CHARACTERIZATION OF FLUORINE-BASED HYDROPHOBIC COATING TOWARDS WATER AGING APPLICATION

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In the present world, coating technology is a reliable and effective modern technology utilize in wide range of applications in various industry including solar panel, eyewear, building glass panel, and many more. The coating applied to surface of these materials required a specific requirement such as water resistance, good adhesive strength, and optically transparent, mainly for physical and chemical protection. The afore mentioned requirements demand coating's material with water repellent properties, low scattering/diffusion coefficient, and good molecular force attraction towards glass surfaces. This can be realized by tailoring the molecular structure and bonding properties of the where the protection can be sustained.

This work details with coating solution preparation adopted to produce roughened surface with water repellent ability aiming to enhance the surface physical and chemical protection. This thesis focuses the coating process using spray coating technique with tetraethyl orthosilicate (TEOS) and heptadecafluorodecyltrimethoxysilane (HFTMS). The coating properties such as water contact angle, surface morphology, transparency, adhesiveness, and refractive index of the coating are characterized carefully by using contact angle instrument, atomic force microscopy (AFM), UV-Vis spectrometer, scratch test, and ellipsometer instruments.

The coating materials are found to have very significant effect on water resistant ability where the present of water repellent agent of HFTMS, with the present of fluorine in the coating materials has been found to produce higher contact angle value. In addition, increasing the surface roughness of the coating, by manipulating the spray setting and water aging cycles, has been found to enhance further the water contact angle of the coating. Thus, the optimized surface roughness and contact angle have been chosen in order to obtain the best water-resistant properties with higher water contact angle even after water aging process. Findings from AFM measurement confirmed that higher

surface roughness coating is achieved after the samples have been through water aging process which promotes the coating material molecules to accumulates and bulking to each other. Other than that, the result from UV-Vis spectrometer has shown that the transmission coefficient of the coated materials is consistent along all samples even sprayed at different setting and after going through water aging process. Interestingly, the refractive index of TEOS samples shows a constant value even after the dipping cycles.

This study shows that the present of fluorine particle in the water resistive agent has introduced the water resistance properties with high contact angle for the sample. Furthermore, controlling the surface roughness by manipulating the spray setting and water aging process, the water contact angle can be increased. In addition, changing the spray process parameter and water aging process have no influence on the optical transparency of the coating. However, the refractive index of the samples varies as the material is reported to contain porous structure smaller than the light wavelength. Therefore, this study shows the use of fluorine in coating material as water repellent agent can permits better water resistive properties when exposed to water molecules. After the sample characterizations and analysis, it was found that sample with alumina number of particles 0.006311849 per μm^2 has shown good properties of hydrophobicity in long term period, and meanwhile, sample with alumina number of particles 0.004176432 per μm^2 has shown good hydrophobicity in short term period.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENCIRIAN SALUTAN KALIS AIR YANG BERASASKAN FLUORIN TERHADAP APLIKASI PENUAAN AIR

Oleh

MOHD NAQIUDIN BIN CHE IBRAHIM

Oktober 2018

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Pada zaman kini, teknologi penyalutan adalah satu teknologi moden yang meluas berguna di dalam bidang industry termasuk panel solar, kaca mata, panel kaca bangunan, dan lain-lain lagi. Salutan yang dikenakan pada permukaan bahan-bahan sebegini memerlukan ciri-ciri tambahan yang lain seperti kalis air, daya lekatan yang bagus, dan telus cahaya,sebagai perlindungan daripada faktor fizikal dan kimia. Ciri-ciri tambahan seperti ini memerlukan bahan salutan yang mempunyai sifat kalis air, perserakan cahaya yang rendah, dan mempunyai daya tarikan molekul yang kuat terhadap permukaan kaca. Perkara ini boleh dicapai dengan mengubah ciri-ciri struktur dan ikatan molekul supaya mampu memberikan perlindungan.

Kajian ini menekankan terhadap penyediaan salutan yang digunakan untuk menghasilkan permukaan yang kasar dengan kemampuan kalis air bagi meningkatkan lagi perlindungan secara fizikal dan kimia. Tesis ini memberikan fokus terhadap proses penyalutan yang menggunakan kaedah teknik penyalutan secara semburan dengan menggunakan bahan *tetraethyl orthosilicate* (TEOS) dan *heptadecafluorodecyltrimethoxysilane* (HFTMS). Ciri-ciri salutan seperti sudut sentuh air, morfologi permukaan, ketelusan cahaya, daya lekatan, dan indek biasan dicirikan dengan menggunakan alatan sudut sentuh air, mikroskopi daya atom (AFM), spektroskopi penyerapan UV-Vis, ujian calar, dan alat elipsometer.

Bahan salutan tersebut ditemui mampu memberikan kesan terhadap keupayaan kalis air dengan menggunakan agen kalis air HFTMS, yang mengandungi fluorin di dalamnya untuk menghasilkan sudut sentuh air yang lebih tinggi. Sebagai tambahan, dengan meningkatkan kadar kekasaran permukaan salutan, dengan cara memanipulasikan tetapan semburan dan kitaran penuaan air, ditemui dapat menghasilkan sudut sentuh air yang lebih tinggi. Justeru itu, kadar kekasaran permukaan dan sudut sentuh air yang optimum telah dipilih untuk memperoleh sifat kalis air yang terbaik dengan sudut

sentuh air yang tertinggi setelah proses kitaran penuaan air. Penemuan daripada AFM membuktikan bahawa kadar kekasaran permukaan yang lebih tinggi dapat dicapai selepas proses penuaan air yang telah mengakibatkan bahan salutan untuk bergumpal dan membesar sesama sendiri. Selain itu, keputusan daripada spektroskopi UV-Vis menunjukkan bahawa kadar ketelusan cahaya bahan salutan adalah tetap dan sama bagi kesemua sampel walaupun sampel-sampel tersebut disembur pada tetapan yang berbeza dan selepas proses penuaan air. Yang menariknya, kadar biasan TEOS adalah juga sama walaupun selepas proses penuaan air.

Kajian ini membuktikan bahawa dengan kehadiran fluorin di dalam agen kalis air dapat menghasilkan sampel kalis air dengan sudut sentuh air yang tinggi. Selanjutnya, dengan mengawal kadar kekasaran permukaan dengan memanipulasi tetapan semburan dan proses penuaan air, sudut sentuh air dapat ditingkatkan. Sebagai tambahan, dengan melakukan perubahan pada tetapan semburan dan proses penuaan air, kadar ketelusan cahaya salutan tidak juga berubah, walau bagaimanapun, indek biasan salutan adalah tidak tetap di seluruh sampel kerana bahan salutan tersebut telah dilaporkan mengandungi liang-liang yang bersaiz lebih kecil daripada panjang gelombang cahaya. Oleh itu, kajian ini membuktikan bahawa penggunaan fluorin di dalam bahan salutan sebagai agen kalis air dapat menunjukkan sifat kalis air yang lebih baik apabila terdedah kepada molekul air. Setelah selesai kajian, didapati sampel dengan jumlah zarah alumina 0.006311849 bagi setiap μm^2 menunjukkan sifat kalis yang bagus bagi tempoh masa yang panjang, manakal, sampel dengan jumlah zarah alumina 0.004176432 bagi setiap μm^2 menunjukkan sifat kalis air yang baik hanya untuk tempoh masa yang pendek.

ACKNOWLEDGEMENTS

In the present world of competition, there is a race of existence in which those are having will to come forward succeed. Project is like a bridge between theoretical and practical working. With this willing I joined this particular project.

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May this thesis help to who those in need in the future.

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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A	Absorbance
α	Radius of the droplet
α	Absorption coefficient
A_L	Liquid cap surface area
AFM	Atomic force microscopy
ASTM	American Society for Testing and Material
b	Length of the path
c	Concentration of the absorbing medium
cP	Dynamic viscosity
cSt	Kinematic viscosity
DC	Direct current
FAS 17	Fluoroalkyl silane
h	Droplet height
HFTMS	Heptadecafluorodecyltrimethoxysilane
I	Intensities of the incident light
I_o	Intensities of the transmitted light
ISO	International Organization of Standardization
K_c	Capillary constant
LBADSA	Low-bond Axisymmetric Drop Shape Analysis
LCD	Liquid crystal display
LED	Light emitting diode
MSE	Mean square error
P	Incident light intensity
P_o	Transmitted light intensity
ρ	Solution density
R	Radius of curvature of the liquid droplet on a surface
R_a	Surface roughness average
R_q	Surface roughness root mean square
tc	Transmission coefficient
t_f	Time taken of the liquid to flow
TEOS	Tetraethyl orthosilicate
UV-Vis	Ultraviolet-visible
W_a	Work of adhesion
γ_L	Liquid surface tension
γ_L^d	Dispersive component for liquid surface tension
γ_L^p	Polarity component for liquid surface tension
γ_{LA}	Surface tension at liquid-air (gas) interphase
γ_{SA}	Surface tension at solid-air (gas) interphase
γ_S	Solid surface energy
γ_S^d	Dispersive component for solid surface energy
γ_S^p	Polarity component for solid surface energy
γ_{SL}	Surface tension at solid-liquid interphase

CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter discusses the general concepts of hydrophobic and its functionality for coating application which makes it significant in everyday life. Besides that, the scientific reviews involved in developing a long-lasting hydrophobic coating is also discussed in this chapter.

Furthermore, this chapter also presents the motivation of this study, problem statements related to coating applications for hydrophobic industry, the objectives of this work, and the outline of this thesis.

1.2 Hydrophobic Coating

Coating or also known as modifying surface is widely used in many fields of modern high technology and it is applied for specific well-defined surface properties ranging from a large area to nanoscale structure (Montemor, 2014). Nowadays, the application or device produced from coating technology involves in generating multibillion-dollar industry especially those that possess transparent properties which suitable for windows panel, eye-wear, and display screen (Prevo *et al*., 2005). The functions of coating are applied onto a material surface to protect it from physical, chemical and environmental damages while introducing some physical, chemical, mechanical, electrical, or magnetic barriers properties toward the materials (Montemor, 2014). There is various coating process in present time that has been developed by manufacturers to meet certain coating criteria such as spin coating, dip coating, spray coating, chemical vapour deposition, electrochemical plating, and roll to roll coating (Aziz & Ismail, 2015).

Generally, hydrophobic coating is applied to protect the material's surface from water in order to prevent corrosion, improve cleanliness of the surface from dirt or dust, increase optical transparency for drivers during rain, solar panels and as a building exterior's materials (Kumar *et al.,* 2015). In nature, plants leave with hydrophobic properties have a clean surface by rolling off the water beads along with the dirt on the leave's surface completely by simple rain shower (Han *et al*., 2008). The requirement for a surface to be stated as hydrophobic is that it must has a water contact angle of more than 90° on its surface.

In order to explain the science behind the hydrophobic properties, the terms of surface tension and surface energy must be used. Surface tension term is used to explain the cohesive and adhesive forces that occur at the air-liquid interphase of a homogenous liquid (Kumar, 2017). At the liquid-liquid interphase, the cohesive force pulls the surrounding molecules towards the centre in every direction thus produces equilibrium force. However, at the air-liquid interphase, the adhesive force between air and liquid is not strong enough as liquid-liquid interphase which then causes an unbalanced force that recognized as surface tension. Figure 1.1 shows the illustration concept for surface tension from balanced and unbalanced forces for liquid molecules at the centre and surface (Quora, 2016). Furthermore, the forces acting on the molecules at the surface produces energy at the surface. In brief, surface energy is defined as the intermolecular (interatomic) energy difference between the bulk of the material and the surface of the material (Kumar, 2017). Figure 1.2 shows the difference between the direction of force acting on the molecules at the surface and molecules between the bulk of a solid material ("Surface Tension", 2013). The direction of the forces acting on the solid surface only happen at one side of the molecule, and thus the resultant force is not equilibrium at the surface. Meanwhile, the direction of forces acting at the bulk of the material happen in all direction thus resultant force is in equilibrium.

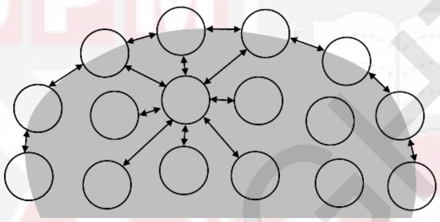

Figure 1.1: Illustration of net cohesive force acting on particle in the middle and surface of a liquid material.

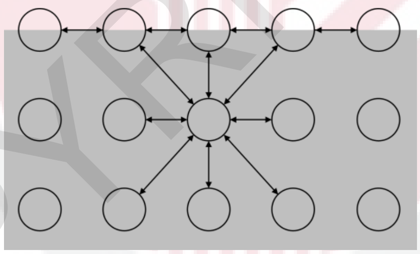

Figure 1.2: Illustration of net cohesive force acting on particle in the middle and surface of a solid material.

Besides material surface energy, surface morphology of the material will also affect the hydrophobic properties of the material at the surface (Valipour M. *et al.*, 2014). Surface roughness is defined as the shorter frequency of real surface relative to the troughs (Keyence, 2012). The relationship between the surface roughness and surface hydrophobicity is explained by the Wenzel and Cassie-Baxter state (Valipour M. *et al.*, 2014). They formulated a mathematical approximation that a rough surface is able to enhance the hydrophobicity and hydrophilicity properties of the surface. Furthermore, to produce rough surface for hydrophobic enhancement, roughening agent can be added to the material and this roughening agent can come from various types of materials such as silica and graphene (Zhang *et al*., 2016: Zhou *et al*., 2012).

There are a few considerations that need to be highlighted to select suitable materials for production of hydrophobic coating. One of the considerations is that, the selected material must meet the purposes of the coating. The materials must have the ability to bind efficiently to the substrate, protect the substrate from environmental damages, and possess low surface energy.

1.3 Tetraethyl Orthosilicate

Tetraethyl orthosilicate (TEOS) is a silane chemical compound commonly used as coupling agent that has the ability to form a durable bond between organic and inorganic materials (Arkles, 2006). TEOS has a hydrolysable group ($O - C_2H_5$ bond) which typically alkoxy, which easily reactive through hydrolysis process and condensed with other silanol group. Besides that, glass substrate also shows excellent bonding performance with the TEOS coupling agent (Arkles, 2006: Arkles, 2014). Figure 1.3 shows the chemical structure of TEOS which exploited as one of the silane coupling agent materials.

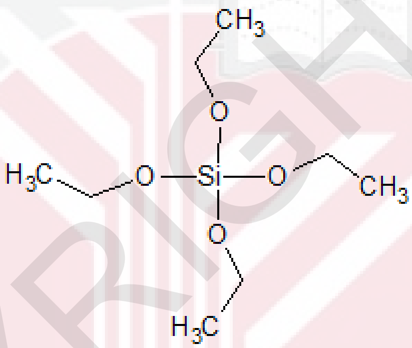

Figure 1.3: Structure of tetraethyl orthosilicate which is used as coupling agent.

Moreover, some researchers have used TEOS as the coupling agent for glass substrate because of the ability of TEOS to form transparent coating (Li *et al*., 2003). TEOS was also found to be easily hydrolysed and suitable to be used as coupling agent to introduce hydrophobic surface with contact angle of ≥90° (Yu *et al*., 2007). Other than that, TEOS coating also shows good anti-corrosion properties on glass material when tested under controlled environment (Liu *et al*., 2005). Thus, the TEOS coating is capable to produce hydrophobic, transparent, and anti-corrosion coating on glass substrate.

Since that TEOS is a silane-based solution so it is easy to mix TEOS with other types of silane-based solution that exhibit different properties. This method is to introduce desired/additional properties to the TEOS coating.

1.4 Fluoro-carbon Silane

Fluoro-carbon silane is a silane attached to a long fluoro-carbon chain. Well known fluoro-carbon silane is heptadecafluorodecyltrimethoxysilane (HFTMS) which contains fluoro-carbon chain and silane at one end and has water contact angle of 115° on smooth surface (Arkles, 2006). Figure 1.4 shows the structure and molecular bonds of HFTMS.

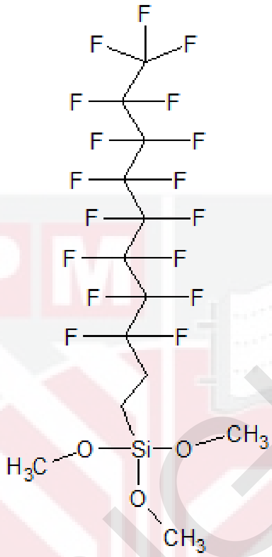

Figure 1.4: Silane with fluoro-carbon chain.

Any molecule with fluorocarbon bond, generally the electronegativity of the structure is high since the carbon-fluorine is packed to itself with bond length about 1.35Å and high bond dissociation energy of 544 kJ/mol (Clark, 2007). This closely packed fluorocarbon chain prevents the electrons to move freely because surrounded by negative charges from the fluorine atoms which lead to repulsion among them. The repulsion force among the fluorine atoms reduces the overall molecular density thus reducing the surface energy of that structure.

Other reasons of why fluorocarbon chains on the surface can introduce low surface energy is basically of the low lattice spacing of 5.9Å (Dalvi & Rossky, 2010). Later in the work, they also stated that the hydrophobicity of a fluorinated surface is due to the fluorocarbons molecules that packed less dense than hydrocarbon molecules on the surface which lead to poorer Van der Waals interaction with water. The result shows that the hydrophobicity of fluorocarbons in terms of geometry is because of their size is much bigger than the hydrocarbons. They also reported that the surface energy of hydrophobic surface is much lower also because of their Lennard-Jones interactions than just electrostatic interactions. The Lennard-Jones interactions is defined as the interaction of attraction and repulsion between a pair of neutral atoms or molecule.

A hydrophobic surface using fluorine-based chemical on cotton fabric dipped with fluorooctyl triethoxysilane (FOS) diluted with mixture of ethanol and water has shown higher contact angle when the concentration of the fluorine in the mixture is increased (Erasmus & Barkhuysen, 2009). They have reported that the method was able to produce a cotton fabric with self-cleaning ability where the water droplets could easily roll-off and carry along the dust on the surface.

Other than that, a surface energy treatment utilising a functionalized silica nanoparticle of ~120 nm in diameter with fluoroalkyl silane (FAS 17) in ethanol solution have been reported by J. Brassard et. al. The functionalized silica nanoparticles were spin coated on glass substrate for multiple times to produce thick hydrophobic coatings. The coated sample showed an increase of water contact angle value as the number of coating layers were added (Brassard *et al*., 2012).

The major or main objective of a coating is to give protection the substrate or give additional finish to the substrate material towards environment. This objective automatically increases the speculation among consumers to understand the coating lifespan and quality under such various environment. Hence, a testing must be done by the innovator to test the coating lifespan and quality so that it can be understood by the consumer.

1.5 Coating Degradation

Coating degradation is a study of coating quality after being exposed to any conditions in order to understand the coating lifetime (Perrin *et al.*, 2009). Besides that, the process of coating degradation could also be used to study samples recovery properties, changes in morphology, and coating transformation (Cui *et al*., 2015). These factors stated can cause great influence on the properties of a hydrophobic coating.

Since this study uses TEOS based hydrophobic coating that reacts quickly with the presence of water through hydrolysis process, thus it is crucial to understand the effect of dried TEOS coating against water degradation. A recent study reveals that TEOS coating is able to be stronger, less packed, and shows suitability properties for hydrophobic coating after in contact with water solution (He *et al*., 2009). Besides that, other researchers also come up with an idea that the coating strength and stiffness increases after undergoing water aging process (Einarsrud *et al*., 2001). Other than that, a technique was also developed in order to study TEOS coating sturdiness after going through water and ethanol aging process (Soleimani Dorcheh & Abbasi, 2008).

The aging instrument and method can be made by dipping the samples in and out of water bath continuously for a period of time and consistently replace the water bath to prevent the removed coating particles from re-adhering the surface (Cui *et al*., 2015). Therefore, the measurement after the aging process is important to study the deformation of the coating properties and quality.

1.6 Motivation of the research

The market and demands for the self-cleaning and hydrophobic surface are increasing along with the new technology advancement. The self-cleaning and hydrophobic surfaces are able to increase water resistive properties of many materials such as metal, electronics, and glass. Besides that, a surface with self-cleaning ability will able to reduce manpower and also operation cost to clean the surface. A self-cleaning surface would not need an extra work to be done on the surface since dust, oil and other particles cannot stick on the surface. An extra work would have to be done in order to maintain the cleanliness of the surface such as hiring workers to wipe off any stuck particles on the surface in order to maintain the performance of the surface. Big cities with high skyscrapers usually pay workers to climb the exterior of the building just to clean the windows and this is a very dangerous and high cost work. This problem can be overcomed by using self-cleaning surface on buildings.

Besides that, spray coating technique is also cost effective, simple, reproducible, and has excellent coating coverage performance when involving rough surface with holes, grooves, trenches and cavities (Yu *et al*., 2006). Spray coating technique has been studied to create a superhydrophobic surface with a contact angle of ≥150° and sliding angle of ≤10°, by using the simple and inexpensive instrument on paper substrate (Ogihara *et al.,* 2012). Spray coating technique was also used to produce superhydrophobic and transparent coating from ZnO solution on glass micro slide (Tarwal & Patil, 2010).

Furthermore, the ability of the coating to withstand weathering effects in various environment situation is also one of the factors to identify the quality of a coating. Since TEOS solution has an excellent performance to bond and form coating layer on glass substrate, the coating is expected to provide excellent protection for the substrate (Arkles, 2006). A high-performance coating is said to provide durable protection from the weather, chemicals, and abrasion or other forces that possibly affecting the substrate (Acrymax Technologies, 2011).

1.7 Problem Statements

The current coating techniques which includes spin coating are showing lots of disadvantages which one of it is bad finishing when involving complex surface topography of the substrate (Yu, 2006). On the other hand, of dip coating technology are demanding clean room for operation, higher chemistry cost, experienced and trained operator, and expensive equipment to operate (Poté, 2016). Besides that, the evaporation rate of the coating solution must be considered when using dip and spin coating technique because these techniques involve the movement of substrate which will enhance the coating evaporation rate if operated at high speed (Yimsiri & MacKley, 2006).

The ability of the hydrophobic surface in mimicking the lotus leaf characteristics to repel water has attracted many attentions as it can introduce to a self-cleaning surface by minimizing the contact area of water droplet and decreasing the adhesion of dust or contaminant (Liu, Liang, Zhou, & Liu, 2012). However, the present hydrophobic surface technology still shows low surface self-cleaning performance and this minimises the application of hydrophobic surface in the industry. Thus, the development for hydrophobic surface with higher contact angle that has higher water repellences to ensure better water protection to improve cleanliness of substrate is demanding (Erasmus & Barkhuysen, 2009).

In order to produce a transparent superhydrophobic coating, the chemical composition of the coating solution must be selected wisely to prevent it from blocking the visible light spectrum. The properties of the coating must possess several requirements such as coating thickness and coating surface roughness. The thickness of the coating must be controlled as it can reduce the light transmission (Kaempgen *et al*., 2005). Besides that, the roughness of the coating surface also needs to be manipulated so that the diffusion of the light is minimal. Light rays might be scattered after hitting the rough surface thus making the coating look opaque (Ogihara *et al*., 2012). Wenzel (1936) and Cassie-Baxter (1944) have studied the effect of surface roughness on superhydrophobic surface in their mathematical model (Bhushan & Nosonovsky, 2010). According to the study, high surface roughness can trap and scatter the light effectively thus reduce the transparency of the coating. Overall, the optimum roughness needs to be studied in order to produce a transparent and hydrophobic surface.

Coating adhesion is due to the summation of interactions of the intermolecular bonding forces in a perfectly bonded system (Rowe, 1987). Adhesion is the strength of the bond between two or more bodies acts at interphase in between coating and the substrate. A good and functioning coating is based on the coating adhesiveness to stay on the substrate (Samimi *et al*., 2011). A peeled off coating due to low adhesion strength can no longer protect the substrate as the substrate is exposed to the surrounding. The functionality of the coating's material depends on the ability of the coating to remain securely attached to the substrate's surface. Coating failures always happened when the coated layer/film got peeled off due to its aging process or when mechanical stress is applied onto it. Environmental effects that strongly influenced the aging process could deform or corrode the surface layer of the coating easily (Cui *et al*., 2015). Furthermore, the adhesiveness between the coating layer and the water (liquid) droplet is also one of the important aspects need to be taken into consideration. The properties of the liquid coating adhesiveness will determine the interaction energy between the coating and water droplet. Hence, the adhesive strength between the substrate-coating layer and liquid-coating layer must be tested to resolve whether the coating has good adhesion and suitability for a variety of applications.

1.8 Objectives of the Research

The main objective of the research project is to deposit and study a silica-based hydrophobic nanocoating mainly TEOS on a silicate glass by using aerosol spray system (patented PI 2017704529) and to characterize it optical and mechanical properties for consumer application.

To achieve this purpose, the research work is further studied and deliberated. Therefore, the objectives of the research are divided into four small objectives to facilitate the research work.

The first objective is to study surface contact angle of water droplet on the coated silica surface. The contact angle is a characterization technique to determine the hydrophobicity of the surface. The contact angle of the water droplet will be measured and analysed at different spray process parameter to find the relationship between contact angle and surface energy. The contact angle is measured by dropping 5μl water droplet on the coating surface. The image of water droplet on the substrate's surface is captured with digital camera and measured in ImageJ software. The contact angle is then used to calculate the surface energy of the coating and then reported and analysed to study the surface hydrophobic properties.

The second objective is to study the surface roughness of the coating. The roughness of the surface is important as the water will sit on the air pocket that has much lower surface energy and particle density. The properties of hydrophobicity and its effect from surface roughness will be studied in order to improve the contact angle of the water droplet. The surface roughness is measured by using atomic force microscopy (AFM). For surface roughness measurement, the scanning area is 10 × 10 μm by using non-contact tapping mode.

The third objective is to investigate the visible light optical transmission and refractive index of the silica based hydrophobic coating on glass substrate. The optical properties of the surface will be measured using Ultraviolet-visible (UV-Vis) Spectrometer for optical transmission, and ellipsometer for refractive index. These optical characteristics of the silica based hydrophobic coating is a crucial measurement to determine the suitability and durability of the coating toward harsh environmental condition when use on the car windshield, eyeglass, and others. The optical transmission and reflection coefficient of the coating will be characterized by visible light wavelength using standard UV-Vis spectrometer, while the refractive index of the coating will be determined using optical ellipsometer.

The final objective is to study the adhesion quality at coating-substrate and liquid-coating interphase. The adhesiveness of the coating at the coating-substrate interphase is tested by using adhesion tape peel test technique according to the American Society for Testing and Material (ASTM) D3359-09, meanwhile for adhesiveness at the coating-liquid interphase is calculated by using Young-Dupre Equation. In ASTM D3359-09 technique, the coating's surface is observed for any detached coating flakes after scratching and tape peeling process. Furthermore, the adhesion at the liquid-coating interphase is determined by taking into account the water contact angle data and coating surface energy data through calculation of using Young-Dupre Equation.

1.9 Thesis Outline

Chapter 1 consist of the introduction of the research. This chapter contains the idea of the development of the hydrophobic coating and its application in real life. Besides that, this chapter also discusses the problems from real life and previous researches which are in the field of coating technology and water repellence coating. The problems focus on coating technology such as dip coating, spin coating, spray coating, and hydrophobic coating. Finally, the objectives of this research are also presented in this chapter.

Chapter 2 discusses current researches and findings related to the hydrophobic coating. The related fabrication methods are mentioned in this section and used as guidance to determine the most effective fabrication method. Besides that, the coating characterization techniques are also discussed in this section. Furthermore, this chapter also contains the development of contact angle measuring instrument to assist in the determination of water contact angle and surface energy of the coating. Other than that, factors that affecting the hydrophobicity of a surface such as surface roughness is also discussed in this chapter.

Chapter 3 introduced the methodology of sample preparation and characterization technique used to measure the physical, optical and hydrophobic properties of the samples in this research. The preparation of the sample’s explanation starts from the making of the coating solution, spray process, drying process, until aging testing. Meanwhile, the characterization methods used in this research includes, contact angle measurement, surface roughness, refractive index, visible light transparency, and coating adhesiveness. Moreover, the data analysing techniques used in interpreting the data are also discussed in this section.

Chapter 4 demonstrated the experimental result of physical, optical and adhesion characterization of the coating. This chapter covers the experimental results and analyzation for both original and aging samples. The experimental results and analyzation in this chapter include the measurement of contact angle, surface roughness, refractive index, visible light transparency, and coating adhesiveness for both original and aging samples.

Chapter 5 is the final chapter of this thesis which presents the conclusion of this research work. All of the findings from the analysed data’s in Chapter 4 are summarized in this chapter to form a conclusion. The conclusion covers all of the measurements which are contact angle measurement, surface roughness, refractive index, visible light, and coating adhesiveness for all original and aging samples. Besides that, this chapter also includes suggestions and improvements that could be done in future works which are related to this field.

REFERENCES

About Optical Coatings. (n.d.). Retrieved from https://www.thomasnet.com/about/optical-coatings-15821200.html

Acrymax Technologies, Inc. - Flexible Solutions in High-Perfomance Coating Systems. (n.d.). Retrieved from http://www.acrymax.com/qualitycoatings.html

Arkles, B. (2006). *Hydrophobicity, Hydrophilicity and Silanes. Paint & Coatings Industry*, (October),114. Retrieved from http://www.gelest.com/goods/pdf/Library/advances/HydrophobicityHydrophilicityandSilanes.pdf

Arkles, B., Maddox, A., Singh, M., Zazyczny, J. and Matisons, J. (2014). Silane Coupling Agents: Connecting Across Boundaries (3rd Edition).

Aziz, F., & Ismail, A. F. (2015). Spray coating methods for polymer solar cells fabrication: A review. *Materials Science in Semiconductor Processing*, 39, 416–425.

Barthlott, W., & Neinhuis, C. (1997*).* Purity of the sacred lotus or escape from contamination in biological surfaces. *Planta*, 202(1), 1–8.

Bayer, I. S., Krishnan, K. G., Robison, R., Loth, E., Berry, D. H., Farrell, T. E., & Crouch, J. D. (2016). Thermal Alternating Polymer Nanocomposite (TAPNC) Coating Designed to Prevent Aerodynamic Insect Fouling. *Scientific Reports*, 6(November), 1–13.

Beers, R. F. & Sizer, I. W. (1951). A Spectrophotometric Method for Measuring the Breakdown of Hydrogen Peroxide by Catalyse. *Journal of Biological Chemistry*, *195*, 133–140.

Bhushan, B., & Nosonovsky, M. (2010). The rose petal effect and the modes of superhydrophobicity. *Philosophical Transactions. Series A, Mathematical, Physical, and Engineering Sciences*, 368, 4713–4728.

Brassard, J.-D., Sarkar, D. K., & Perron, J. (2012). Fluorine Based Superhydrophobic Coatings. *Applied Sciences*, 2(2), 453–464.

Brinker, C. J. (1988). Hydrolysis and Condensation of Silicates: Effects on Structure. *Journal of Non-Crystalline Solids*, 100(3), 31–50.

Brown, L. M., Springer, J., & Bower, M. (1992*).* Chemical substitution for 1,1,1-trichloroethane and methanol in an industrial cleaning operation. *Journal of Hazardous Materials*, 29(2), 179–188.

Butt, H. J., Golovko, D. S., & Bonaccurso, E. (2007). On the derivation of young's equation for sessile drops: Nonequilibrium effects due to evaporation. *Journal of Physical Chemistry B*, 111(19), 5277–5283.

Butt, H., Graf, K., & Kappl, M. (2003). *Physics and chemistry of interfaces*. Weinheim, Germany: Wiley-VCH.

C. Jeffrey Brinker, G. W. S. (1990). *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*. Sol-Gel Processing, Academic Press, San Diego.

Cai, S., Zhang, Y., Zhang, H., Yan, H., Lv, H., & Jiang, B. (2014). Sol − Gel Preparation of Hydrophobic Silica Antireflective Coatings with Low Refractive Index by Base / Acid Two-Step Catalysis, 8–13.

Chandler, D. (2005). Interfaces and the driving force of hydrophobic assembly. Nature, 437(7059), 640-647.doi:10.1038/nature04162

Chou, T., & Cao, G. (2003*).* Adhesion of Solgel Derived Organic Inorganic Hybrid Coating on Polyester. *Journal of Sol-Gel Science and Technology*.

Clark, J. (2007). *Intermolecular Bonding and The Physical Properties of PTFE*. Retrieved from https://www.chemguide.co.uk/qandc/ptfe.html

CSC Scientific Company (2018). *Viscosity, Testing the Flowability of Liquid Products*. Retrieved from http://www.cscscientific.com/viscosity

Cui, J., Daniel, D., Grinthal, A., Lin, K., & Aizenberg, J. (2015*).* Dynamic polymer systems with self-regulated secretion for the control of surface properties and material healing. *Nature Materials*, 14(June), 1–6.

Dalvi, V. H., & Rossky, P. J. (2010). *Molecular origins of fluorocarbon hydrophobicity*. Proc. Natl. Acad. Sci. U.S.A., 107(31), 13603–13607.

De Coninck, J., Dunlop, F., & Rivasseau, V. (1989). On the microscopic validity of the Wulff construction and of the generalized Young equation. *Communications in Mathematical Physics*, 121(3), 401–419.

Einarsrud, M. A., Nilsen, E., Rigacci, A., Pajonk, G. M., Buathier, S., Valette, D., … Ehrburger-Dolle, F. (2001). Strengthening of silica gels and aerogels by washing and aging processes. *Journal of Non-Crystalline Solids,* 285(1–3),1–7.

Erasmus, E., & Barkhuysen, F. A. (2009). Superhydrophobic cotton by fluorosilane modification. *Indian Journal of Fibre and Textile Research*, 34(4), 377–379.

Fung, R. M., & Parrott, E. L. (1980). Measurement of Film-Coating Adhesiveness, 69(4), 1979–1981.

Gao, L. C., & McCarthy, T. J. (2006). Contact angle hysteresis explained. *Langmuir*, 22(14), 6234–6237.

Grimsley, G. R., & Pace, C. N. (2004). Spectrophotometric determination of protein concentration. *Curr Protoc Protein Sci*, Chapter 3, Unit 3 1.

Ha, J. W., Park, I. J., & Lee, S. B. (2008). Antireflection surfaces prepared from fluorinated latex particles. *Macromolecules*, 41(22), 8800–8806.

Hallab, N. J., Bundy, K. J., O'Connor, K., Moses, R. L., & Jacobs, J. J. (2001*)*. Evaluation of Metallic and Polymeric Biomaterial Surface Energy and Surface Roughness Characteristics for Directed Cell Adhesion. *Tissue Engineering*, 7(1), 55–71.

Han, J. T., Kim, S. Y., Woo, J. S., & Lee, G. W. (2008). Transparent, conductive, and superhydrophobic films from stabilized carbon nanotube/silane sol mixture solution. *Advanced Materials*, 20(19), 3724–3727.

Hattori, A. (1997). Measurement of glass surface contamination. *Journal of Non-Crystalline Solids*, 218, 196–204.

He, F., Zhao, H., Qu, X., Zhang, C., & Qiu, W. (2009*)*. Modified aging process for silica aerogel. *Journal of Materials Processing Technology*, 209(3), 1621–1626.

Hegde, N. D., & Venkateswara Rao, A. (2006). Organic modification of TEOS based silica naerogels using hexadecyltrimethoxysilane as a hydrophobic reagent. *Applied Surface Science*, *253*(3), 1566–1572.

Heinke, W., Leyland, A., Matthews, A., Berg, G., Friedrich, C., & Broszeit, E. (1995). Evaluation of PVD nitride coatings, using impact, scratch and Rockwell- C adhesion tests. *Thin Solid Films*, 270, 431–438.

Hejda, F., Solar, P., & Kousal, J. (2010). Surface Free Energy Determination by Contact Angle Measurements – A Comparison of Various Approaches. *WDS'10 Proceedings of Contributed Papers*, (3), 25–30.

Hiromoto, S., & Tomozawa, M. (2011). Hydroxyapatite coating of AZ31 magnesium alloy by a solution treatment and its corrosion behavior in NaCl solution. *Surface and Coatings Technology*, 205(19), 4711–4719.

Holgerson, P., Sutherland, D. S., Kasemo, B., & Chakarov, D. (2005*)*. Patterning and modification of PDMS surface through laser micromachining of silicon masters and molding. *Applied Physics A: Materials Science and Processing*, *81*(1), 51–56.

Hołowacz, I., Podbielska, H., Bauer, J., & Ulatowska-Jarza, A. (2005). Viscosity, surface tension and refractive index of tetraethylorthosilicate-based sol- gel materials depending on ethanol content. *Optica Applicata*, *35*(4), 691–699.

Hopper, M. L. (1999). Automated one-step supercritical fluid extraction and clean-up system for the analysis of pesticide residues in fatty matrices. *Journal of Chromatography A*, 840(1), 93–105.

Ishizaki, T., & Sakamoto, M. (2011). Facile formation of biomimetic color-tuned superhydrophobic magnesium alloy with corrosion resistance. *Langmuir*, 27(6), 2375–2381.

Kaempgen, M., Duesberg, G. S., & Roth, S. (2005). Transparent carbon nanotube coatings. *Applied Surface Science*, 252(2), 425–429.

Kakani, S. L., & Kakani, A. (2004). *Material Science*, 657.

Kawaguchi, M., Fukushima, T., & Miyazaki, K. (1994). The Relationship Between Cure Depth and Transmission Coefficient of Visible-light-activated Resin Composites. *Journal of Dental Research*, 73(2), 516–521.

Kelly, P. J., Zhou, Y., & Postill, A. (2003). A novel technique for the deposition of aluminium-doped zinc oxide films. *Thin Solid Films*, 426(1–2), 111–116.

Keyence. (2012). Introduction to Surface Roughness Measurement.

Kim, H. J., Lee, C. H., & Hwang, S. Y. (2005). Fabrication of WC-Co coatings by cold spray deposition. *Surface and Coatings Technology*, 191(2–3), 335–340.

Klein, R. J., Biesheuvel, P. M., Yu, B. C., Meinhart, C. D., & Lange, F. F. (2003). Producing Super-Hydrophobic Surfaces with Nano-Silica Spheres. *Zeitschrift Fur Metallkunde*, 94(4), 1–12.

Koohyar, F. (2013). Refractive Index and Its Applications. *Journal of Thermodynamics & Catalysis*, 4(2), 7544.

Kumar, D., Wu, X., Fu, Q., Ho, J. W. C., Kanhere, P. D., Li, L., & Chen, Z. (2015). Hydrophobic sol-gel coatings based on polydimethylsiloxane for self-cleaning applications. *Materials and Design*, 86, 855–862.

Lamour, G., Hamraoui, A., Buvailo, A., Xing, Y., Keuleyan, S., Prakash, V., … Borguet, E. (2010). Contact angle measurements using a simplified experimental setup. *Journal of Chemical Education*, 87(12), 1403–1407.

Li, C. (2016). Refractive Index Engineering and Optical Properties Enhancement by Polymer Nanocomposites, (May 2014).

Li, W., Seal, S., Megan, E., Ramsdell, J., Scammon, K., Lelong, G., … Richardson, K. A. (2003). Physical and optical properties of sol-gel nano-silver doped silica film on glass substrate as a function of heat-treatment temperature. *Journal of Applied Physics*, 93(12), 9553–9561.

Liu, X., Liang, Y., Zhou, F., & Liu, W. (2012). Extreme wettability and tunable adhesion: biomimicking beyond nature? *Soft Matter*, 8(7), 2070.

Liu, Y., Moevius, L., Xu, X., Qian, T., Yeomans, J. M., & Wang, Z. (2014). Pancake bouncing on superhydrophobic surfaces, 10(June), 515–519.

Liu, Y., Sun, D., You, H., & Chung, J. S. (2005). Corrosion resistance properties of organic-inorganic hybrid coatings on 2024 aluminum alloy. *Applied Surface Science*, 246(1–3), 82–89.

Long, J., & Chen, P. (2001). Surface characterization of hydrosilylated polypropylene: Contact angle measurement and atomic force microscopy. *Langmuir*, 17(10), 2965–2972.

Lou, M. S., Chen, J. C., & Li, C. M. (1998). Surface roughness prediction technique for CNC end-milling. *Journal of Industrial Technology*, *15*(1), 1–6.

Mahajan, A. M., Patil, L. S., Bange, J. P., & Gautam, D. K. (2004). Growth of SiO2 films by TEOS-PECVD system for microelectronics applications. *Surface and Coatings Technology*, 183(2–3), 295–300.

Montemor, M. F. (2014). Functional and smart coatings for corrosion protection: A review of recent advances. *Surface and Coatings Technology*, 258, 17–37.

Nuyttens, D., Baetens, K., De Schampheleire, M., & Sonck, B. (2007). Effect of nozzle type, size and pressure on spray droplet characteristics. *Biosystems Engineering*, 97(3), 333–345.

Ogihara, H., Xie, J., Okagaki, J., & Saji, T. (2012). Simple method for preparing superhydrophobic paper: Spray-deposited hydrophobic silica nanoparticle coatings exhibit high water-repellency and transparency. *Langmuir*, 28(10), 4605–4608.

Paint & Coating Industry. (2001, May 31). *Dynamic Surface Tension and Surface Energy in Ink Formulations and Substrates*. Retrieved from https://www.pcimag.com/articles/85879-dynamic-surface-tension-and-surface-energy-in-ink-formulations-and-substrates

Perrin, F. X., Merlatti, C., Aragon, E., & Margaillan, A. (2009). Degradation study of polymer coating: Improvement in coating weatherability testing and coating failure prediction. *Progress in Organic Coatings*, 64(4), 466–473.

Poté, M. (2016). Dip Coating vs. Spin Coating, 1–9.

Prabakar, S., & Assink, R. A. (1997). Hydrolysis and condensation kinetics of two component organically modified silica sols. *Journal of Non-Crystalline Solids*, 211(1–2), 39–48.

Prevo, B. G., Hwang, Y., & Velev, O. D. (2005). Convective Assembly of Antireflective Silica Coatings with Controlled Thickness and Refractive Index, (2), 3642–3651.

Puertas Arbizu, I., & Luis Pérez, C. J. (2003). Surface roughness prediction by factorial design of experiments in turning processes. *Journal of Materials Processing Technology*, 143–144(1), 390–396.

Quéré, D. (2002). Rough ideas on wetting. *Physica A: Statistical Mechanics and Its Applications*, 313(1–2), 32–46.

Rhee, S. K. (1977). Surface energies of silicate glasses calculated from their wettability data. *Journal of Materials Science*, 12(4), 823–824.

Rohrig, B. (2017). *No-Hit Wonder! D30*. In ChemMatters (Vol. 1, pp. 8–10).

Rosenberger, F., Iwan, J., Alexander, D., & Jin, W. (1992). Gravimetric capillary method for kinematic viscosity measurements. *Review of Scientific Instruments*, 63(9), 4196–4199.

Rowe, R. C. (1988). Adhesion of film coatings to tablet surfaces -a theoretical approach based on solubility parameters. *International Journal of Pharmaceutics*, 41(3), 219–222.

Rulison, C. (2000). *Two-component surface energy characterization as a predictor of wettability and dispersability*. KRUSS Application Note AN213, 49(40). Retrieved from

Samimi, A., & Zarinabadi, ‹. S. (2011). An Analysis of Polyethylene Coating Corrosion in Oil and Gas Pipelines. *Journal of American Science*, 7(71), 1032–1036.

Satas, D., & Tracton, A. A. (Eds.). (2001). *Coatings Technology Handbook (Second ed.)*. New York, USA: Marcel Decker.

Schrader, M. E. (1995). Young- Dupre Revisited. *Langmuir*, 11(6), 3585–3589.

Sklodowska, A., & Matlakowska, R. (1997). Influence of exopolymers produced by bacterial cells on hydrophobicity of substrate surface, 11(11), 837–838.

Soleimani Dorcheh, A., & Abbasi, M. H. (2008). Silica aerogel; synthesis, properties and characterization. *Journal of Materials Processing Technology*, 199(1), 10–26.

Soon, C. F., Omar, W. I. W., Nayan, N., Basri, H., Narawi, M. B., & Tee, K. S. (2013). A Bespoke Contact Angle Measurement Software and Experimental Setup for Determination of Surface Tension. *Procedia Technology*, 11(Iceei), 487–494.

Stalder, A. F., Kulik, G., Sage, D., Barbieri, L., & Hoffmann, P. (2006). A snake-based approach to accurate determination of both contact points and contact angles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 286(1–3), 92–103.

Stalder, A. F., Melchior, T., Müller, M., Sage, D., Blu, T., & Unser, M. (2010). Low-bond axisymmetric drop shape analysis for surface tension and contact angle measurements of sessile drops. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 364(1–3), 72–81.

Tarwal, N. L., & Patil, P. S. (2010). Superhydrophobic and transparent ZnO thin films synthesized by spray pyrolysis technique. *Applied Surface Science*, 256(24), 7451–7456.

Tian, C. S., & Shen, Y. R. (2009). Structure and charging of hydrophobic material/water interfaces studied by phase-sensitive sum-frequency vibrational spectroscopy. *Proceedings of the National Academy of Sciences*, 106(36), 15148–15153.

Tompkins, H. G., & McGahan, W. A. (1999). *Spectroscopic ellipsometry and reflectometry*. New York, United States of America: Wiley.

Valipour M., N., Birjandi, F. C., & Sargolzaei, J. (2014). Super-non-wettable surfaces: A review. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 448(1), 93–106.

Vazquez, G., Alvarez, E., & Navaza, J. M. (1995). Surface Tension of Alcohol + Water from 20 to 50 °C. *Journal of Chemical and Engineering Data*, 40(3), 611–614.

Vincent, A., Babu, S., Brinley, E., Karakoti, A., Deshpande, S., & Seal, S. (2007). Role of catalyst on refractive index tunability of porous silica antireflective coatings by sol-gel technique. *Journal of Physical Chemistry C*, 111(23), 8291–8298.

Wang, H., Fang, J., Cheng, T., Ding, J., Qu, L., Dai, L., … Lin, T. (2008). One-step coating of fluoro-containing silica nanoparticles for universal generation of surface superhydrophobicity. *Chemical Communications (Cambridge, England)*, (7), 877–879.

Wankhede, R. G., Thanawala, K., Khanna, A., & Birbillis, N. (2013). Development of Hydrophobic Non-Fluorine Sol-Gel Coatings on Aluminium Using Long Chain Alkyl Silane Precursor, 3(4), 224–231.

Washburn, E. W. (1921). The dynamics of capillary flow. Physical Review, 17(3), 273–283.

Webb, N. (2014). *External Influences on Liquid Viscosity and Your Spray System*. Retrieved from https://www.otpnet.com/external-influences-on-liquid-viscosity-and-your-spray-system/

Williams, D. L., Kuhn, A. T., Amann, M. A., Hausinger, M. B., Konarik, M. M., & Nesselrode, E. I. (2010). Computerised measurement of contact angles. *Galvanotechnik*, 101(11), 2502–2512.

Wojcik, A. B., & Klein, L. C. (1995). Transparent inorganic/organic copolymers by the sol-gel process: Thermal behavior of copolymers of tetraethyl orthosilicate (TEOS), vinyl triethoxysilane (VTES) and (meth)acrylate monomers. *Journal of Sol-Gel Science and Technology*, 5(2), 77–82.

Wu, G., Wang, J., Shen, J., Yang, T., Zhang, Q., Zhou, B., … Zhang, F. (2000). Novel route to control refractive index of sol-gel derived nano-porous silica films used as broadband antireflective coatings. *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, 78(2–3), 135–139.

Xu, Q. F., Wang, J. N., & Sanderson, K. D. (2010). A general approach for superhydrophobic coating with strong adhesion strength. *Journal of Materials Chemistry*, 20(28), 5961.

Xu, R., Pope, E. J. A., & Mackenzie, J. D. (1988). Structural Evolution of Sol-Gel Systems Through Viscosity Measurement. *Journal of Non-Crystalline Solids*, 106, 242–245.

Yimsiri, P., & MacKley, M. R. (2006). Spin and dip coating of light-emitting polymer solutions: Matching experiment with modelling. *Chemical Engineering Science*, 61(11), 3496–3505.

Yu, L., Lee, Y. Y., Tay, F. E. H., & Iliescu, C. (2006). Spray coating of photoresist for 3D microstructures with different geometries. *Journal of Physics: Conference Series*, 34(1), 937–942.

Yu, M., Gu, G., Meng, W. D., & Qing, F. L. (2007). Superhydrophobic cotton fabric coating based on a complex layer of silica nanoparticles and perfluorooctylated quaternary ammonium silane coupling agent. *Applied Surface Science*, 253(7), 3669–3673.

Zhang, S., Wang, Y. S., Zeng, X. T., Khor, K. A., Weng, W., & Sun, D. E. (2008). Evaluation of adhesion strength and toughness of fluoridated hydroxyapatite coatings. *Thin Solid Films*, 516(16), 5162–5167.

Zhang, Y., Qu, S., Cheng, X., Gao, X., & Guo, X. (2016). Fabrication and Characterization of Gecko-inspired Dry Adhesion, Superhydrophobicity and Wet Self-cleaning Surfaces. *Journal of Bionic Engineering*, 13(1), 132–142.

Zhou, Y., Xu, F., Jiang, G., Wang, X., Hu, R., Wang, R., … Chen, W. (2012). Superhydrophobic and high adhesive performance of functionalized graphene films. *Powder Technology*, 230, 247–251.