**SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING**

**UNIVERSITI SAINS MALAYSIA**

# CHARACTERIZATION AND WETTABILITY OF SUPERHYDROPHOBIC FILLED PLASTICIZED POLYVINYL CHLORIDE

By

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Dissertation submitted in partial fulfillment
of the requirements for the degree of Bachelor of Engineering with Honours
(Materials Engineering)

Universiti Sains Malaysia

**JULY 2017**

# DECLARATION

I hereby declare that I have conducted, compiled the research work and written the dissertation entitled **"Characterization and Wettability of Superhydrophobic Filled Plasticized Polyvinyl Chloride"**. 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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# ACKNOWLEDGEMENTS

First and foremost, I would like express my special thanks of gratitude to my supervisor Professor Hazizan Md. Akil for supporting me a lot interm of academically or mentally during conducting this research. Moreover, despite of being an advisor to complete this project he also has give me the golden opportunity to express myself to understand a lot of thing. I was really in debt to him for the sharing of his expertise, experience in this whole time.

Other than that, special thank to Madam Siti Nor Binti Din, Postgraduate student for helping, encouraging and teaching me a lot until the end of the research. She has being very patient on spending her time in updating the progress of my work. She has been very kind and helpful by have suggesting a lot of ideas to finalizing this research within the limited time frame.

Furthermore, I also would like to thanks to all technician, Mr Khairi, Mr Azam, Mr Meor and Mr Syafiq for helping me a lot during conducting the experiment in this research. I really appreciate all of the advices and opinion that have being given to me. A part from that, special acknowledgement is to be given to Prof Dr. Ir. Srimala A/P Sreekantan for the briefing of the project. She has given the guideline for the entire final year students and teaches us generally regarding the writing skill and the correct technique to have proper thesis writing.

Last but not least, I also would like to thanks to my family and friends for the supportive, motivation and encouragement that have been given to me in competing this project.

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| PCC | Precipitated Calcium Carbonate |
| AFM | Atomic Force Microscopy |
| FESEM | Field Emission Scanning Electron Microscopy |
| WCA | Water Contact Angle |
| LAWS | Low Aromatic White Spirits |
| DINP | Diisononyl Phthalate |
| ZnO | Zinc Oxide |
| PVC | Polyvinyl Chloride |
| FTIR | Fourier Transform Infrared Spectroscopy |

# LIST OF SYMBOLS

| | |
|---|---|
| $^{o}$ | Degree |
| Θ | Contact Angle |
| $>$ | Greater than |
| $<$ | Smaller than |
| $\boldsymbol{\gamma_{SL}}$ | Solid-Liquid Interface |
| $\boldsymbol{\gamma_{SV}}$ | Solid-Vapor Interface |
| $\boldsymbol{\gamma_{LV}}$ | Liquid-Vapor Interface |
| $r$ | Roughness Factor |
| F | Force |
| Min | Minute |
| mg | Mass x Gravitational Force |
| $f$ | Frictional Force |
| rpm | Revolution per Minutes |
| phr | Part per Hundred |
| µl | Micro-liter |
| cm | Centimeter |

# PENCIRIAN DAN KEBOLEHBASAHAN SUPERHIDROFOBIK POLIVINIL KLORIDA BERPLASTIK YANG MENGANDUNGI PENGISI

## ABSTRAK

Pada masa kini, permukaan superhidrofobik telah menjadi tumpuan dalam industri penyelidikan. Ini kerana permukaan superhidrofobik dapat digunakan dalam pelbagai aplikasi seperti salutan, tekstil dan bidang bioperubatan. Istilah superhidrofobik menerangkan sifat kebolehbasahan yang lemah pada permukaan dengan sudut sentuh lebih besar daripada $150^o$. Objektif kajian ini adalah untuk menyediakan superhidrofobik (PVC) berplastik dengan penambahan mendakan kalsium karbonat (PCC) yang telah disalut dengan asid stearik. Tujuan pengisi perlu disalut adalah untuk menurunkan tenaga permukaan zarah pengisi. Kesan penambahan pengisi pada sebatian pemplastik PVC dianalisis dengan kekuatan tegangan. Tambahan pula, kebolehbasahan dan permukaan morfologi telah dinilai menggunakan imbasan elektrod mikroskop (FESEM), pengukuran sudut sentuh dan mikroskop daya atom (AFM). Selain daripada itu, untuk mempertingkatkan lagi kekasaran permukaan, teknik menggosok kertas pasir dengan 500 grit ke atas sampel lapisan telah digunakan. Kesimpulan yang boleh dibuat ialah penambahan pengisi dan pelarut mengurangkan kekuatan dan fleksibiliti sebatian PVC berplastik. Peningkatan jumlah pengisi akan meningkatkan modulus dan keliatan, manakala kesan penambahan pelarut adalah bertentangan daripada itu. Penambahan pengisi dapat meningkatkan sudut sentuh PVC berplastik dari $89.39^o$ sehingga $126.67^o$. Peningkatan pengisi bersama-sama dengan kesan dari gosokkan kertas pasir juga dapat meningkatkan kekasaran. Walau bagaimanapun, sudut kenalan yang diperolehi masih tidak mencapai sasaran superhidrofobik dengan sudut sentuh,$\theta$ lebih daripada $150^o$.

# CHARACTERIZATION AND WETTABILITY OF SUPERHYDROPHOBIC FILLED PLASTICIZED POLYVINYL CHLORIDE

## ABSTRACT

Nowadays, superhydrophobic surfaces have become an interest in research industry. This is because the superhydrophobic surface able to be used in various applications such as coating, textile and biomedical field. The term superhydrophobic is describing the poor wettability of a surface with the contact angle greater than $150^o$. The objective for this research is to prepare superhydrophobic plasticized PVC filled with precipitated calcium carbonate (PCC) that was coated with stearic acid. The used of the coated filler is to lower down the surface energy of the filler particles. The effect of filler addition on plasticized PVC compounds was analyzed by tensile strength. Furthermore, the wettability and surface morphology were evaluated using field emission scanning electrode microscopy (FESEM), contact angle measurement and atomic force microscopy (AFM). Other than that, to further improved the surface roughness, technique of rubbing sandpaper with 500 grit on the coating sample was being used. It can be inferred that the addition of filler and solvent reduces the strength and flexibility of plasticized PVC compounds. The increase in filler loading will increase the modulus and toughness, while solvent introduced an opposite effect to the compound. The addition of filler was able to increase the contact angle of the plasticized PVC from $89.39^o$ up to $126.67^o$. The increase in fillers along with the effect of sandpaper rubbing also increases the surface roughness which is one of the critical factors in enhancing the hydrophobicity of the compounds. However, the contact angle obtained are still not reaching the target of superhydrophobic with contact angle,$\theta$ greater than$150^o$.

# CHAPTER 1

# INTRODUCTION

## 1.1 Research Background

In the world of engineering, the concept of making people's life easy and solving their difficulty is an important key portion to become successful engineers. There are a lot of challenges that related in the world of engineers, failure such as corrosion, clouding mist on the window for automobiles, harsh flow out of ketchup in a bottle, anti-soiling architectural coatings, and regular cleaning schedule of an object can be resolved using the technology of surface improvement and superhydrophobic surface is one of the method to solved this problems.

The term superhydrophobic is usually used as descriptors of surfaces properties. The superhydrophobic surfaces exhibit the properties of intense water-repellent which will prevent the absorption of water or be wetted by water. The surface are said to be superhydrophobic due to the minimal contact angle between the surface and the liquid dropped. The contact angle and roll off angle should be higher than $150^o$ for it to become superhydrophobic.

According to Elena *et al.,* (2013) the interest on superhydrophobic was started by the discovery of the self-cleaning properties on lotus leaves which depend on the hierarchical roughness. Since then the interest have grown higher among researchers to study more about superhydrophobic surfaces. The first demonstration reported in artificial superhydrophobic surfaces was done in the mid of 1990s. Researchers have come with various ways to fabricate rough surfaces which display the properties of superhydrophobic surfaces.

In current practices, realizing the great application perspective, various methods was used to induced superhydrophobic behavior on the surface of material in past ten years, such as the phase separation method, solution method, sol–gel method, plasma treatment process, electrospinning method, template method, layer-by-layer self assembly, and many more. Unfortunately most of the method used is highly complicated, required high cost, special apparatus and equipment and some are using toxic and non-environmentally such as fluorosilanes (Duan *et al.*, 2014). Therefore, developing a superhydrophobic surface using low cost production is important and necessary.

Moreover, for the surface to become superhydrophobic it needs to have the combination between low surface energy and high surfaces roughness which will then creating the wetting behavior of superhydrophobic surface (micro-nanostructure) to be better. Low surface energy is needed to overcome the interaction of liquid drop on the superhydrophobic surfaces whereas the surface roughness is to provide the slippery behavior of the surfaces.

The surface energy is describing the atoms and molecules which is near the surfaces that are being bonded with smaller amount neighboring atoms and molecules. Thus, it makes those atoms or molecules on the surface to be higher energy. This high energy is being called as the free surface energy which will make this part to be more active to interact with anything in contact. The free surface energy can be interpreted as the energy needed to create a new surface with a unit area and it quantifies the disruption of chemical bonds that occurs when a surface is created (Nosonovsky *et al.*, 2008). Thus, to create a superhydrophobic surfaces the free surface energy need to be reduced.

The theory behind the roughness of superhydrohobic surface can be described as it creates the pores due to the formation of micro or nano-particle that will lead toward the entrapment of air. Water droplet on such a surface could only in contact with the tips of the particles surface, and it could not penetrate into the pores due to the air pockets trapped in the pores. Therefore, air itself served as a part of the surface and the interface beneath the water drop could be considered as a composite surface (Hong *et al.,* 2008). Hence, increasing of the amount of nanoparticle on the surface would lead toward a better superhydrophobic properties since more air can be trapped on the surfaces itself, thus increase the surface roughness and adhesion of the surface.

There are lots of applications in superhydrophobic field such as in biomedical for utensil purposed, self-cleaning textile, and coating technologies for protection purposes. In this research of studies, focus will be more on superhydrophobic coating application. The coating produced should be low in cost, facile to be fabricated, high strength and of course having the superhydrophobic properties on it. Therefore, plasticized PVC polymer was chosen since PVC is the world leading synthetic polymer (Ramos *et al.,* 2005) that fit with the various applications nowadays. It is one of the most widely used and economically relevant thermoplastic materials. (Hesamoddin *et al.,* 2016)

## 1.2 Problem Statement

Plasticized PVC is the material which is very suitable for coating purposes. In current practices, the layer of plasticized PVC is being used in some automobile industry especially for protective coatings to prevent the open exposed areas such as underbodies, wheel coat, wheel arches and rocker panel. All of this part on automobile industries will have an advantage if the surface of the part is having superhydrophobic behavior on it. This is because superhydrophobic surface have the self-cleaning properties which make it easy for cleaning purposes rather than just protecting the internal surfaces. However, PVC which has been added with plasticizer for flexibility application tends to become hydrophilic. The solid-water interface of modified PVC is one fourth of the unmodified interface which shows the hydrophilic behavior on the modified surfaces (Balakrishnan *et al.*, 2005).

Moreover, Emelyanenko *et al.*, (2015) have reported that another challenge creating superhydrophobic coatings is that the superhydrophobic coatings layer is unable or even withstand slight finger touch and friction. Therefore, it is still a great challenge to prepare robust superhydrophobic surfaces for especially under the rigorous real application environment. The surface roughness of the material surfaces is the key factor other than the surfaces energy for the surface to become superhydrophobic surface. Most of functional surfaces currently available can be easily damaged by routine use, resulting in the immediate loss of the chemical functionalities, surface-structure and related chemical or physical properties.

## 1.3 Objectives

Therefore, the aim for this research is to produce superhydrophobic plasticized PVC with high mechanical strength and able to withstand the superhydrophocity behavior even with the presence of friction on the surfaces to compete with the current demand for coating purposes. The specific objective for this project are:

a) To prepare superhydrophobic plasticized polyvinyl chloride (PVC) filled with coated precipitated calcium carbonate (PCC).
b) To determine the strength of the superhydrophobic filled plasticized PVC.

c) To investigate the effect of PCC and solvent on surface properties and wettability of plasticized PVC.

## 1.4 Thesis Outline

This thesis is consisting of five consecutive chapters. Chapter 1 describes a concise introduction, problem statement and objectives of the research. In this chapter reader are expected to get the general idea of the whole content of this thesis writing. Readers are also being introduced with several important keywords for further and easy understanding. Next is Chapter 2 which comprises a full review on the formation of superhydrophobic surface of plasticized PVC, fundamental concepts of superhydrophobic and functional applications of superhydrophobic plasticized PVC coating are discussed. Furthermore, Chapter 3 explains the information on the experimental procedures that is used in this research. In this chapter it also comprised the experimental design and the method of testing and characterizing the plasticized superhydrophobic surfaces. It covers a brief explanation on the characterization equipment, their operation principles and sample preparation. In this research, there are 5 characterizations being used which is tensile test, contact angle measurement, Fourier Transform Infrared Spectroscopy (FTIR), Atomic Force Microscopy (AFM), and Field Emission Scanning Electron Microscope (FESEM) analysis. Moreover, Chapter 4 describes to the readers about the experimental results and brief discussion on the synthesized superhydrophobic plasticized PVC and their parameters. Finally, Chapter 5 is devoted to the conclusions of this research work and suggestions for future work.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

Surface analysis is a study of a surface behavior towards the chemical and physical phenomenon between two phases. The phases can exist in same phases (solid-solid, liquid-liquid) or in different phases (solid-liquid, solid-gas, solid-vacuum). One of the most important properties related to the surface analysis is the wettability of the surfaces (Joneydi *et al.,* 2013). Wettability is explaining the behavior of solid-liquid interface. It involved the measurement of the water contact angle as the main data analysis. Woodward and Roger, (2008) explained that the wettability angles can be devided into three types which is hydrophilic ($<90^o$), hydrophobic ($90^o$-$150^o$) and superhydrophobic ($>150^o$).

If we are looking at the nature occurrence, there are several plants that can be observed that have the superhydrophobic properties on their surfaces such as Giant Alocasia, Lotus leaves, Taro leaves, Water Strider’s legs and Water Lettuce. This phenomenon is being called as the ‘lotus effect’ (Figure 2.1). Firstly, the surface leaves was covered with waxes which is made from hydrocarbon compound with high resistive towards wetting. The function for this wax is to lowering the surfaces energy of the leaves. Secondly, the surface structure of the leaves has entrapped air between water droplet and surface due to the papillae formation. The papillae structure will create a roughness on the surface. The two combinations contributes to less wetting between water droplets and the surface, thus creating highly water repellent surfaces which will lead towards increasing of the water contact angle (Ma and Hill, 2006).

**Figure 2.1:** Superhydrophobic can be observed on the lotus leaf (Lotus Effect)

As mentioned before in the previous chapter, superhydrophobic surfaces can be achieved by controlling two parameters which is surface roughness and surface energy. According to Chen *et al*., (2009), roughness and surface microstructure is a vital factor to produce superhydrophobic surface. This factor can be achieved by utilizing the difference in solubility or additive addition in the materials compound. Other than that, for surface energy of the solid surfaces it is related to the formation of adhesive bond between the two interfaces. The higher adhesive bond will result the liquid on the interface to be simply wet the surfaces since formation of a new surface of a liquid on the solid surfaces can be easily formed (Packham *et al.,* 2003). Therefore, in superhydrophobic view, the surface energy of the surfaces must be lower to minimize the wettability.

## 2.2 Basic wetting of hydrophobic surfaces

Originally the term hydrophobic or hydrophilic was only used to describe water since the word “hyro” means “water” in greek. However, nowadays this term was not only used to describe water anymore but also valid for describing the contact of a solid surface with any liquid. The hydrophobic properties having the contact angle of more than $90^o$ between the water or any other liquid on the solid surfaces whereby to achieve a superhydrophobic surface the contact angle must be greater than $150^o$ (Refer Figure 2.2). The higher the contact angles produce the higher the repellency ability of the surface that prove the superhydrophobic surface have being achieved.

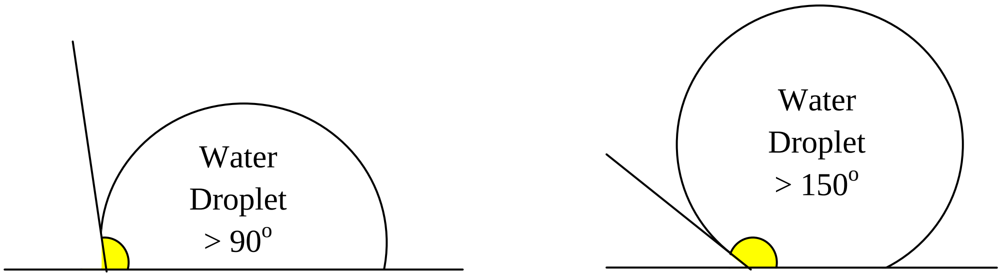


**Figure 2.2**: Schematic illustration showing a macroscopic water droplet on a hydrophobic surface with a contact angle higher than 90° and a superhydrophobic surface displaying a contact angle above 150°.(Hansson, 2012)

### 2.2.1 Surface Tension and Contact Angle—Young's Equation

The contact angle is defined as the angle formed from the contact of the liquid-solid interface and the liquid vapor interface (it was obtained from geometrical drawing of a tangent line from the contact point along the liquid-vapor interface in the droplet profile). The interface with the existence of solid, liquid and vapor is called the "three phase contact line". Figure 2.3 shows five contact angle of liquid drop which spreads on solid surface.

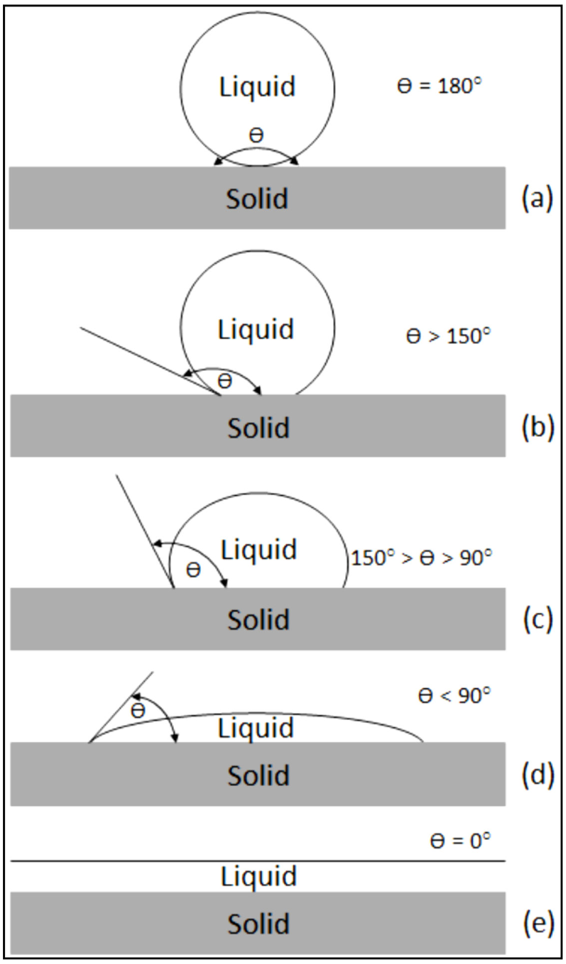


**Figure 2.3:** Five types of wetting on solid surfaces: (a) complete non-wetting (b) superhydrophobic (c) hydrophobic (d) hydrophilic and (e) complete wetting (modified after Jastrzebski 1980 (Victor, 2012)

From the figure, the contact angle which is less than 90° represent the wetting of the surface is excellent and the liquid is spread evenly through the solid surface, as the contact angles which if bigger than 90° indicate that wetting of the surface is poor due to the minimum contact surface between the two interfaces. For instance, complete wetting of surface shows the contact angle of 0°, as the liquid droplet turns into a flat puddle. For contact angle more than 150° it shows that the surface is superhydrophobic with almost no contact between them. Furthermore, contact angles are not limited to the liquid vapor interface on a solid; they are also applicable to the liquid-liquid interface on a solid.

According to Woodward and Roger, (2008) the rounded shape of a liquid droplet is depending on the surface tension of the liquid. The rounded shape of a small droplets and bubbles gives the minimum surface area for a fixed volume cases. The reason why the water droplet can maintaine to be spherical is due to the existence of intermolecular force that acting around the outermost layer between neighboring molecules to balance the net force. This intermolecular force will contract the surface and this contraction is called surface tension which responsible for the shape of liquid droplets (Woodward *et al.*, 2013). In practical, the external forces such as gravity deform the droplet; consequently, the contact angle is determined by a combination of surface tension and external forces (usually gravity). Theoretically, the contact angle is expected to be characteristic for a given solid-liquid system in a specific environment.

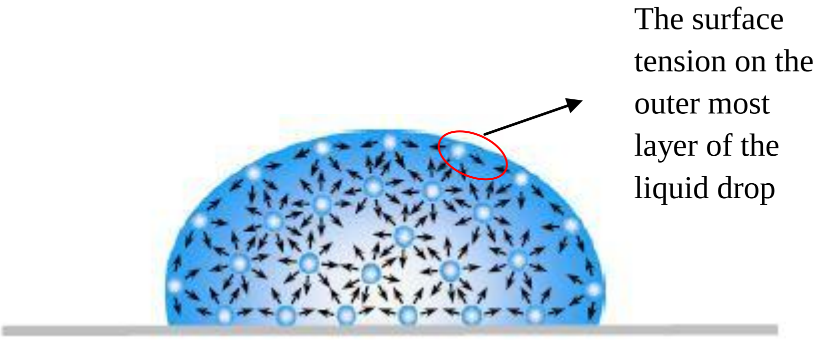


**Figure 2.4:** Surface tension is caused by the unbalanced forces of liquid molecules at the surface, (Woodward *et al.*, 2013).

### 2.2.2 Contact Angle Hysteresis

Based on Young’s equation which practical to a specific liquid-solid system, three thermodynamic parameters which is ‘$\gamma_{lv}$’ , ‘$\gamma_{sv}$’, and ‘$\gamma_{sl}$’ was used to verify a single and unique contact angle ‘$\theta_Y$’ (Refer Figure 2.5). Unfortunately, there are many existing of metastable states droplet on a solid, and the experimental contact angles are usually not equal to '$\theta_Y$' (Young's contact angle). The limitation of this equation is that it can only valid for static state whereas in real trend of a wetting case it is more than just a static state. Liquid tend to spread its new surface and to wet the new surface of the solid thus the measurement of a single static contact angle to characterize wetting behavior is no longer sufficient. When the three-phase contact line is in motion, it will produce contact angle which is called the "dynamic" contact angle (Diaz *et al.*, 2010).

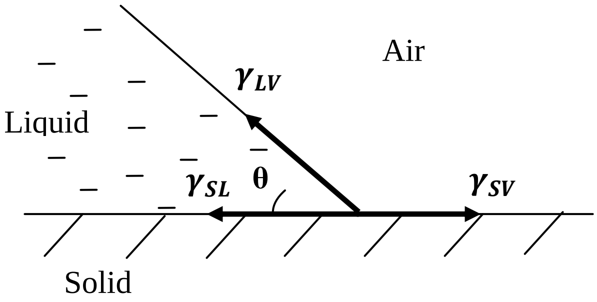


**Figure 2.5:** The three-phase contact line

Specifically, the contact angle form by expanding and contracting the fluid are alluded to as the advancing contact angle '$\theta_{adv}$' and the receding contact edge '$\theta_{rec}$'. These angle falls inside a range, with the advancing angle moving toward the maximum value, and the receding angle is moving toward a minimum value (Duursma *et al.*, 2010). Dynamic contact angle can be measured at different rates of speed. At a low speed, it ought to be close or equivalent to an appropriately measured of static contact angle. The contrast between the advancing angle and the receding angle is known as the hysteresis (H):

$$H = \theta_{adv} - \theta_{rec} \text{ ............................ } (2.1)$$

Where '$\theta_a$' advancing contact angle and '$\theta_r$' is receding contact angle

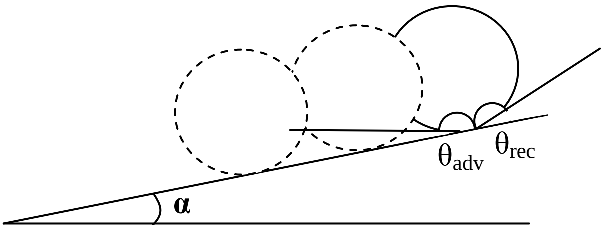


**Figure 2.6:** The tilted angle, α of a liquid droplet, the advancing angle, '$\theta_{adv}$' and receding contact angles, '$\theta_{rec}$'.

The contact angle hysteresis is crucial in analyzing superhydrophobic for solid–liquid interface. The contact angle hysteresis is the difference between the advancing and receding angle, which are two stable values. If a drop sits on a tilted surface (Figure 2.6), the contact angles at the front and back of the droplet correspond to the advancing and receding contact angle, respectively. The advancing angle is greater than the receding angle, which results in contact angle hysteresis. Contact angle hysteresis occurs due to surface roughness and heterogeneity.

### 2.2.3 Cassie–Baxter wetting hypothesis and Wenzel capillarity-induced wetting transition

There are two types of models which can be used to explain the superhydrophobic phenomenon namely; Cassie–Baxter and Wenzel wetting models. Based on the Cassie-Baxter model, there are presences of air pockets which exist below the water droplet. The hydrophobicity of the surfaces is supported because the drop sits somewhat on the air.

According to the Wenzel model the roughness will boost the wetting area of the solid surfaces, which likewise geometrically adjusts the hydrophobicity. A standout amongst the most talked about points in the field now is the Cassie–Wenzel regime transition practical on a several surface relieves under applied external pressure. The equation (2.2) describing the Wenzel state as follows:

$$\cos \theta w = r cos\ \theta \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2.2)$$

Where ‘r’ is roughness factor = Actual Surface area and ‘$\theta$’ is the Wenzel apparent contact angle which corresponds to the stable equilibrium.

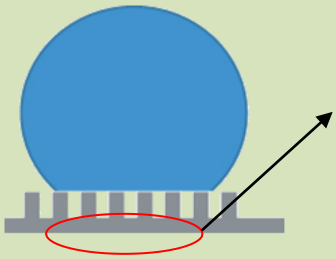
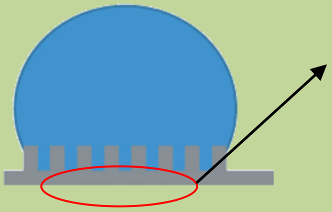
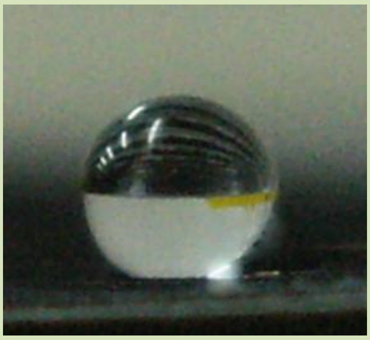
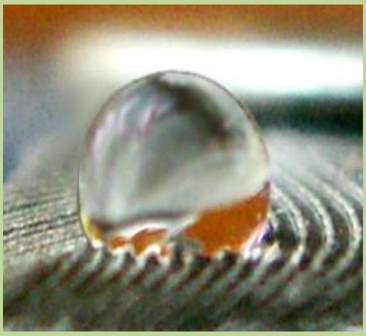
(Celia *et al.* 2013) state that roughness factor ‘r’ emphasizes the effect of the surface chemistry determined by the term cos $\theta$. When $\theta$ <90°, an increase in roughness factor r reduces ‘$\theta w$’, but if $\theta$ >90°, an increase in roughness leads to an increase in ‘$\theta w$’.

In the Cassie-Baxter state, the droplet is suspended on the surface asperities. The liquid does not penetrate into the protrusions of the surface features. In the Cassie-Baxter equation, the apparent contact angle is the result of all contributions of different phases:

$$\cos \theta_{CB} = f_1 \cos \theta_1 + f_2 \cos \theta_2 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots..... \ (2.3)$$

where ‘$f_1$’and ‘$f_2$’ are the surface fraction of the phase 1 and 2, respectively, and ‘$\theta_1$’ and ‘$\theta_2$’ the contact angle of phase 1 and 2, respectively (Nosonovsky & Bhushan 2009). Table 2.7 show the illustration of the difference between Cassie-Baxter and Wenzel state

**Figure 2.7:** The difference between Cassie-Baxter State and Wenzel State, (Bormashenko *et al.*, 2007)

| **Cassie-Baxter State** | **Wenzel State** |
|---|---|
| <br>Air trap exist between the two interface | <br>Complete fill of water droplet |
|  |  |

## 2.3 Plasticized PVC

Polyvinyl chloride or known as "PVC" was first documented and characterized more than 100 years ago; however PVC having properties of poor thermal stability and it was not widely used until about 1930. The major drawback of PVC was improved by the addition of plasticizer which make it to become an important commercialize polymer (Ramos, 2008). Nowadays synthetic polymer have grown to be the number one of the world's leading synthetic polymers, with a total production of about 15 million tonnes in. According to Aruna (2016) pure PVC exists as a rigid polymer with a glass transition temperature ($T_g$) of 70-82 °C which limiting its applicability. In order to obtain the desired durability and flexibility below 82°C the PVC is mixed with a variety of plasticizers.

Different plasticizers exhibit different characteristics in both the ease with which they form the plasticized PVC and in the resulting mechanical and physical properties of the flexible PVC. The nature of the plasticizer with respect to its molecular structure, size, polarity, glass transition temperature, and its interaction with the polymer control the effectiveness of the plasticizer, both with respect to the flexibility introduced and to the retention of the plasticizer in the polymer. The most commonly plasticizers used are synthetic esters of phthalic acid such as di(isononyl) phthalate (DINP) and many others. Phthalates provide PVC compatibility, a high gelling capacity, good water resistance, and low cost. The existence of polarizable benzene in the structure of DINP makes it to become highly effective to bond with PVC structure thus improves the flexibility of the polymer chains (Aruna, 2016).

Naturally plasticized PVC is made off a synthetically or physically cross-linked polymer. Usually they have considerably physical properties. These physical properties can be further increase by adding the solvent into the PVC mixing component. In particular, with increasing solvent density in the mixing formulation will improved the polymer molecular chain by compressed or entangle it. The solvent entanglements of the polymer chain will improve the physical properties by increasing the molecular weight of the polymer. The increase in molecular weight will expand the polymer dimensions. For a plasticizer to be effective, it must be mixed homogeneously and incorporated into the PVC polymer matrix. This is typically affected by heating and mixing until either the resin dissolves in the plasticizer or the plasticizer dissolves in the resin. The plasticized material is then molded or shaped into the desired end product.

## 2.4 Methods to Prepare Superhydrophobic Surfaces

There are several techniques that can be used to prepare superhydrophobic surfaces such as phase separation method (Lieu *et al.,* 2014), template method (Yuan *et al.,* 2007) and sol gel method (Mahadik *et al.,* 2010). Most of the technique used to produce superhydrophobic surfaces are either complicated, use a special apparatus or required high cost in term of fabricate it of in process making. Thus, developing a facile and low cost approach to obtain a superhydrophobic surface from a common hydrophobic material or complete wetting material is commercially important and scientifically challenging.

### 2.4.1 Phase Separation Method

Phase separation is one of the methods used to produce superhydrophobic surfaces on polymeric materials. The advantages of using this method is because it is easy, efficient and low cost and the possibility to create various substrates by casting and coating. Phase separation method is one of the methods to produce rough surface on superhydrophobic layer. It was formed by multi-component mixture of raw material. It occurred when a stable mixture is being disturbed by some change such as pressure or temperature drop making it to become unstable and separated into two phases. Bicontinuous is a structure that may occurred to enhance the separation process by forming porous interpenetrate network between both new phases. The bicontinuous structure is consists of a lot of formation of pores and it can be control by the rate of solidification. These structures have being used as filter for many years and only proceed with superhydrophobic surfaces by Nakajima *et al.,* (2001) to produce rough superhydrophobic surfaces using sol-gel method. The phase separation structure having a microscale structure and it may have a possibility to collapse during drying due to the shrinkage of the size dimension.

Aruna *et al.,* (2012) have produced a superhydrophobic surface on polystyrene (PS) using phase separation method. In the research tetrahydrofuran (THF) was used as a solvent and different alcohol as non-solvents. The result is quite promising because the water contact angle can achieve up to $159^o$. Another research was done by Pi *et al.,* (2013) which have prepared a polylactic acid (PLA) superhydrophobic film by creating microphase separation on the film during drying and forming polyethylene oxide (PEO) micro-domains on the surfaces, resulting a porous and rough surfaces structure.

In this method, the microstructure of the polymer surfaces is proportional to the degree of phase separation. However, this method has several disadvantages such as specific humidity, suitable solvent and non-solvent, or low surface energy raw material. Another major problem of this method is the stability of the superhydrophobic surfaces is difficult to control and it cause by many factors. The disadvantages of fabrication superhydrophobic surfaces using this method need to be considered to choose in the most effective method among others.

Based on Figure 2.8, the phase separation state can clearly be observed at which the solvent are being gathered at certain region surrounded by a criss-cross of polymer networks. This phase separation cannot occur spontaneously, instead it need to be enhance by the addition of solvent which will then promote the phase separation in the polymer structure. For example, Wei *et al.,* (2010) was using ethanol as solvent in fabricate superhydrophobic fluoropolymer films. The result from this work is that the contact angles of the polymer keep increasing with respect to the increment of ethanol. The additions of ethanol will decreasing down the surface energy and spontaneously change the copolymer chains which will then increase the surface roughness of the polymer surfaces.

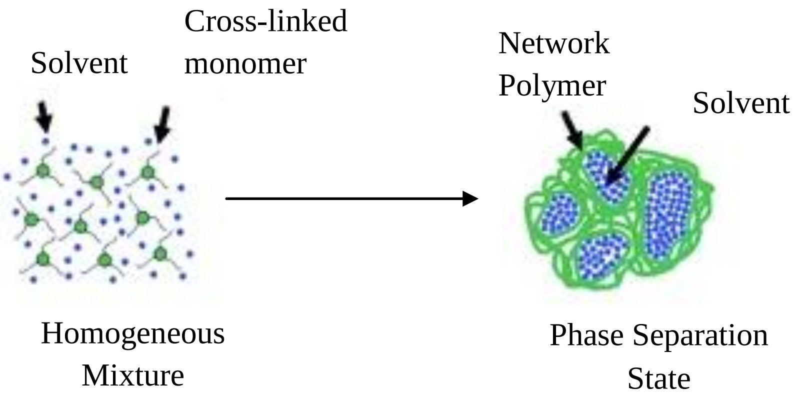
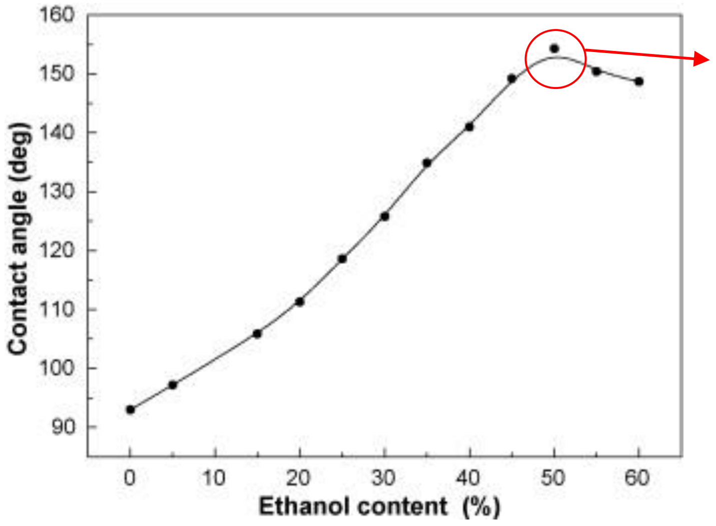


**Figure 2.8:** The phase separation occurs in polymer structure (Gelb *et al*., 2000)

To further describe the experimental work by Wei *et al.,* (2010) as mentioned earlier, the addition of ethanol will make some of the PVC to precipitate out of the polymer solution and form some PVC aggregates or particle. The higher amount of ethanol added, the higher PVC nano-particle smaller size will be formed. The deposited PVC particle will act as nuclei that aggregated the PVC rich phase around it in order to decrease the surface tension. After solidification occur, the intense phase will form a matrix phase whereas the PVC poor phase will form a porous structure. However, when the amount of ethanol added is too much, most of the PVC will precipitates out of the polymer PVC solution instantly and form large segregates instead of nano-particles, and this is not practical in creating superhydrophobic PVC surface (Refer Figure 2.9)



Maximum limit in addition of ethanol

**Figure 2.9:** Relationship between the amount of ethanol added and the water contact angle of the surface layer (Chen *et al.*, 2009)

### 2.4.2 Template Method

This method is inspired from the self-cleaning of superhydrophobic surface in nature such as lotus and taro leaf. This is the first method used to practiced superhydrophobic on the PVC surfaces. Other type of polymer produced by this method includes polystyrene (PS) and polydimethylsiloxane (PDMS). By using this method, the water contact angle and the sliding angle of the superhydrophobic PS surface were 158° ± 1.6° and 3°, respectively. Thus, it can be concluded that template method is one of the promising methods to produce superhydrophobic that can be used surfaces. The PS surface was still superhydrophobic when brought into contact with dark ink, fresh blood and even viscous glue water. SEM demonstrates that the surface structure includes many uniform papillae with the distances across extending from 10 to 15 µm, which is like the surface structure of common taro leaf. Such an extraordinary surface morphology may bring about the superhydrophobic properties.

Moreover, Yean *et al.,* (2007) having a research related to Sun's investigation which is a biomimetic taro-leaf-like polystyrene (PS) film with superhydrophobic surface was obtained by replicating the surface pattern of a natural taro leaf. The result for both researches is able to produce the superhydrophobic surfaces with contact angle of $150^o$-$160^o$. Other than that, Sun *et al.,* (2005) have also developed an easy and low cost technique to produce a superhydrophobic lotus-leaf-like on PDMS surface using a natural lotus leaf as template, and the resulting PDMS has the same superhydrophobicity as a natural lotus leaf. In fact, taro leaf has also has excellent superhydrophobic property.

### 2.4.3 Sol Gel Method

For the benefit of simple operation, minimal effort and unrivaled homogeneity, the ordinary sol-gel handle has turned into a planned technique to get readily nano-porous materials and has been broadly utilized. Su *et al.,* (2011) have specified that sol–gel technique is a straightforward and low cost approach to prepare superhydrophobic coatings or films. Yan *et al.,* (2011) have investigated that the sol gel technique can be used to produce superhydrophobic surfaces based on Wenzel or Cassie–Baxter's hypothesis. This method involves a chemical deposition at which the chemical solution or sol is being used as a precursor on the selected substrate to form a gel-like system. This type of technique is more promising in producing transparent and superhydrophobic films on material surfaces. For this method to be successful, extra control over the process like spin-coating is necessarily important in the fabricating procedures.

Nowadays, majority of the researcher is focusing on sol–gel based on silica sol–gel. The reason is because using this method the contact angle can be achieved up to 172°. This angle is already good enough to be considered as superhydrophobic. Moreover, the contact angle of silica film can retain the superhydrophobic behavior at temperature of 550 °C. The silica film was prepared by setting the molar ratio of methyltriethoxysilane (MTES), trimethylmethoxysilane (TMMS), methanol (MeOH), water ($H_2O$) stable at 1:0.09:12.71:3.58, respectively with 13 M $NH_4OH$. Then, the films were prepared with different deposition time which is from 5 to 25 h. To further improve the contact angle of the silica film 10% trimethylchlorosilane (TMCS) is added which will act as a silylating agent in hexane solvent for 24 h.

Another research have been explained by Latthe *et al.,* (2010) which portrays the room temperature synthesis of adherent and permeable superhydrophobic silica film on glass substrates utilizing methyltriethoxysilane (MTES) as hydrophobic reagent by sol–gel handle. The covering sol was set up by keeping the molar ratio of tetraethoxysilane (TEOS), methanol (MeOH), water ($H_2O$) steady at 1:22.09:6.25, separately, with 0.01 M NH4F catalyst all through the trials and the MTES/TEOS molar proportion (M) was differed from 0 to 0.43. The static water contact edge as high as 160° and water sliding point as low as 3° was acquired for silica film arranged from M = 0.43. The surface morphological review demonstrated the permeable structure with pore sizes going from 250 to 300 nm. The superhydrophobic silica film held their superhydrophobicity up to a temperature of 290 °C or more than this temperature, the film progressed toward becoming superhydrophilic.

## 2.5 Application of Superhydrophobic Surfaces

Superhydrophobic surfaces are actively studied across a wide range of applications and industries such as biomedical, coating technologies and in textile applications. Nowadays the research regarding superhydrophobic are being improved from time to time. According to the report in grandviewresearch.com which was published on September 2016 the global superhydrophobic coating in current market is at USD 5.77 million in 2015. This is due to the high demand of peoples all across the world which attracted to the properties of the surfaces which can repel water and humidity and also self-cleaning properties.

### 2.5.1 Biomedical

In biomedical arena superhydrophobic technologies was being used as a substrates to control protein adsorption, cellular interaction, and bacterial growth, as well as platforms for drug delivery devices and for diagnostic tools. The reason why this material was proposed is to create a stable or metastable air layer at the material surface, which lends itself to a number of unique properties. These activities are catalyzing the growth of new materials, applications, and fabrication techniques, as well as collaborations across material science, chemistry, engineering, and medicine given the interdisciplinary nature of this work. The analysis begins with a research of superhydrophobicity, and then explores biomedical applications that are utilizing superhydrophobicity in depth including material selection characteristics, in vitro performance, and in vivo performance (Falde *et al.*, 2014).

Recently medical surface incorporation has developed an effective superhydrophobic coating technology that can be used to coat gloves, fabrics, and general equipment used in medical applications, where a clean surface that resists