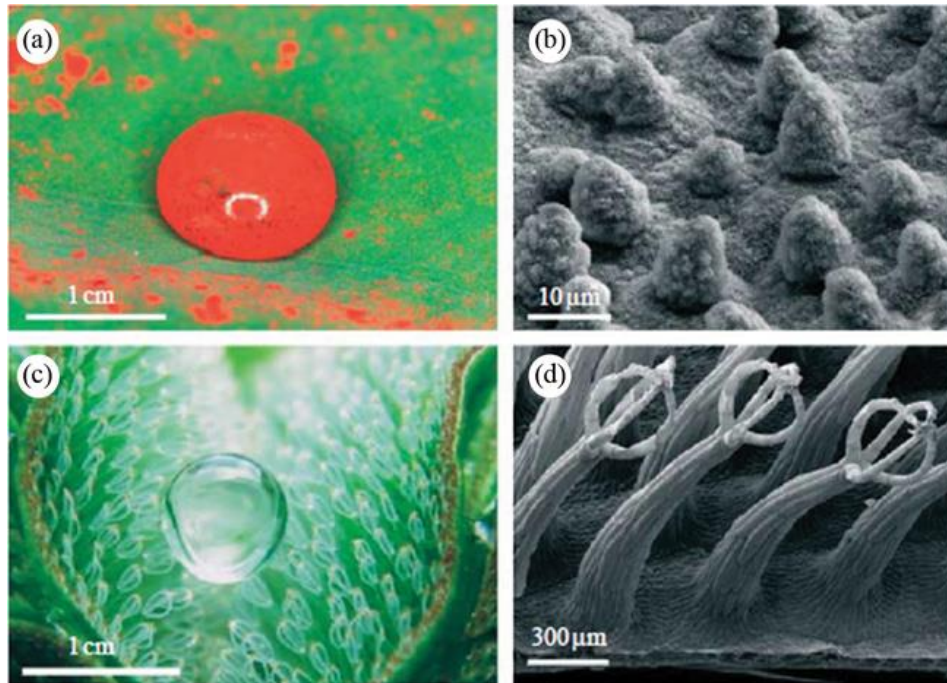
Figure 2.7 : (a- b) Superhydrophobic and self-cleaning leaves of the lotus and (c-d) the superhydrophobic and air-retaining leaves of the water fern Salvinia biloba. In (a) the lotus leaf has been contaminated with dirt of Sudan red; a water droplet rolling over the surface collecting these lipoidic contaminations is shown. (c) The microstructure of the lotus leaf, with its papilla cells and a dense covering of epicuticular wax tubules, is shown. (d) The large hairs on the leaves of the water fern genus Salvinia are multicellular and form a crown-like nano-structure, shown in the SEM micrograph (Cohen et al., 2016)

2.4.2 Artificial Superhydrophobic surfaces fabrication

Since studies on natural plant leaves showing super-hydrophobic properties indicate the importance of the surface morphologies for constructing the super-hydrophobic surfaces with hierarchical unitary structure. When a rough surface has a low surface free energy, it tends to have an enhanced hydrophobicity. Therefore, the principle to realise super-hydrophobicity has been based on a rough surface with a low free energy. In the last decades, fabrication of artificial super-hydrophobic surface has been extensively studied with the combination of nanoparticles incorporate in low surface energy material.

2.4.2.1   Silane coupling agent

Silane are silicon material that can react with inorganic substrate to form stable covalent and organic substitution that alters the physical interactions of treated substrate. They are commercially applied to the surface of inorganic substrate to improve water repellence, added to organic fillers to improve dispersibility in organic polymer and used for surface modification of inorganic materials. Silane are available in range of fluoroalkyl-substituted silanes and non-fluorinated alkyl silane.

A silane that contains at least one carbon-silicon bond (Si-CH$_3$) structure is known as an organosilane. The basic organosilane molecular structure [X-R-Si(OR')$_3$] consists a nonreactive group (X) or organofunctional group which is a non-hydrolyzable such as alkyl or amino. The alkoxy group (OR') such as methoxy and ethoxy are hyrolyzable group which reacts and provide linkage with inorganic or organic substrate. Meanwhile, spacer (R) can be either an aryl or alkyl chain. The good wetting properties

enhance by silicon-carbon bond (Si-CH$_3$) which is very stable and non-polar, also with the presence of Si-alkyl group which ensures low surface energy and hydrophobic effects (De Buyl, 2007). Table 2.3 shows intrinsic WCA of various silane group on smooth surface and widely used in fabricating hydrophobic surface especially for textile.

Table 2.3: WCA of various silane group

Silane group	WCA (^{o})	Surface energy (mJ/m^2)
Polydimethylsiloxane (PDMS)	116	15.7
Poly(tetrafluoroethylene)	110	18.5
Poly(propylene)	108	31.0
Poly(ethylene)	103	33.0
Poly(styrene)	94	34.0

Common surface treatment are fluorinated compounds such as Heptadecafluorodecyltriethoxysilane and Poly (tetrafluoroethylene) has fluoroalkyl substituents with vary structure were employed due to longer straight-chain of fluoroalkyl substituents and attached to the siloxane backbone. Methyl-substituted alkylsilanes and fluorinated alkylsilanes provide better hydrophobic surface treatments than linear alkyl silanes which beneficial for the enhancement of water-repellency (Arkles, 2006a). This is because in order to generate a hydrophobic surface the organic substitution of the silane must be nonpolar, more subtle distinctions can be made. The hydrophobic effect of the organic substitution can be related to the free energy of transfer of hydrocarbon molecules from an aqueous phase to a homogeneous hydrocarbon phase. In terms of van der waals interaction, the entities that present

sterically closed structures that minimize van der Waals contact are more hydrophobic than open structures that allow van der Waals contact (Arkles, 2006b).

Since fluorinated compound have potential risk for human health and environment due to fluorine-containing molecule, development of eco-friendly non-fluroalkyl has been done in recent research, according to EPA Much evidence suggesting that the inclusion of fluoride in drinking water has beneficial as well as adverse effects on human health was obtained. So, lowering surface energy by non-fluorinated compound with long chain hydrophobic silane like polydimethylsiloxane (PDMS), is the one of the effective methods in research nowadays (Wankhede et al., 2013).

Based on the literature studies, the use of Polydimethylsiloxanes (PDMS) has higher water contact angle compared to the other silane types used to modified hydrophobic surface. PDMS was usually used as low surface energy material to replace the fluorine material in fabricating hydrophobic surface due to its linear repeating monomer $[SiO(CH_3)_2]$ as in Figure 2.8. Chemically, the structure presents methyl (CH_3) moieties at its surface, rendering it hydrophobic and making it an ideal substrate for creating a super-hydrophobic surface. Moreover, the properties of non-toxic, optical transparency, and high thermal stability of PDMS has allow the products to be applied in various areas (Stanton et al., 2012).
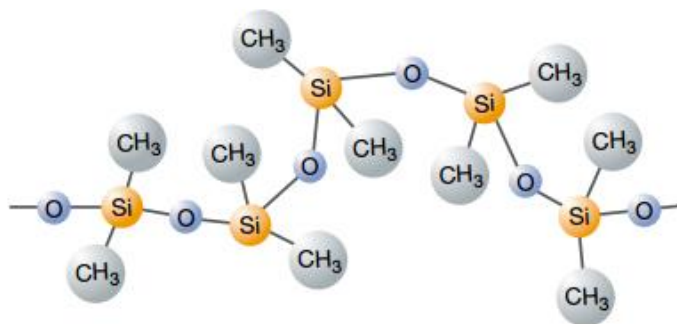
Figure 2.8: Chemical structure of Polydimethylsiloxanes (PDMS)

2.4.2.2   Mechanism of organosilane on substrate

The mechanism of organosilane in any application are involved the silane molecules to undergo hydrolysis and condensation reactions. Silane coupling agents react with water in hydrolysis process to form silanol groups and oligomers are formed through partial condensation. The silanol oligomers then create hydrogen bond to the surface of the substrate which are inorganic or metallic materials. Finally, the inorganic materials put through a drying process and robust chemical bonds are formed through a dehydration condensation reaction as illustrated in Figure 2.9. When a silane coupling agent is used for surface treating an inorganic material, it will to promote adhesion between the inorganic material and organic materials .Example of inorganic material such as glass, glass is composed of silica, soda, lime and also impurities that are usually mineral salts (Speight, 2017). Silane will acts by improving the wettability and compatibility with the substrate. Apart from that, some researcher has discover the superhydrophobic coating using PDMS with silica nanoparticles has shown the great adhesion of glass substrate (Saharudin et al., 2018). Therefore, later work polydimethylsiloxane (PDMS) was used in this project.
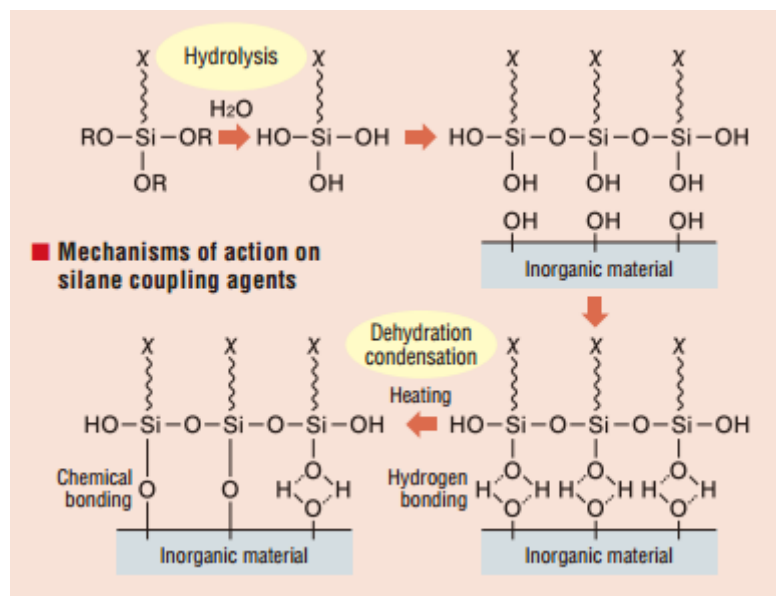
Figure 2.9: The mechanism of silane coupling agent to an inorganic substrate (Arkles, 2006c)

2.4.2.3   Nanoparticles incorporate in silane

Another approached in order to create hydrophobicity is by addition nanoparticles which provide a nano-roughness surface (Khanna, 2015). In order to achieve the hydrophobic properties, the substrate must have optimum texture roughness, mimicking a "lotus leaf" structure. Some researchers have conclude that the key of surface roughness are depends on different structure, different scale either in micron or nano and also types of particles for its application.

In recent decades, coating with super-hydrophobic property has been studied intensively. Researches have made significant progress for many applications in the industry. These are summarized in Table 2.4. As seen application of ZnO, TiO2, SiO2, CNT, Fluorinated GO nanoparticles could enhance the surface roughness, because aggregation of nanoparticles minimize the contact area, thus enhancing the super-