SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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INVESTIGATION OF SUBMICRON PARTICLES INCORPORATE IN SILANE TO IMPROVE HYDROPHOBICITY WITH THE POTENTIAL APPLICATION IN BATIK INDUSTRY

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **"Investigation of Submicron Particles Incorporated in Silane to Improve Hydrophobicity with the Potential Application in Batik Industry"**. 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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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscope
Ag	Silver
APTMS	(3-Aminopropyl)trimethoxysilane
BOD	Biochemical Oxygen Demand
C	Carbon
$CaCO_3$	Calcium carbonate
CVD	Chemical Vapor Deposition
DMDEOS	Dimethyldimethoxysilane
FAS	Fluoroalkylsilane
FESEM	Field Effect Scanning Electron Microscope
FTIR	Fourier Transform Infrared
HDTMS	Hexadecyltrimethoxysilane
HMDS	Hexamethyldisilazane
HMT	Hexamethylenetetramine
KOH	Potassium hydroxide
ICDD	International Centre for Diffraction Data
MTMS	Methyltrimethoxysilane
O	Oxygen
OTES	Octyltriethoxysilane
PDMS	Polydimethylsiloxane
pH	Potential of hydrogen
PTMS	Phenyltrimethoxysilane

PVP	Polyvinylpyrrolidone
RMS	Root Mean Square
RTV	Room Temperature Vulcanized
Si	Silicon
SiO_2	Silicon dioxide
TEOS	Tetraethylorthosilicate
TiO_2	Titanium dioxide
UV	Ultraviolet
WCA	Water contact angle
XRD	X-ray Diffraction
Zn	Zinc
ZnO	Zinc 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
cm	Centimeter
µm	Micrometer
nm	Nanometer
C	Celcius
rpm	Revolution per minute
min	Minute
h	Hour
g	Gram
ml	Mililiter
%	Percentage
λ	Wavelength
kV	Kilovolt
Å	Angstrom

KAJIAN GABUNGAN SUBMICRON PARTIKEL DALAM SILANA UNTUK MENINGKATKAN SIFAT HIDROFOBIK DENGAN POTENSI APLIKASI DALAM INDUSTRI BATIK

ABSTRAK

Lapisan hidrofobik banyak digunakan dalam industri automatif, elektronik, perubatan, salutan cat, tekstil dan pelbagai industri lain. Fokus utama dalam projek ini adalah untuk memperbaikikan sifat hidrofobik dengan menggabungkan partikel ke dalam silana bagi memenuhi kedua-dua keperluan permukaan hidrofobik iaitu permukaan yang kasar dan tenaga permukaan rendah. Dalam projek ini, partikel zink oksida (ZnO) telah digabungkan ke dalam Polydimethylsiloxane (PDMS) yang digunakan sebagai pelopor hidrofobik kerana ciri-cirinya yang tidak fluorin dan bahan permukaan tenaga rendah. Partikel telah didepositkan ke atas substrat kain melalui kaedah penyalutan celup. Kesan daripada komposisi dan morfologi ZnO partikel yang berbeza pada kebolehbasahan telah menunjukkan peningkatan sudut sentuhan air hingga 144º dengan morfologi ZnO kepingan berkomposisi 0.10 g. Pelbagai penyelidikan telah dijalankan dalam beberapa dekad dalam mewujudkan tekstil kalis air. Namun, aplikasi hidrofobik bagi menggantikan lilin parafin dalam pembuatan batik masih belum diterokai. Larutan silikon (SS) yang diekstrak daripada abu kepala sawit telah ditambah ke dalam larutan PDMS/ZnO untuk merumuskan larutan yang mempunyai sifat yang sama dengan lilin parafin. Komposisi terbaik PDMS/ZnO/SS iaitu 30PZF:70SS telah mencapai sudut sentuhan air sehingga 146º dan menunjukkan hidrofobik yang baik dengan menghalang penembusan pewarna. Justeru itu, bagi projek ini, aplikasi hidrofobik untuk menggantikan lilin paraffin telah berjaya difabrikasi dan mempunyai sudut sentuhan air yang hampir dengan superhidrofobik

($>150^{\circ}$). Kaedah yang mudah untuk menyingkirkan lapisan hidrofobik juga dicapai dengan merendam ke dalam larutan penimbah pH 4 dan 10 selama 48 jam.

INVESTIGATION OF SUBMICRON PARTICLES INCORPORATE IN SILANE TO IMPROVE HYDROPHOBICITY WITH THE POTENTIAL APPLICATION IN BATIK INDUSTRY

ABSTRACT

Hydrophobic coatings are widely used in automotive, electronic, medical, paint coating, textiles and many other industries. 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, zinc oxide (ZnO) particle was incorporate in Polydimethylsiloxane (PDMS) which used as the hydrophobic precursor due to its properties of non-fluorinated and low surface energy material. The ZnO particles were deposited on cloth substrate by dip-coating method. The effect of ZnO particles amount and different morphology on wettability has shown that ZnO flake particles with composition of 0.10 g have improved the WCA up to 144º. Various research has been directed in several decades towards the creation of water repellent textiles. However, application of hydrophobic barrier to replace paraffin wax in batik making has not been explored yet. Silica solution (SS) which extracted from oil palm ash were added into PDMS/ZnO hydrophobic solution to formulate solution that have similar properties to paraffin wax. 30PZF:70SS is best composition of PDMS/ZnO/SS which has exhibit WCA up to 146º and demonstrated good hydrophobic barrier by resisting dye penetration. Therefore, in this project, application of hydrophobic to replace paraffin wax was successfully fabricated and exhibit WCA nearest to exhibit super-hydrophobic (>150º). Simple method to remove the hydrophobic also achieved by immersed the hydrophobic coating into buffer solution with pH 4 and 10 for 48 hours also discovered.

CHAPTER 1

INTRODUCTION

1.1 Background

Hydrophobic surface properties such as self-cleaning, anti-wetting, anti-microbial and anti-corrosion 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. The term of hydrophobic defines the interaction of the boundary layer between solid phase with liquid or vapor water. Traditionally, a hydrophobic surface is a surface that has the ability not to absorb water or be wetted by water. Theoretically, surface with water contact angle (WCA) is larger than 90° describe as hydrophobic surface. In contrast, super-hydrophobic surfaces have a water contact angle greater than 150º and shows a minimal contact angle between the water droplet and the substrate (Arkles, 2006).

Hydrophobicity is the physical property that provides water repellence and non-wettability of a solid surface. The hydrophobic coating has been achieved in many ways with different kinds of materials by mimicking the surface roughness of lotus leaves and low surface energy. The surface structure of the leaves enables entrapment of air between water droplets and the surface (Ramaratnam et al., 2008). Meanwhile, low surface energy attained from non-polar molecules. This contributes to less wetting and adherence between the water droplets and the surface, thus creating a highly water repellent surface.

The attractive features of hydrophobicity behaviour on solid surface clearly is very important and can be exploited in a variety of applications including in electronic, medical, paint coating, textiles and many other industries. Self cleaning glass, anti-corrosion coatings and waterproof textiles are some of the potential areas for its application (Yazdanshenas and Shateri-khalilabad, 2013). Typically, fabricating hydrophobic textiles involve the treatment of the textile with selected low surface energy material purposely to prevent properties changes of the textiles (Bhattcharyya, 2014).

Various research has been directed in several decades towards the creation of textiles which are water repellent, dust resistant and anti-bacterial. However, its application as a hydrophobic barrier to replace paraffin wax in batik making has not been explored yet. Research in substituting paraffin wax is essential to reduce large volume of solid suspended discharge from paraffin wax that cause clogging issue on batik waste water treatment system.

Perceiving impacts of batik process to environment, it is time to seizure this problem by decreasing the amount of suspended solid that had been discharged to the river (Nordin and Bakar, 2012). Due to the presence of wax in batik wastewater during the batik production process, a substitute material to replace paraffin wax is necessary to reduce the discharge quantity of solid suspended into river. The wax patterning technique can inspire by new technique of developing hydrophobic barriers from selected low surface energy materials. This alternative in replacing paraffin will give significant impact in lowering the water pollution statistic comes from batik industry.

1.2 Problem statement

In the fabrication of hydrophobic surface, two major factors must be considered which are low surface energy and surface roughness (Latthe et al., 2014). Surface nano roughness dependent on the size and the morphology of particle. Nevertheless, limited research reported on the effect of different morphology wettability behaviour.

In current research, employed of fluroalkysilane (FAS) is preferable because it can provide better hydrophobic surface treatments than linear alkyl silanes which beneficial for the enhancement of water-repellency. However, FAS has adverse affect to human health and environment due to fluorine-containing molecule. Development of eco-friendly non-fluroalkyl with excellent hydrophobic properties must be discover.

Textile wastewater is rated as the most polluting among all in the industrial areas. Textile wastewater contents of complex and variable combination of polluting substances such as inorganic, organic, elemental and polymeric products (Kusumastuti, 2016). In 2014, The Compendium of Environment Statistics (CES) had presented the statistic on status of river water quality status based on main pollutants. Suspended solid also one of the components that contribute to the water pollution, besides Biochemical Oxygen Demand (BOD) and Ammonium Nitrogen. This situation has lead about 29.3% that cause water pollution in Malaysia (Ho Mei Kei, 2015). The environmental issue caused by batik wastewaters has led to the death of flora and fauna. Usually individual that involved in batik industry and exposed to hot wax usually will face health problems like allergic, sensitive and itchy skin effected by colouring and batik waxes (Yaacob et al., 2016). This problem requires innovative solutions to replace the usage of wax as hydrophobic agent. This study will explore the hydrophobic coating potential application in batik making.

In the finishing process of batik making, all the wax that has been applied was remove. However, there is only a few research discussed on the removal of hydrophobic coating. Since the application of this hydrophobic is to replace the paraffin wax in batik making, the suitable method to remove the hydrophobic coating is required to be easily adapted in the batik industry.

1.3 Objectives

The main objectives of this project

1. To investigate effect of morphology on wettability by synthesis ZnO particles with different morphology.
2. To formulate hydrophobic coating based on Polydimethylsiloxane (PDMS), hexane, silica solution and ZnO particles with different shape and concentration.
3. To study the properties of optimum hydrophobic coating by measuring water contact angle (WCA), atomic force microscopy (AFM), Fourier Transform Infrared Spectroscopy (FTIR) analysis, UV aging, acid-base stability and explore the potential application of the hydrophobic coating to replace wax in batik industry.

1.4 Thesis Overview

This thesis is organized with five chapters consequently. Chapter 1 describes a brief introduction, problem statement and objectives of the research. Chapter 2 a comprehensive review on the formation of hydrophobic solution, fundamental concepts of hydrophobic and functional applications of hydrophobic coating are discussed. Chapter 3 details the experiment procedures that are used in this study. This includes the experimental design, synthesis of hydrophobic solution 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 synthesized superhydrophobic coating solution. 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 chapter describes the basic concept of hydrophobic surfaces and the fundamental in wetting properties that are necessary to understand non-wetting effect. This effect could provide benefit advancement in the engineering technology and other industry applications. This review begins with a brief discussion of the fundamentals of hydrophobicity and then followed by fabrication method. Current available materials of creating hydrophobic surface will be discussed. Finally, potential applications of hydrophobic surface also have been elaborated.

2.2 Definition of hydrophobicity and super-hydrophobicity

The concepts of hydrophobicity and super-hydrophobicity are of vital importance both for fundamental purpose as well as in industrial applications. Interest in this type of surface property has grown substantially during the past years to understanding of the criteria for forming hydrophobic surfaces and recognition of its potential as liquid barrier in different applications. Solid surfaces are often defined in terms of hydrophilicity or hydrophobicity which describes the materials ability to be wet by water. A surface which is easily wet by water is referred to as hydrophilic while a surface which is unwettable is considered to be hydrophobic. These different behaviours can be correlated to the surface energies of both the water and the solid material. The simplest explanation of hydrophilic shows robust affinity towards water, hydrophobicity is a surface having static water contact angle higher than 90^{o}, while a super-hydrophobic surface is theoretical to exhibit a contact angle higher than 150^{o} as shown in Figure 2.1 (Nuraje et al., 2013).

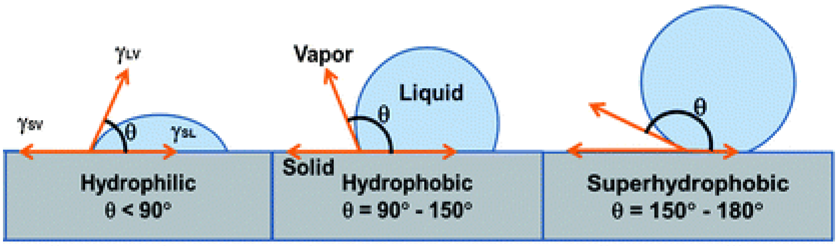

Figure 2.1: Schematic illustration showing a macroscopic contact angle of water droplet on a hydrophilic, hydrophobic and super-hydrophobic surface (Nuraje et al., 2013)

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 distinguishing property of materials and depends strongly on both the surface energy and roughness. Wetting is the ability of a liquid to freely wet a solid surface, which resulted from intermolecular interactions when the two are brought together (Quéré, 2008). At the liquid-solid interface, if the liquid-solid molecular interaction is stronger than the liquid-liquid one, the adhesive forces are stronger than the cohesive forces, leading to surface wetting. In contrast, if the cohesive forces are stronger than the adhesive forces and the liquid tends to bead-up, not wetting the solid surface.

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) is defined 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. 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, while a non-wettable surface is described as hydrophobic surface.

Table 2.1: Contact angle and the surface wettability

Contact angle ($\boldsymbol{\theta}$)	**Degree of wetting**	**Strength of**	
		solid/liquid interactions	**liquid/liquid interactions**
$\theta = 0$	Perfect wetting	Stronger	Weaker
$0 < \theta < 90^o$	High wettability	Stronger	Stronger
		Weaker	Weaker
$90^o \leq \theta \leq 180^o$	Low wettability	Weaker	Stronger
$\theta = 180^o$	Perfect non wetting	Weaker	Stronger

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) :

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \qquad \text{... Equation 2.1}$$

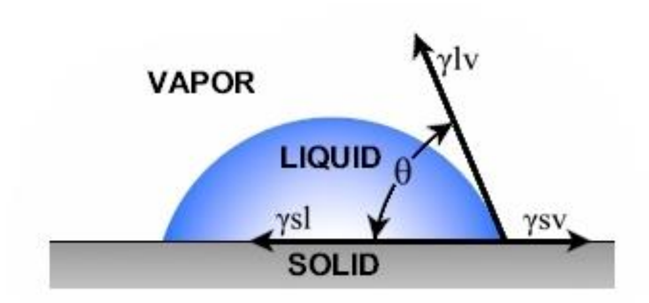

Figure 2.2: Wetting behaviour of smooth surface

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 - the 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:

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

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.

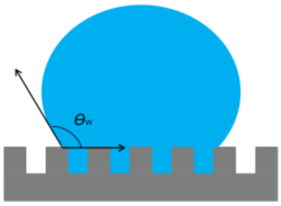

Figure 2.3: Sketch of water drop on a rough surface (Wenzel model)

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).

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 2.4).

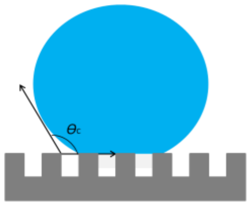

Figure 2.4: A water drop suspended on a rough surface, with air trapped between asperities (Cassie-Baxter model)

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):

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

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 them, 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". It is also challenging for a 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, there are air pockets trapped underneath, and the surface is made "slippery". Therefore, both Wenzel and Cassie-Baxter approaches cannot be applied on a rough surface at the same time. 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 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. In reality, surfaces often exhibit wetting behaviour intermediate to those of the Wenzel and Cassie-Baxter 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. 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).

2.4 Natural and artificial super-hydrophobic surfaces

2.4.1 Natural super-hydrophobic 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 stimulated extensive research to make artificial super-hydrophobic surfaces and use them for variety of applications.

Lotus leaf is a classic example among naturally displaying super-hydrophobic surfaces, 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. 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 2.5 show SEM images of Lotus leaf with hierarchical structures.

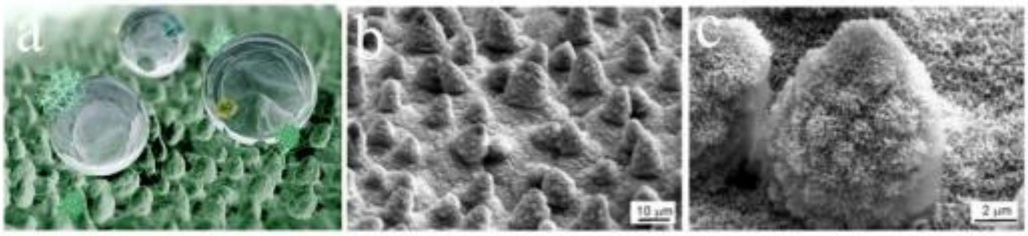

Figure 2.5: a) Sphere like water droplets on a non-wettable lotus leaf. (b) low and (c) high magnification SEM images of the structure on the lotus leaf (Koch et al., 2008).

2.5 Super-hydrophobic 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.

2.5.1 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 2.2 shows intrinsic WCA of various silane group on smooth surface and widely used in fabricating hydrophobic surface especially for textile.

Table 2.2: WCA of various silane group

Silane group	WCA (º)
Polydimethylsiloxane (PDMS)	116
Heptadecafluorodecyltriethoxysilane	115
Poly(tetrafluoroethylene)	110
Methyltrimethoxysilane (MTMS)	110
Hexamethyldisilazane (HMDS)	99
Dimethyldimethoxysilane (DMDEOS)	93
Phenyltrimethoxysilane (PTMS)	84
Octyltriethoxysilane (OTES)	70

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, 2006).

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. 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 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 2.6. 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).

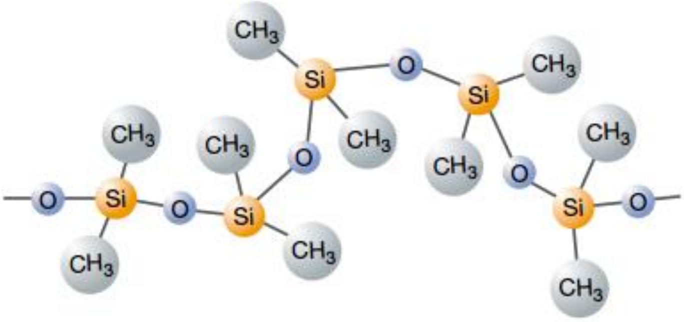

Figure 2.6: Chemical structure of Polydimethylsiloxanes (PDMS)

2.5.1.1 Mechanism of organosilane on substrate

The mechanism of organosilane in any application are involed 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 illustatrated in Figure 2.7. 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. Silane will acts by improving the wettability and compatibility with the substrate.

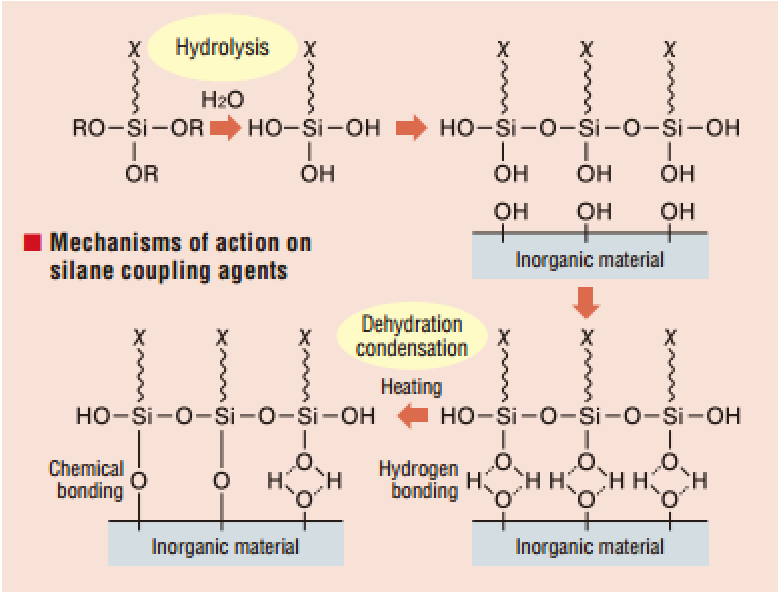

Figure 2.7: The mechanism of silane coupling agent to an inorganic substrate

2.5.2 Nano/micro-particles incorporate in silane

Another approach in order to create hydrophobic surface was achieved by addition of nanoparticles which provide a nano/micro-roughness surface (Khanna, 2015). In order to achieve the hydrophobic properties, the substrate must have optimum texture roughness. 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 2.3 consists of research nanoparticles incorporate in silane on different types of substrate and method. Nanoparticles addition is to enhance the surface roughness, thus leading to a significant increase in contact angle and hence achieve super-hydrophobic surface. Despite of employing various types of nanoparticles, particles size embedded in silane also important to provide surface roughness.

Table 2.3: Silane group with different nano/micro-particles

Silane group	Nano particles	Particle size (nm)	RMS roughness (nm)	Substrate	Method	WCA (º)	Reference
PDMS	Modified silica	N/A	N/A	Fabric	Dip-coating	171	(Zhou et al., 2012)
PDMS	$CaCO_3$	100-200	76.5-354	Glass	Spray	120-160	(Yuan et al., 2014)
Hexadecyltrimethoxysilane (HDTMS)	Ag	53	N/A	Fabric	Dip-coating	158	(Shateri-Khalilabad et al., 2013)
Hexadecyltrimethoxysilane Led	Ag	100-300	N/A	Fabric	Dip-coating	157.3	(Xue et al., 2012)
OTES, Tetraethyl orthosilicate (TEOS)	Silica	100	N/A	Fabric	Sol-gel, Dip-coating	156	(Liu et al., 2014)
PDMS	ZnO	14	N/A	Glass	Spray	155	(Chakradhar et al., 2011)
HDTMS	Silica	N/A	N/A	Fabric	Sol-gel, dip-coating	154.9	(B. Liu et al., 2015)
Poly(tetrafluoroethylene)	Modified silica	20-30	N/A	Glass	Spray	154	(Basu and Dinesh Kumar, 2011)
APTMS	Ag	30-80	N/A	Fabric	Dip-coating	153.2	(Guo et al., 2013)
MTMS	Silica	7-40	1100-2200	Glass	Sol-gel, spin-coating	153	(Cho et al., 2010)

OTES, TEOS	Silica	88	38.5	Fabric	Dip-coating	152.8	(Yazdanshenas and Shateri-khalilabad, 2013)
Hexadecyltrimethoxysilane	Silica	30-200	N/A	Fabric	Sol-gel, dip-coating	145-152	(Xu et al., 2011)

Therefore, from the summary of recent research shows that silane incorporate with nanoparticle exhibit higher WCA compared to WCA of intrinsic silane. Thus, in order to possess super-hydrophobicity properties, introduce of nanoparticles are required to provide nano roughness on the substrate. Sol-gel method with dipping technique is the most preferable method to fabricate super-hydrophobic surface due to low cost and high homogeneity which lead to transparent coating.

2.5.2.1 Nanostructure surface roughness

Although it is certain that surface energy is one of important factors which determines surface wettability, superhydrophobic cannot be obtained only by lowering the surface energy. In superhydrophobic surface, surface roughness plays a crucial role because air trapping in the surface roughness drastically amplifies surface hydrophobicity. Hierarchical surface roughness is especially effective to make surface superhydrophobic. Some nanoparticles such as those based on SiO_2, ZnO, $CaCO_3$ and Ag can be applied to the surface of substrates to produce roughness in the micro or nano scale.

In fabrication of transparent hydrophobic glass, SiO_2 are preferable because of because of its low cost and particularly has high visible transmittance properties. However, in the present study, textile industry focused on ZnO based-fabric possesses excellent properties of antibacterial activities and UV protection. Also, ZnO has probably the richest family of structures morphology as shown in Figure 2.8 including rods, flakes, whiskers and tube. Moreover, morphology influences other properties such as wettability, another significant characteristic of ZnO covered surfaces bringing great advantages in a wide variety of applications in industry (Li et al., 2017).

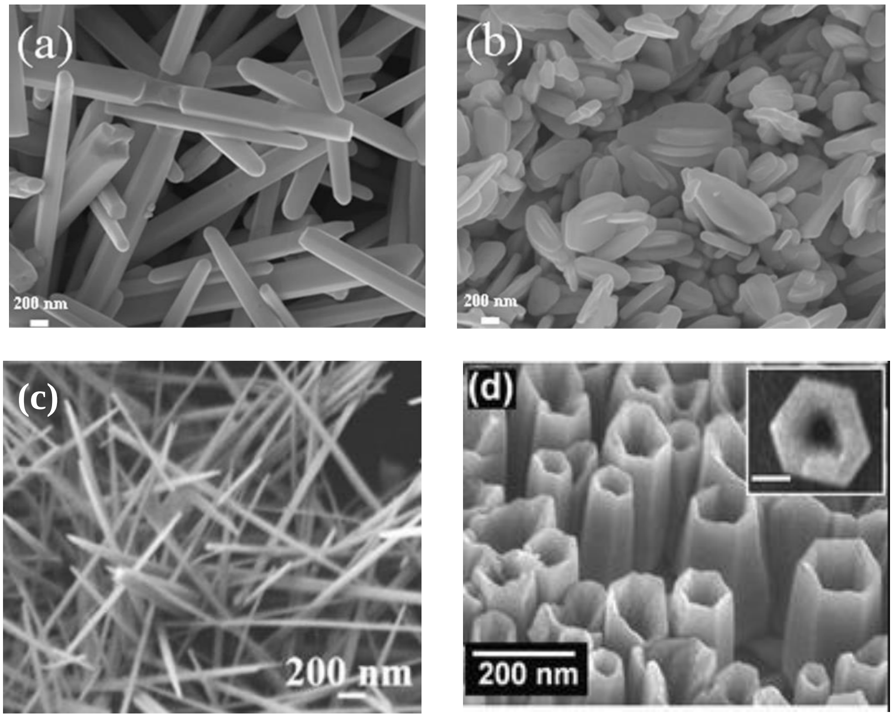

Figure 2.8: ZnO various morphology (a) rods, (b) flakes, (c) whiskers and (d) tubes

Nanoparticles size, shape and composition may influence the wetting behaviour. Most research study on the size and composition that contribute to RMS (root mean square) roughness. However, limited understanding towards the effect of nanoparticles shape on wetting behaviour. In a research by Ramaratnam et al. (2008), a variety of rough surface were created on the model silicon wafer substrate using different dilution rates of the silica nanoparticles of approximately 150 nm size. The RMS values were plotted against WCA data as shown in Figure 2.9 has identified the RMS values that give the highest WCA. For nano-level roughness, this RMS value was chosen as the empirical optimum value. As observed in Figure 2.9, the optimum RMS value was found to be around 40 to 50 nm in order to achieve WCA between 117º to 128º.

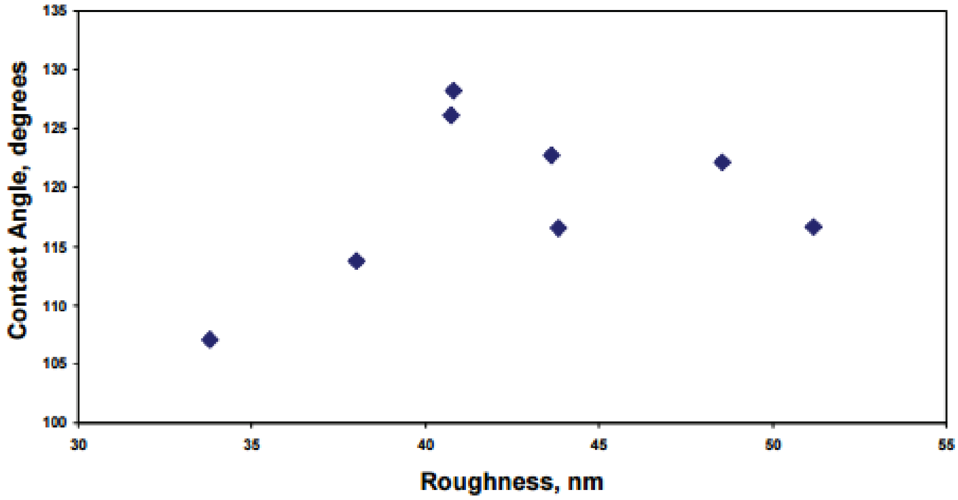

Figure 2.9: WCA against RMS roughness plot of silicon wafer modified with silica nanoparticles (Ramaratnam et al., 2008)

2.5.3 Wet chemical process

Many elegant methods have been employed to fabricate super-hydrophobic surfaces on fabrics. The most common synthesis techniques to construct rough coatings for the formation of hydrophobic materials using wet chemical process include sol-gel, aggregation or assembly of colloids, chemical bath deposition, chemical vapour deposition, plasma etching and electrospinning. For the coating methods, dip-coating and spray methods are the most reported methods in fabricating hydrophobic surfaces. The fabrication process and coating techniques describe also has their requirement and durability properties as shown in Table 2.4.

Table 2.4: Common techniques to construct hydrophobic coating

Process/Method	Time scale and requirement	Properties
Sol-gel process	Moderate	Transparent and homogeneous nanoparticles deposition

Assembly of colloids	Slow	Double-surface roughness and low transparency
Chemical bath deposition	Slow and temperature requireemnt	Moderate durability
Chemical vapor deposition	Slow and need heating	Separation of oil or organic contamination from water
Plasma etching process	Moderate and require specific equipment	Sellf-cleaning
Electrospinning	Slow and solvent required	Porous membrane
Dip-coating method	Slow	Mechanical and environmental stability
Spray method	Rapid and scalable under ambient condition	Moderate stability, easy reparability

2.5.3.1 Sol-gel

Sol-gel process is a wet-chemical technique widely used in the fields of materials science. The sol-gel process can be described as the formation of an oxide network through poly-condensation reactions of a molecular precursor in a liquid. A sol is typically a stable suspension with colloidal particles or polymers in it. Mainly for the fabrication of materials starting from a colloidal that acts as the precursor of an integrated network of either discrete particles or network polymers. These particles interrelate typically through either van der Waals forces or hydrogen bonds (Song and Rojas, 2013).

Sol-gel technique has been commonly used for the fabrication super-hydrophobic surfaces. Variety of alkylsilane precursors have been employed to create super-hydrophobic surfaces by sol-gel method. S. Liu et al. reported a very simple one-step approach to fabricate transparent and self-cleaning super-hydrophobic coatings via the sol–gel processing of long-chain fluoroalkylsilane as shown in Figure 2.10. The coating surface exhibited a coarse, wrinkled, hill-like morphology similar to the microstructure of the lotus leaf (rough micro-scale papillae), this promising for super-hydrophobicity. An optically transparent and super-hydrophobic coating on glass was prepared by the simple one-step sol–gel processing of long chain FAS.

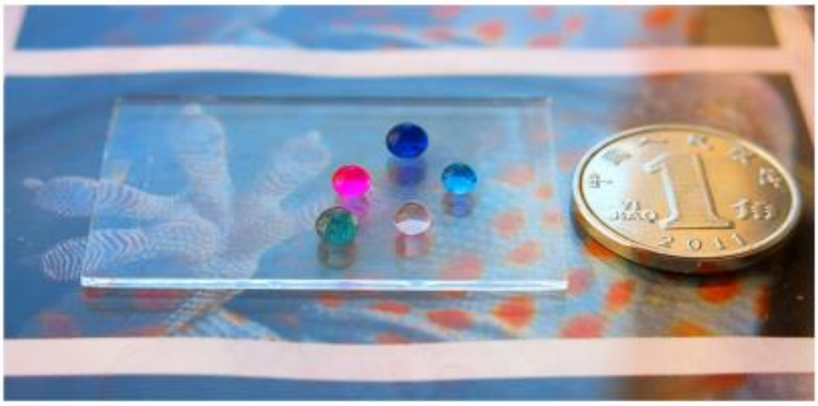

Figure 2.10: Optical photograph of water drops on FAS super-hydrophobic coating (S. Liu et al., 2015)

2.5.3.2 Assembly of colloids

Rough surfaces can also be formed using colloidal particles. The particles stick together utilizing the attractive Van der Waals forces, electrostatic forces between particles and particles to the substrate. Ming et al. reported a simple way to fabricate super-hydrophobic films with dual-size hierarchical structure originated from well-defined raspberry-like particles. The fabrication step is sketched in Figure 2.11(a). First, uncured epoxy groups is prepared with a conventional cross-linked film based on an epoxy-amine system is prepared with available for further surface grafting. Then, raspberry-like silica particles functionalized by amine groups are deposited onto the epoxy films.

The surface topography could be controlled by the deposition parameters. This method generates a double structured roughness on the epoxy film. Finally, a low surface energy layer of monoepoxy end capped PDMS is grafted onto the raspberry-like particles to render the film surface hydrophobic. The raspberry like particle has twolevel roughness, the micro scale roughness is contributed by the large silica particles forming the core of the raspberry-like particles, whereas on each of the micro scale structures there is a nano scale silica bead, that supplied the second roughness in Figure 2.11(b). This dual scale hierarchical structure mimicked the surface of a lotus leaf. It has a static contact angle of 154° and a roll off angle less than 3°. The advantage of particle aggregation method is that it can easily achieve both nano and micro scale roughness in a conformal and controlled way. However the interaction of the particles itself and the adhesion of the aggregated particle to the substrate are quite weak. Moreover, due to the random roughness, the transparency of the coating is usually low.

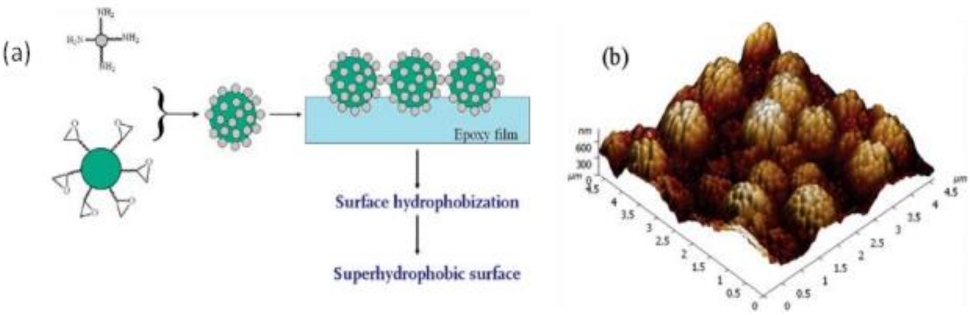

Figure 2.11: Preparation of superhydrophobic films based on rasberry-like particles (b) AFM 3D images for PDMS-covered epoxy-based film containing raspberry-like particles (Ming et al., 2005)

2.5.3.3 Chemical bath deposition

Research reported by Li et al., of forming covalently bonded flower-like TiO2 nanoparticles on cotton fabrics by in-situ growth via a chemical bath deposition method, in which the cotton were immersed in the reaction mixture for several hours at 80ºC. Then a self-assembling process of fluoroalkylsilane (FAS) was carried out to construct a robust super-hydrophobic fabric. The obtained composite fabric is capable to be adapted for the design of multifunctional fabrics with good anti-UV, effective self-cleaning, efficient oil-water separation, and microfluidic management applications.