CHEMICAL MODIFICATION OF NATURAL RUBBER WITH FLUOROALKYSILANE FOR OIL/WATER SEPARATION

BY

MISS JITTRAPORN SAENGKAEW

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE (CHEMISTRY)

DEPARTMENT OF CHEMISTRY

FACULTY OF SCIENCE AND TECHNOLOGY

THAMMASAT UNIVERSITY

ACADEMIC YEAR 2017

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THESIS

BY

MISS JITTRAPORN SAENGKAEW

ENTITLED

CHEMICAL MODIFICATION OF NATURAL RUBBER WITH FLUOROALKYLSILANE FOR OIL/WATER SEPARATION

was approved as partial fulfillment of the requirements for the degree of Master of Science (Chemistry)
on November 14th, 2017

Chairman

(Assistant Professor Chantip Samart, D.Eng.)

Advisor

(Assistant Professor Suwadee Kongparakul, Ph.D.)

Member

(Napida Hincharern, Ph.D.)

Dean

(Associate Professor Somchai Chakhatrakan, Ph.D.)

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ABSTRACT

A superhydrophobic/superoleophilic stainless steel mesh with excellent oil/water separation efficiency was successfully via simple and environmental friendly method by coating of encapsulation particles. The natural rubber-encapsulated silica (NR/SiO₂) can undergo the chemical reaction with fluoroalkylsilane (FAS) under alkaline conditions at 4-8°C to provide the NR/SiO₂ modified with FAS. Firstly, the natural rubber was encapsulated with inorganic silica shell using tetraethyl orthosilicate (TEOS) as a silica precursor. The thermal behavior investigated by thermogravimetric analysis (TGA) showed the thermal stability enhancement of natural rubber after encapsulated with silica shell. The morphology of NR/SiO₂ from TEM images revealed rubber core fully covered by silica shell. Secondly, the surface of NR/SiO₂ was modified with trimethoxy(3,3,3-trifluoropropyl) silane (FAS-3) or 1H,1H,2H,2H-perfluorodecyltrimethoxysilane (FAS-17) group. The water contact angle (WCA) of unmodified meshed including uncoated mesh, NR coated mesh and NR/SiO₂ coated mesh are 77.5°, 85.2° and 0°, respectively. In the meanwhile, the water contact angle (WCA) of meshes after dip-coated with NR/SiO₂ modified FAS-3 and NR/SiO₂ modified FAS-17 are 138° and 153.9°, respectively. Furthermore, the modified mesh exhibits excellent oil/water
separation efficiency (>99.74%) solely by gravity, even after being cycled 30 times. Therefore, the coating surface with NR/SiO$_2$ modified FAS is applicable to use as coating material for oil/water separation.

**Keywords:** Natural Rubber, Encapsulation, Fluoroalkylsilane, Silica, Superhydrophobic, Superoleophilic, Stainless steel mesh, Oil/water separation
ACKNOWLEDGEMENTS

This thesis has been well succeeded owing to the kind support and cooperation from many persons as follows:

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Miss Jitraporn Saengkaew
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<td>AFM</td>
<td>Atomic Force Microscope</td>
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<tr>
<td>ATR-FTIR</td>
<td>Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethylammonium Bromide</td>
</tr>
<tr>
<td>DRC</td>
<td>Dry Rubber Content</td>
</tr>
<tr>
<td>DTG</td>
<td>Derivative Thermogravimetric Analysis</td>
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<tr>
<td>FAS</td>
<td>Fluoroalkylsilane</td>
</tr>
<tr>
<td>FAS-3</td>
<td>Trimethoxy(3,3,3-trifluoropropyl)silane</td>
</tr>
<tr>
<td>FAS-17</td>
<td>1H,1H,2H,2H-Perfluorodecyltrimethoxysilane</td>
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<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
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<tr>
<td>MAS</td>
<td>Magic-Angle Spinning</td>
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<td>NMR</td>
<td>Nuclear Magnetic Resonance Spectroscopy</td>
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<td>NR</td>
<td>Natural Rubber</td>
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<td>NR coated mesh</td>
<td>The mesh was dip-coated with NR latex.</td>
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<tr>
<td>NR/SiO₂ coated mesh</td>
<td>The mesh was dip-coated with NR/SiO₂ latex.</td>
</tr>
<tr>
<td>NR/SiO₂ modified FAS-3 coated mesh</td>
<td>The mesh was dip-coated with NR/SiO₂ modified FAS-3 latex.</td>
</tr>
<tr>
<td>NR/SiO₂ modified FAS-17 coated mesh</td>
<td>The mesh was dip-coated with NR/SiO₂ modified FAS-17 latex.</td>
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<tr>
<td>NRL</td>
<td>Natural Rubber Latex</td>
</tr>
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<td>OCA</td>
<td>Oil Contact Angle</td>
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<td>OM</td>
<td>Optical Microscope</td>
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<tr>
<td>Symbols/Abbreviations</td>
<td>Terms</td>
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<tr>
<td>PETMP</td>
<td>Pentaerythritol tetra (3-mercaptopropionate)</td>
</tr>
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<td>PFDTDS</td>
<td>1H,1H,2H,2H-Perfluorodecyltrichlorosilane</td>
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<tr>
<td>PFOTDS</td>
<td>1H,1H,2H,2H-Perfluorooctyltriethoxysilane</td>
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<td>SDS</td>
<td>Sodium Dodecyl Sulfate</td>
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<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
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<td>TEOS</td>
<td>Tetraethyl Orthosilicate</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analyzer</td>
</tr>
<tr>
<td>TMTVSi</td>
<td>2,4,6,8-Tetramethyl-2,4,6,8-Tetravinylcyclotetrasiloxane</td>
</tr>
<tr>
<td>WCA</td>
<td>Water Contact Angle</td>
</tr>
<tr>
<td>η</td>
<td>Oil/Water Separation Efficiency</td>
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<tr>
<td>m_{water}</td>
<td>The water content determined by the titration method</td>
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<tr>
<td>m_{collected}</td>
<td>The weight of the collected oil after separation process</td>
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CHAPTER 1
INTRODUCTION

1.1 The Purpose of the Investigation

A pollution from oily wastewater is happening every day since industrial oily wastewater, household waste and oil spill accidents keep doing damage to environment. Therefore, oil/water separation has become a worldwide challenge [1]. The methods of treatment oily wastewater have many approaches such as gravity separation, coagulation, oil skimmer, filtration, centrifugal machine, flotation, absorbing materials and combustion [2-6]. On the other hand, the most of the methods involve complicated processing steps, long processing time and secondary pollution during the process. The separating materials stand out from a simple, universal and environmentally friendly for oil and water separation [7]. In addition, the surface with hydrophobic/oleophilic wettability has triggered research in the field of filtration [8-9]. The separating materials with special wettability and micro-nanoscale structure have attracted increasing ability of hydrophobic/oleophilic property. The material, which is modified with fluoroalkylsilane (FAS) features low-surface-energy material due to hydrophobic fluoro-compound ending group. Many types of hydrophobic surface have been created by researchers in recent years. For example, the PU sponges that exhibit superhydrophobicity/superoleophilicity (WCA = 157° and OCA = 0°) are fabricated by chemical vapor deposition (CVD) of tetraethyl orthosilicate (TEOS) and then dip-coated in a fluoropolymer (FP) aqueous solution. The sponges show excellent reusability and oil stability of oil absorbent. The superhydrophobic PU sponge is very promising materials for oil absorption and oil/water separation [10]. The research presents fabricating a novel fluorinated polybenzoxazine (F-PBZ) modified nanofibrous membrane optimized to achieve gravity driven oil/water separation. The membrane was prepared by a facile combination of electrospun poly(m-phenylene isophthalamide) (PMIA) nanofibers and an in situ polymerized F-PBZ functional layer with SiO$_2$ nanoparticles (SiO$_2$ NPs) [11]. Hence, FAS is often to modify with polymer
and in order to achieve hydrophobicity or superhydrophobic property [12]. The modified materials are applied to self-cleaning, oil absorption and oil/water separation materials.

Natural rubber (NR) is an important polymer from natural resource in Thailand. In addition, the NR latex system is outstanding green system more than another polymer [13]. The chemical structure of NR (cis-1,4-polyisoprene) is generally known as hydrophobic polymer and FAS is well known as low surface materials. In this research, the natural rubber-encapsulated silica (NR/SiO$_2$) was modified with FAS to improve hydrophobic and oleophilic characteristic of oil/water separation materials. The different types of FAS groups including trimethoxy(3,3,3-trifluoropropyl)silane (FAS-3) and 1H,1H,2H,2H-perfluorodecyl-trimethoxy silane (FAS-17) were used in this study. The separation efficiency and reusability of mesh were discussed. The mesh characteristics such as functionality, morphology, thermal stability and hydrophobic properties of stainless steel mesh were characterized.

### 1.2 Objectives

The objective of thesis can be summarized follows:

1. To synthesis natural rubber-encapsulated silica (NR/SiO$_2$) and NR/SiO$_2$ modified fluoroalkylsilanes (FAS).
2. To study the properties of NR/SiO$_2$ and NR/SiO$_2$ modified fluoroalkylsilanes (FAS).
3. To study the application of NR/SiO$_2$ modified fluoroalkylsilanes (FAS).

### 1.3 Scope of the Investigation

The experimental procedure for this research was presented as follows:

1. Synthesis of natural rubber-encapsulated silica (NR/SiO$_2$) latex via sol-gel process. The effect of various type of surfactants (anionic, cationic and nonionic), temperature (6-50°C), reaction time (20 and 240 min), TEOS to NR
weight ratios (1:50 and 4:50) and flow rate of adding TEOS (1.0 and 4.0 mL/min) were studied.

2. Synthesis of NR/SiO$_2$ modified fluoroalkylsilanes (FAS). The effect of various type of FAS (Trimethoxy(3,3,3-trifluoropropyl)silane; FAS-3 and 1H,1H,2H,2H-perfluorodecyltrimethoxysilane; FAS-17) and FAS-3 concentration (0.105, 0.157, 0.209 and 0.262 mmol) were studied.

3. Study the properties of NR/SiO$_2$ and NR/SiO$_2$ modified fluoroalkylsilane synthesis. The chemical structures were determined by Fourier transform infrared (ATR-FTIR) spectroscopy, a real-time in situ mid-infrared measurements and $^{29}$Si solid-state NMR spectroscopy. The morphologies were observed by transmission electron microscope (TEM) and thermal propertied were examined by thermogravimetric analysis (TGA). The particles sizes of NR/SiO$_2$ and NR/SiO$_2$ modified fluoroalkylsilanes synthesis were determined.

4. Study the properties of modified mesh. The morphologies of modified mesh were observed by optical microscope (OM), atomic force microscope (AFM) and scanning electron microscope equipped with energy-dispersive spectroscopy (SEM-EDS). The hydrophobicity and oleophilicity of uncoated and coated mesh were determined by oil and water contact angle.

5. Study the oil/water separation efficiency and reusability with modified stainless steel mesh. The effect of various type of non-polar liquids (hexane, dodecane, toluene, gasohol 95 and diesel) and oil/water mixture ratios (75%, 50% and 25% v/v) were studied.
CHAPTER 2
REVIEW OF LITERATURE

2.1 Oil

An oil can be defined as any neutral, nonpolar chemical substance, which exhibits both hydrophobicity (water fearing) and oleophilicity (miscible with oils). Oil is viscous liquid at ambient temperature, high carbon, high hydrogen, volatility and customarily flammable. The structure of oil consists of different hydrocarbons that composes the range from a light gas to heavy solid. In addition, each of oil types differ in their structure, volatility, viscosity and toxicity. The viscosity of oil is a measure of its resistance to flow. Volatility can be referred to oil evaporation in the air [14].

The various types of oil will affect the environment differently. Therefore, the character of various oily wastewater can be described into 4 basic types [15].

- **Type 1: Very Light Oils**

  The very light oils such as gasoline and jet fuels are highly and volatile that these are usually complete within 1 to 2 days after oil pollution. These oils are also high soluble toxic compounds and high flammable. The boiling point of very light oils are range between 30 and 200°C. A water can mix with very light oils that these will destroy aquatic life and environments around there.

- **Type 2: Light Oils**

  The light oils for example home heating, No. 2 fuel oil, light crude and diesel are moderately volatile. These oils have a typical boiling point range of 200-300°C. The concentration of soluble toxic compounds is medium. Light oil will affect around intertidal zone with long-term contamination potential.
• **Type 3: Medium Oils**

  The medium oils (most crude oils) are less volatile. The boiling point of medium oils are range 300-500°C. About two-thirds of the amount oils will evaporate within 24 hours. A water is less likely to mix with medium oils. These oils can be served a long-term pollution of intertidal zone. The fur-bearing mammal and waterfowl are affected from medium oils also.

• **Type 4: Heavy Oils**

  The heavy oils such as No. 6 fuel oil, heavy crude oils and bunker C are less evaporation or dissolution. In general, boiling point of heavy oils is over around 500°C. A water does not readily mix with heavy oils. These oils can cause contamination of intertidal zone and possible long-term pollution of sediments. The fur-bearing mammal and waterfowl are affected from ingestion and coating of heavy oils. In addition, shoreline cleanup of this type is difficult.

2.2 Oily Wastewater Treatment Methods

Oily wastewater is polluted oil and water mixture in composition and it cannot be used for productive process. Industrial oily wastewater, household waste and oil spill accident can create serious environmental problems. Nowadays, the methods of treatment oily wastewater should be developed. Oily wastewater treatment methods may be used singly of chemical, physical, biological, electrical or combination method responding on the aims of treatment, type of polluted oil, location of pollution and wastewater characteristic. The method for oily wastewater treatment can be subjected to 5 methods including thermal treatment, chemical treatment, biological treatment, electrolytic treatment and physical treatment [16-24].

2.2.1 Thermal Treatment

*In situ* burning is a simple method for cleaning up oil spill in near shore zone, on water surface, wetlands and other area situation. This method can rapidly reduce the volume of oil pollution and eliminate to the transport, collect, and store of
recovered oil. The procedure time to clean up can be shortened; therefore, it can reduce oil spread on the water and protect aquatic life. However, in situ burning can produce pollution during process. It has the potential to impact animal and human health from toxic smoke; hence this method is technique more suitable for use away from populated zone. Moreover, carbon dioxide (CO₂), unburned oil and some smoke particulate as a residue will remain after in situ burning process [16, 17]. The oily wastewater treatment by in situ burning method is shown in Figure 2.1 and 2.2.

![Figure 2.1](image1) Oil spill cleanup process by in situ burning method [18].

![Figure 2.2](image2) Fireproof boom for in situ burning method [19].
2.2.2 Chemical Treatment

Chemical treatment is the most widely used that it usually includes coagulation or acidification and follows by flocculation. This method uses chemical (chemical agents such as surfactants, acid chemicals, base chemicals, solvents and other compounds) designed to change its chemical and/or physical properties of oily wastewater, which is enhanced degradation and reduced physical contact with biota and objects. Normally, oily wastewater requires large amounts of acid to adjust the pH below 4. Hence, the problems of method are corrosion, slowly removes oil from environment and high volumes of sludge toxic [20]. The oily wastewater treatment by chemical treatment is shown in Figure 2.3.

![Chemical treatment](image)

**Figure 2.3** Oily wastewater treatment by chemical treatment [21].
2.2.3 Biological Treatment

Bioremediation is the process of the microbial metabolism from small organisms such as fungi, yeasts and bacteria. This method, either aerobic or anaerobic, has successfully been used in the cleanup of oily wastewater. This method presents naturally; however, treatment time is longer than other methods and has residual toxic to biota and corals [20]. The oily wastewater treatment by biological treatment is shown in Figure 2.4.

Figure 2.4 Oily wastewater treatment process by biological treatment [22].
2.2.4 Electrolytic Treatment

The electrolytic process of treating oily wastewater uses an electrolytic cell, which immerses in the oily wastewater composed electrolytes. The electrolytes that have positive and negative charges are ionic compounds conducting electricity in aqueous solution. This method presents a green alternative of cleanup method and electrochemical approach to waste removal are many. However, electrolytic treatment has the disadvantage about iron electrodes because the color of polluted solution during and after treatment is changed to green and yellow generated from $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$, respectively [23]. The oily wastewater treatment by electrolytic treatment is shown in Figure 2.5.

![Figure 2.5 Oily wastewater treatment diagram of electrochemical pilot-scale plant](image-url)
2.2.5 Physical Treatment

Physical methods of oily wastewater treatment use the natural force such as electrical attraction, gravity and van der Waal forces for removal of waste. Generally, the chemical structures of the target substances are not changed by physical treatment. In some case, physical states are changed as agglomerate or vaporization. Physical treatments include separating materials, gravity separation, flotation, adsorption materials and sedimentation. The physical method of oily wastewater treatment by separating materials is shown in Figure 2.6.

![Figure 2.6](image.jpg)

**Figure 2.6** The physical treatment by separating materials [8].

2.3 Surface Wettability

The wettability of solid interfaces bases on their surface roughness and surface energy. The surface properties are important for applicable oil/water separation. Thus, in this section will start with describing the basic concept of surface wettability including surface energy, surface roughness and creating hydrophobic surfaces.
2.3.1 Surface Energy

The Young’s law (Equation 2.1) describes the surface wetting behavior of a liquid on a flat and rigid surface [25].

\[ \gamma_{SL} + \gamma_{LG} \cos \theta_Y = \gamma_{SG} \]  \hspace{1cm} (Equation 2.1)

In which \( \gamma_{SL}, \gamma_{LG} \) and \( \gamma_{SG} \) are the surface free energies between solid-liquid, liquid-gas, and solid-gas, respectively. The \( \gamma_{SL} \) can be described by the following Equation 2.2;

\[ \gamma_{SL} = \gamma_{SG} + \gamma_{LG} - \sqrt{\gamma_{SG} \cdot \gamma_{LG}} \]  \hspace{1cm} (Equation 2.2)

The degree of wetting and the contact angle (\( \theta_C, CA \)) according to Young’s law, equation is shown schematically in Figure 2.7.

![Figure 2.7 Schematic of the parameters in Young’s law.](image)

The water contact angle (\( \theta_C \)) of the hydrophobic and the hydrophilic are larger than 90° and less than 90°, respectively.

A surface is called as superhydrophobic surface when the water contact angle (WCA) is higher than 150°. Superhydrophobic surface has been correlated to low surface energy and high surface roughness. However, the smooth surface as low-energy surfaces just exhibit the highest water contact angle around 110° to 120°.
In addition, the contact angles (CA) are based on the surface free energy (SFE) and time of liquid spreads on the surfaces. The wettability of liquid on solid surface can determine by adhesive work ($W_a$) that results from the molecular interactions between the solids and liquids and cohesive work ($W_c$) of the liquids molecules among themselves (Figure 2.8). Table 2.1 shows that the wettability will be defined by the relative strength of the adhesive (solid/liquid) and cohesive (liquid/liquid) force. The CA presents nearly complete wetting from strong adhesion and weak cohesion of work. As adhesive force weaken and cohesive force strengthen, the CA is increased.

![Figure 2.8](image)

**Figure 2.8** The interactions between the liquid and the solid surface [26].

<table>
<thead>
<tr>
<th>CA (°)</th>
<th>Wetting</th>
<th>Adhesive force</th>
<th>Cohesive force</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Complete</td>
<td>Strong</td>
<td>Weak</td>
</tr>
<tr>
<td>60</td>
<td>High</td>
<td>Strong</td>
<td>Weak</td>
</tr>
<tr>
<td>90</td>
<td>Moderate</td>
<td>Weak</td>
<td>Weak</td>
</tr>
<tr>
<td>120</td>
<td>Low</td>
<td>Weak</td>
<td>Strong</td>
</tr>
<tr>
<td>180</td>
<td>None</td>
<td>Weak</td>
<td>Strong</td>
</tr>
</tbody>
</table>

Table 2.1 Wettability of various contact angle

(ramé-hart instrument co.)
The $W_a$ and $W_c$ are related with the surface free energy (SFE), following to Equation 2.3 and 2.4, respectively.

\[ W_a = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \quad \text{(Equation 2.3)} \]

\[ W_c = 2(\gamma_{LV}) \quad \text{(Equation 2.4)} \]

In which, the $\gamma_{LV}$, $\gamma_{SV}$ and $\gamma_{SL}$ are the liquid-vapour, solid-vapour and solid-liquid interfaces.

The difference between the cohesive work ($W_c$) and adhesive work ($W_a$) can explain the spreading coefficient ($S$), which is explained as the difference between the surface free energy of the solid surface when wet and dry [27]. The spreading coefficient ($S$) related to work of adhesion and cohesion, according to Equation 2.5.

\[ S = W_a - W_c = [\gamma_{SV}]_{\text{dry}} - [\gamma_{LV} + \gamma_{SL}]_{\text{wet}} \quad \text{(Equation 2.5)} \]

Owens and Wendt created the concept about the SFE at liquid-vapor and solid-vapor interfaces. Therefore, the SFE is consisted in two components including the Lifshitz-van der Waals component (dispersive contribution, $\gamma^d$) and Lewis acid-base component (polar contribution, $\gamma^p$) [28]. The $\gamma^p$ and $\gamma^d$ for the SFE can be explained in the Equation 2.6 and 2.7 for liquids and solids, respectively.

\[ \gamma_{LV} = \gamma_{LV}^d + \gamma_{LV}^p \quad \text{(Equation 2.6)} \]

\[ \gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p \quad \text{(Equation 2.7)} \]

The interfacial energy of two phases can be approximated by:

\[ \gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2(\sqrt{\gamma_{SV}^d \gamma_{LV}^d} + \sqrt{\gamma_{SV}^p \gamma_{LV}^p}) \quad \text{(Equation 2.8)} \]

By combining with the Young equation, $\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$ obtains:

\[ \frac{\gamma_{LV}(1+\cos \theta)}{2\sqrt{\gamma_{LV}^d}} = \sqrt{\gamma_{SV}^d \gamma_{LV}^d} + \sqrt{\gamma_{SV}^p \gamma_{LV}^p} \quad \text{(Equation 2.9)} \]
where \( \gamma \) is the surface free energy. The superscripts d and p refer to the dispersive and polar contribution to the surface free energy of material and the subscripts SV, LV and SL refer to the solid-vapor and liquid-vapor and solid-liquid surfaces, respectively.

The linear relation written in terms of the independents variable \( \left( \frac{\gamma_{LV}^p}{\gamma_{LV}^d} \right)^{1/2} \) and of the dependent variable \( \frac{\gamma_{LV}(1 + \cos \theta)}{2 \sqrt{\gamma_{LV}^d}} \), allows us to define the square root of the dispersive and polar contribution. When surface tension of component is known, the two unknowns \( \gamma_{SV}^p \) and \( \gamma_{SV}^d \) are simultaneously solved by linear, referred to as the Owens-Wendt equation.

In addition, the harmonic mean prefers for low surface energy such as polymers, water, organic liquids and organic pigments [29]. The harmonic mean can be used to calculate the dispersive and polar components of the surface energy by measuring the angles of two liquids, water(A) and dodecane(B).

The two equations are then:

\[
W_{SL(A)} = \gamma_{LV(A)}(1 + \cos \theta_A) = \frac{4\gamma_{LV(A)}^d\gamma_{SV}^d}{\gamma_{LV(A)}^d + \gamma_{SV}^d} + \frac{4\gamma_{LV(A)}^p\gamma_{SV}^p}{\gamma_{LV(A)}^p + \gamma_{SV}^p} \tag{Equation 2.10}
\]

\[
W_{SL(B)} = \gamma_{LV(B)}(1 + \cos \theta_B) = \frac{4\gamma_{LV(B)}^d\gamma_{SV}^d}{\gamma_{LV(B)}^d + \gamma_{SV}^d} + \frac{4\gamma_{LV(B)}^p\gamma_{SV}^p}{\gamma_{LV(B)}^p + \gamma_{SV}^p} \tag{Equation 2.11}
\]

where \( W_{SL}, \gamma_{LV} \) and \( \gamma_{SV} \) are work of adhesion between solid-liquid phase, liquid-vapour interfaces and solid-vapour interfaces. The superscripts d and p refer to the dispersive and polar contribution to the surface free energy of material and the subscripts A and B refer to water and dodecane, respectively.

Moreover, the harmonic mean is used also for the polar components. The justification of this assumption is not necessarily solid, but is necessary here to obtain an analytical solution. This set of equations may be converted to two second degree equations as given below.

\[
a^d(\gamma_{SV}^d)^2 + b^d\gamma_{SV}^d + c^d = 0 \tag{Equation 2.12}
\]

\[
a^p(\gamma_{SV}^p)^2 + b^p\gamma_{SV}^p + c^p = 0 \tag{Equation 2.13}
\]
where the constants are

\[
\begin{align*}
\ a^d &= ABBA - AABA & \text{(Equation 2.14)} \\
\ b^d &= CBA - CABA - DABA + DABA & \text{(Equation 2.15)} \\
\ c^d &= DBCA - DCA & \text{(Equation 2.16)} \\
\ a^p &= ABA - ABA & \text{(Equation 2.17)} \\
\ b^p &= BBA - BABA - DABA + DABA & \text{(Equation 2.18)} \\
\ c^p &= DBBA - DABA & \text{(Equation 2.19)} \\
\end{align*}
\]

and

\[
\begin{align*}
\ A_i &= \gamma_{LV_i}(3 - \cos \theta)/4 & \text{(Equation 2.20)} \\
\ B_i &= \gamma_{LV_i}[\gamma_{LV_i}^d - \gamma_{LV_i}(1 + \cos \theta)/4] & \text{(Equation 2.21)} \\
\ C_i &= \gamma_{LV_i}^d \left[\gamma_{LV_i}^p - \gamma_{LV_i}(1 + \cos \theta)/4\right] & \text{(Equation 2.22)} \\
\ D_i &= \gamma_{LV_i}^d \gamma_{LV_i}^p \gamma_{LV_i} \left[(1 + \cos \theta)/4\right] & \text{(Equation 2.23)} \\
\end{align*}
\]

for i is A(water) and B(dodecane), respectively and \( \gamma \) is the surface free energy. The superscripts \( \text{p} \) and \( \text{d} \) refer to the polar and dispersive contribution to the surface free energy of a given material and the subscripts LV refer to the liquid–vapor surfaces.

The roots of the second degree equations are found in the usual way and obtain the positive roots [30-31].

2.3.2 Surface Roughness

The hypotheses of rough surface are explained by Wenzel and Cassie–Baxter model [32]. The Wenzel model explains the wetting, which the liquid fills the cavities of the surface as presented in Figure 2.9(a). The Wenzel model can be described by the following in Equation 2.24 when \( \theta^* \) is the apparent contact angle, \( \theta \) is the static contact angle if the surface would be ideally smooth and \( r \) is the ratio between the actual surface area and the projected surface area. Thereby, the static contact angle will rise, if the surface area is roughened surface.

\[
\cos \theta^* = r \cos \theta \quad \text{(Equation 2.24)}
\]
The Cassie-Baxter model is shown in Figure 2.9(b). The air is trapped in the pockets between water and solid surface. The rough surface is considered to be a porous hydrophobic material unfavorable for the liquid to penetrate. This leads to the entrapment of air, which can be considered as a hydrophobic phase.

A drop in the Wenzel state has been shown to adhere more to the substrate with compared to a drop in the Cassie-Baxter state, even if it exhibits a higher static contact angle due to the filling of the surface cavities by water. The air-pockets in the Cassie-Baxter state give fewer points of contact, which lead to low adhesion and lower contact angle hysteresis. Consequently, this gives lower sliding angles and a better water repelling surface.

Figure 2.9 Illustrations of (a) Wenzel and (b) Cassie model.
2.3.3 Creating Hydrophobic Surfaces

The creation of surface as hydrophobic or superhydrophobic surface is interesting. Because the materials can repel water with high efficient and can be used widely application such as self-cleaning materials, oil adsorption, oil separation, waterproof materials.

The hydrophobic surfaces can be designed by combining low surface energy and roughness surface such as silica, fluoroalkylsilane (FAS) groups, polymer of inorganic-containing compound (PDMS) and polymer of fluoro-containing compound (PTFE).

- Silica
Silica combining of tetrahedral \((\text{SiO}_4)\) is connected by Si-O-Si bridges. Silica materials have a silanol group \((\text{Si-OH})\) on their surfaces thereby the silica surface is an easily modified. The sol-gel process is the method for the fabrication of oxide structure. The concept of sol-gel reaction including hydrolysis and condensation reaction is shown in Equation 2.25-2.27.

Hydrolysis reaction
\[
\text{(RO)}_3\text{Si-OR} + \text{H}_2\text{O} \longrightarrow (\text{RO})_3\text{Si-OH} + \text{ROH} \quad \text{(Equation 2.25)}
\]

Alcohol condensation
\[
(\text{RO})_3\text{Si-OH} + \text{RO-Si(OR)}_3 \longrightarrow (\text{RO})_3\text{Si-O-Si(OR)}_3 + \text{ROH} \quad \text{(Equation 2.26)}
\]

Water condensation
\[
(\text{RO})_3\text{Si-OH} + \text{HO-Si(OR)}_3 \longrightarrow (\text{RO})_3\text{Si-O-Si(OR)}_3 + \text{H}_2\text{O} \quad \text{(Equation 2.27)}
\]

The silica surface exhibits hydrophilic from silanol groups, which occurs through hydrogen bonding. To reduce interaction with the water, the surface is heated, hydroxyl group removed [33] or surface modified. Hydrophobic silica is achieved by the lowering extent of interaction with water and the lowering of surface free energy (SFE) (Figure 2.10). The lowering extent of interaction with water and the lowering of SFE can be increased of hydrophobic surface [34].
Fluoro-containing groups

An alkyl and fluorinated alkyl groups exhibit very low surface energy of interaction with water and can be achieved to superhydrophobic surfaces. Table 2.2 shows the relative hydrophobic properties of the surfaces for flat surfaces. The superhydrophobic properties depend on magnitude of roughening [35].

Table 2.2 Water contact angles (WCA) for flat surfaces composed pure arrays of CF₃, CF₂, CH₃ and CH₂ terminal groups. Calculation was made by considering surface energies [36]

<table>
<thead>
<tr>
<th>Surface Terminal Group</th>
<th>Water contact angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CF₃-</td>
<td>120</td>
</tr>
<tr>
<td>-CF₂-</td>
<td>108</td>
</tr>
<tr>
<td>-CH₃-</td>
<td>111</td>
</tr>
<tr>
<td>-CH₂-</td>
<td>94</td>
</tr>
</tbody>
</table>

Fluoro-containing compounds exhibit hydrophobic characteristic owing to their low surface energy. It is also high reactivity also, which enables relatively high bonding strength towards the sample surface. Types of fluoro-containing chemicals such as fluorosilanes, fluoro plasma and fluorocarbons can be used to modify materials with hydrophobic characteristic.

Figure 2.10 Functionalization of a silica substrate with the lowing of SFE group and provide for the hydrophobic surface [34].
Figure 2.11 Chemical structure of 1H,1H,2H,2H-perfluorodecyltrimethoxysilane.

Figure 2.11 shows 1H,1H,2H,2H-perfluorodecyltrimethoxysilane structure. The alkoxy silanes part of the molecule and the CF$_{17}$-terminated chain are hydrophilic and hydrophobic group, respectively. The modifying of fluoro-containing groups via hydrolysis and condensation reaction can render the hydrophilic part of the molecule to react with some surface species.

Figure 2.12, the hydrated siloxy-chains include hydroxyl groups, which can react with hydroxyls surface through dehydration reactions. The hydrophilic part of the molecules is bound to the surface and the hydrophobic fluorinated chains reveal on the surface for repelling water.

Figure 2.12 The reaction of surface (hydroxyl groups) with a hydrolyzed fluoro-containing molecule; R as a hydrophobic fluoro chain [34].
• Polydimethylsiloxane (PDMS)

Polydimethylsiloxane (PDMS) is a polymer built up of dimethylsiloxane (Figure 2.13). These exhibit heat resistant properties, inert properties and mechanical properties that can be tuned by controlling the length of the polymer chains, branching and crosslinking. The chemical structure of PDMS has methyl groups, which reside at the interface rendering low surface energy and hydrophobic characteristic. The polymer is low surface energy but it is poor adhesion towards other surfaces often as a problem [37].

\[
\text{CH}_3 \quad \text{Si} \quad \text{O} \quad \text{CH}_3
\]

Figure 2.13 Chemical structure of a PDMS.

• Poly(tetrafluoroethylene) (PTFE)

Poly(tetrafluoroethylene) (PTFE) provides very low surface energy due to an insufficiency in favorable water on the polymer surface. The PTFE exhibits hydrophobicity, which it cannot interact with water because of no substantial access to the C-F bonds (Figure 2.14). PTFE is a high molecular weight and it is a solid state at room temperature; however, it can be shaped quite easily by heating. In addition, the roughness surface can be increased the hydrophobic property of surface materials [38].

\[
\text{F} \quad \text{C} \quad \text{F} \\
\text{C} \quad \text{C} \\
\text{F} \quad \text{F}
\]

Figure 2.14 Chemical structure of a PTFE.
2.4 Encapsulation

There are many of microparticles, which include microcapsules, coated granules, granular matrices and microspheres (Figure 2.15) among others.

![Figure 2.15 Morphologies of microparticles; (a) core shell microcapsule, (b) polynuclear core and homogeneous shell microcapsule, (c) mononuclear core and multi-shell microcapsule, (d) polymer matrix (microsphere), where the active is homogeneously or heterogeneously dispersed [39].](image)

The microcapsules contain within the core and surround with membrane or shell. It has one or several of cores and shells. The core may be liquid, solid, polymer, gaseous or other compounds. The shell can be an inorganic, an organic, a metal oxide or polymer. The membrane of capsule materials will protect the core compound from volatilization and harmful reactions to outside environment.

Encapsulation has a wide range of applications including industries, food products, pharmaceutics, cosmetics, perfume, printing, agriculture, adhesives, and dyes [39]. There are many techniques for microencapsulation, such as emulsification, coacervation, fluidized-bed coating, spray-drying, spray-cooling/chilling, freeze-drying, liposome entrapment and extrusion. [40-41].

The molecular level can achieve different performances and properties of microparticles (microcapsules and microspheres). For example, if it enhances hydrophobic compound, the surface of the microcapsule will increase rough surface and low surface energy.
The natural polymers for using are proteins (including albumin and gelatin) and polysaccharides (including starch, cellulose, chitosan and dextran) [42]. The synthetic polymers for using are polycyanoacrylates, polyesters, polystyrene, polyurethanes, polymethylacrylates, amino resins, polyacrylamide and polyamides [43-44]. Inorganic materials for microcapsule preparations include zeolites, silica, inorganic oxides and ceramics [45].

Natural rubber (NR) is an important polymer, which is derived from *Hevea brasiliensis*. NR consists *cis*-1,4-polyisoprene as a major compound (Figure 2.16). The system of NR has two systems including latex and solution system. For the solution system uses organic solvents, which affects in humans, animals and environments. While, liquid latex is preserved with ammonia to prevent bacterial growth when harvested from the tree. The commercial source of NR latex comprises of about 36% of rubber fraction, 5% of non-rubbers components such as protein, lipid, and sugar with water accounting for the remaining 59%. Thus, the NR latex system has advantageous over the NR solution system and other polymers to use. Because, latex system is free organic system, environmentally friendly; moreover, it is simple procedure.

![Chemical structure of cis-1,4-polyisoprene.](image)

2.5 Literature Review

Many techniques of treatment oily wastewater include *in situ* burning, chemical dispersant, biological dispersant, separating material, gravity separation, flotation, adsorption material and sedimentation. However, most methods involve complicated processing step, long processing time and secondary pollution during the process. The
separating materials stand out a simple, universal and environmentally friendly for oil/water separation [7]. Several researches have been reported the separating materials, which are modified with inorganic, organic or polymer.

Examples of separating materials have been reported in the literature including stainless steel mesh, copper mesh, polyethylene (PE), cotton and textile substrate. Wang et al. 2012 [46] reported a simple method for preparing superhydrophobic/superoleophilic stainless steel mesh. The mesh was modified with microstructured ZnO films. The modified mesh shows good selectivity and good recyclability for many applications, for example water treatment, liquid transportation and oil/water separation.

Song et al. 2014 [47] presented superhydrophobic/superoleophilic stainless steel mesh for filtration and collection of oil/water mixture. The mesh was modified with CuCl$_2$ and HCl. The modified mesh collects floating oil, which is in a container without pumping or pouring. The mesh presents excellent oil collection efficiency (>94%) and high purity (>99 wt %) of various oil including heavy mineral oil and motor oil. Hence, modified mesh can be demonstrated for pouring and gravity-driven separation material of oil/water mixing.

Yu et al. 2015 [8] studied the method of fabricated hydrophobic mesh, which was etched with FeCl$_3$ solution and coated with n-octadecylthiol (ODT). The mesh as stainless steel mesh shows high oil selectivity for variety of organic solvents and oil. The water contact angle of mesh is 145°. The mesh has been developed as material for continuous separation of oil/water mixture. The separation efficiency of mesh is more than 99.0 wt % with 10 cycles.

Liu et al. 2016 [7] reported that the copper mesh shows high oil/water separation efficiency of over 93% with recycled 10 times. Moreover, the mesh presents chemical stability and self-cleaning. This mesh exhibits superhydrophobicity (WCA = 155.5°) and superoleophilicity (OCA = 0°). The copper mesh was fabricated by electrodeposition and coating with lauric acid. These processes provide inexpensive and can use for large-scale system.
Zhao et al. 2016 [48] reported easily scaled-up and low-cost method of fabricating oil/water separation materials. The membrane was prepared by scarping and then prick ing the polyethylene (PE) membrane, which exhibited superhydrophobic, with a water contact angle of 153.4°. The membrane is used for oil/water separation solely by gravity, especially these useful in harsh condition such as highly acidic, alkaline and salty conditions. The separation efficiency is over 99.5% with 30 times. The membrane can be reused and exhibited very fast separation by gravity. Therefore, it presents high performance for use in consumer and industrial.

Sasmal et al. 2014 [49] prepared superhydrophobic surfaces via simple free-standing method with copper nanoparticles for water/oil separation, self-cleaning and roll-off. The types of substrates such as cotton, textile, wool, glass, silicon substrate and transparency sheet are studied. The surface of materials can exhibit high water contact angle (164 ± 2°), excellent self-cleaning and roll-off attribute.

From the literature review, the separating materials for treatment oily wastewater exhibit good oil collected efficiency. Furthermore, the referred articles are examples of research involving to use of fluoro-containing compounds, silica particles or combining of two compounds to achieve superhydrophobic surfaces and excellent oil collected efficiency. These have been a successful approach in many cases. The silica particles are used to create the roughness surface. The fluoro-containing compounds are contributed to low-surface energy property. Zhang et al. 2011 [50] reported a simple, versatile and inexpensive method to produce superhydrophobic and superoleophilic polyester textile through chemical vapor deposition (CVD) of trichloromethylsilane (TCMS). The treated textile is used for oil/water separation and selective oil absorption. The combination of superwetting properties of textiles makes them excellent materials for oil/water separation.

Tai et al. 2012 [51] studied new method for fabrication of free-standing carbonaceous composite membrane by using electrospinning technique followed by carbonization and calcination. The carbon nanofiber (CNF) membrane was prepared by mixing polyacrylonitrile (PAN), carbon nanofiber and TEOS as silica precursor. The
carbonaceous nanomaterials present excellent chemical inertness and thermal from hydrophobic/oleophilic characteristic. As a result, CNF membrane exhibits thermal stability, superhydrophobic and superoleophilic properties that it presents WCA of 144.2° ± 1.4° and OCA of 0°. The thermal and chemical stability tests confirm that the membrane is resistant from temperature up to 350°C and wide range of pH values (2-14). The membrane possesses excellent oil water separation with a gravity driven process.

Chen et al. 2015 [52] studied stainless meshes with number 145, 150 and 400 that were prepared via two-steps method. Firstly, the mesh was spray coating with thiol-ene hybrid consisting of pentaerythritol tetra(3-mercaptopropionate) (PETMP), 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (TMTVSi) and then fumed with silica nanoparticles. The morphology of mesh shows microscale roughness from nanoparticle aggregation. The mesh exhibits superhydrophobic (> 150°) and low roll-off angle (< 5°). The material coating also exhibits high separation efficiency with more than 99.85%, excellent pH and temperature resistance after curing.

Si et al. 2015 [53] prepared FIBER aerogels by electrospun nanofibers and freeze-dry method. It presents high elasticity in three-dimensional (3D) nanofibrous networks and superhydrophobicity. In the research study, superelastic (density <30 mg cm⁻³) and superhydrophobic (CA = 162°) characteristic aerogels are developed via PAN membranes and SiO₂ membranes. The PAN and SiO₂ nanofibers are building block to networks. The SiO₂ nanoparticles are introduced to increase porous of aerogels and cross-linking agent as benozoxaine (BAF-a). The FIBER aerogels can efficiency separate water in oil emulsions with using gravity-driven and self-priming pump (maximum of 8140 ± 220 L m⁻² h⁻¹). The aerogels also provided widely applicable in 3D macroscopic form for cleanup of oil spills and fuel purification.

Recently, Arslan et al. 2016 [54] prepared perfluoro functionalized cellulose acetate electrospun nanofibrous mats (FS/CA-NF) that exhibits superhydrophobic characteristic (WCA about 150°). The electrospun nanofibrous mats was functionalized with 1H,1H,2H,2H perfluorooctyltriethoxysilane (FS) via sol-gel process under basic
condition. The cellulose acetate (CA) structure has –OH group that can react through the chemical reaction with FS hybrid. The research presents novel hybrid material for oil/water separation. The hybrid sponge materials can separate oil/water mixture for many cycles therefore it has high potentials in wide application such as oil spill cleaning and oil/water separation.

Yokoi et al. 2014 [55] presented process of preparing superhydrophobic surfaces by coating the flouro-compound (1H,1H,2H,2H-perfluorodecytrichlorosilane, PFDTS) treated and then chemical etching step with SiO₂ nanoparticles, which modified with 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFOTS). This found that the fabricated mesh presents the superhydroobicity, with WCA of over 150°, low sliding angle of lower 25° and transmittance remains 79% after abrasion test under 100 cycles and 10 kPa of pressure. In addition, the mesh also exhibits acidic and basic resistance with wide range of pH (pH 2-14) and the surface of fabricated mesh can be used as oil/water separation materials.

Wu et al. 2015 [10] reported that the PU sponges with superhydrophobicity/superoleophilicity (WCA = 157° and OCA = 0°) were fabricated by chemical vapor deposition (CVD) of tetraethoxysilane (TEOS) and then dip-coated in a fluoropolymer (FP) aqueous solution. The sponges show excellent oil stability, and reusability of oil absorbency. PU sponges with superhydrophobic are very promising materials for oil absorption and oil/water separation.

Tang et al. 2015 [11] presented fabricating a novel fluorinated polybenzoxazine (F-PBZ) modified nanofibrous membrane that optimized to achieve gravity driven oil/water separation. The membrane was prepared by a facile combination of electrospun poly(4-phenylene isophthalamide) (PMIA) nanofibers and an in situ polymerized of F-PBZ layer with SiO₂ nanoparticles (SiO₂ NPs).

Oikawa et al. 2015 [56] prepared fluoroalkylated vinyltrimethoxysilane oligomer silica/talc nanocompoudes (R₁-VM-SiO₂/Talc) with variety of guest molecules such as perfluoro-2-methyl-3-oxahexanoic acid (R₁-COOH), 2-hydroxy-4-methoxybenzophenone (HMB), 3-(hydroxysilyl)-1-propanesulfonic acid (THSP), bisphenol AF and
bisphenol A (BPA) that were encapsulated into the Rf-VM-SiO₂/Talc core. The Rf-VM-SiO₂/Talc/Organic composites can prepare through sol-gel process under alkaline conditions. The gust molecules can provide to control wettability. For example, encapsulation of THSP as gust molecules into Rf-VM-SiO₂/Talc core can impart the superoleophobic/superhydrophilic properties. On the other hand, the encapsulation of HMB as gust molecules into Rf-VM-SiO₂/Talc core can afford the superoleophilic/superhydrophobic properties. Therefore, Rf-VM-SiO₂/Talc/Organic composites have high significant as a wide application material for oil/water separation.

This literature reviews make up the background for the choice of silica and fluoro-containing compounds for creating superhydrophobic/superoleophilic coating and encapsulation to modify surface properties in this study. The simple process is desired in order to make it industrially, applicable and economically feasible. In this work, the natural rubber (cis-1,4-polyisoprene) latex was encapsulated with silica (NR/ SiO₂), which has silanol group to interact with fluoroalkylsilane (FAS). Consequently, NR/SiO₂ modified FAS exhibits superhydrophobic/superoleophilic characteristic. The separating material can be used in application for oil/water separation and the process presents green system from using NR latex.
CHAPTER 3
RESEARCH METHODOLOGY

3.1 Chemicals

High ammonia natural rubber latex (NRL), 60% DRC : Rubber Research Institute, Thailand
Tetraethyl orthosilicate (TEOS), AR grade : Sigma-Aldrich
Ammonia solution, 25% v/v : Sigma-Aldrich
IGEPAL® CO-630, AR grade : Sigma-Aldrich
\( N^1-(3\text{-Trimethoxysilylpropyl})\text{diethylenetriamine}, \) AR grade : Sigma-Aldrich
Trimethoxy(3,3,3-trifluoropropyl)silane, ≥97.0% : Sigma-Aldrich
1\(H\),1\(H\),2\(H\),2\(H\)-perfluorodecyltrimethoxysilane, AR grade : Sigma-Aldrich
Methanol, AR grade : QRÈC
Cetyltrimethylammonium bromide (CTAB), AR grade : Ajax Finechem
Sodium dodecyl sulfate (SDS), AR grade : J.T.Baker Triton™
X-100, AR grade : ACROS
Hexane, AR grade : Sigma-Aldrich
Dodecane, AR grade : Sigma-Aldrich
Toluene, AR grade : Sigma-Aldrich
De-ionized water : ELGA water purifier

All chemicals were used without purification.
3.2 Equipment

- Particle Size Analyzer: Horiba Nano Partica SZ-100
- Attenuated Total Reflection: Perkin Elmer Spectrum 100
- Fourier Transform Infrared Spectrometer (ATR-FTIR)
- A Real-Time in Situ Mid-Infrared Measurements: Mettler-Toledo ReactIR 15
- $^{29}$Si Magic-Angle Spinning (MAS) NMR: Varian Unity Inova 300 NMR
- Transmission Electron Microscope (TEM): JEOL JEM-2100 and TECNAI 20
- Scanning Electron Microscope (SEM): JEOL JSM-5410 LV
- Thermogravimetric Analyzer (TGA): Mettler-Toledo TGA/SDTA 851°
- Optical Microscope (OM): Olympus BX50
- Contact Angle Measurement: Theta Lite TL100
- Atomic Force Microscope (AFM): Park System NX10

3.3 Preparation of Natural Rubber-Encapsulated Silica (NR/SiO$_2$)

Natural rubber-encapsulated silica (NR/SiO$_2$) was synthesized by one-pot procedure: 0.5 g of surfactant (cationic, anionic or nonionic) was dissolved in deionized water (DI water) and 15% dry rubber content (DRC) of natural rubber latex (NR latex) was drop-wised within 25 min through a dropping funnel. Then, TEOS with various concentration was drop-wised into the solution and continuously stirred at 6-50°C for 4 h to form homogeneous milky mixture. The NR/SiO$_2$ latex was stored at 4°C. The effect of surfactant types (cationic, anionic and nonionic), TEOS to NR weight ratios (1:50 and 4:50), temperature (6, 27 and 50°C), reaction time (20 and 240 min) and flow rate of adding TEOS (1 and 4 mL/min) were studied. The chemical structure of anionic, cationic and nonionic surfactant is shown in Figure 3.1.
3.4 Preparation of NR/SiO₂ Modified Fluoroalkylsilane (FAS)

The mixture containing 20 μL of methanol, 20 μL of TEOS, FAS with various content and 1000 μL of natural rubber-encapsulated silica (NR/SiO₂) from section 3.3 was stirred at 6°C for 5 h. The NR/SiO₂ modified with FAS latex was stored at 4°C. The effect of FAS types (FAS-3 and FAS-17) and FAS-3 concentration (0.105, 0.157, 0.209 and 0.262 mmol) were studied. The chemical structures of FAS-3 and FAS-17 are shown in Figure 3.2.
3.5 Characterization

3.5.1 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared (FTIR) spectra were obtained by Attenuated total reflection fourier transform infrared (ATR-FTIR) spectrometer (Perkin Elmer Spectrum 100, USA) in the wavenumber of range 4000 to 650 cm\(^{-1}\). The NR latex modified sample was dried at 60°C and cut into a square shape (0.3 cm × 2.0 cm × 2.0 cm) and placed onto a sample holder. A real-time \textit{in situ} mid-infrared measurements were carried out by a Mettler-Toledo ReactIR 15 instrument equipped with 6.3 mm AgX Fiber Conduit, DiComp (diamond) probe sensor and a liquid N\(_2\) MCT detector.

3.5.2 Nuclear Magnetic Resonance (NMR) Spectroscopy

\(^{29}\)Si magic-angle spinning (MAS) NMR spectra were recorded on a Varian Unity Inova 300 NMR spectrometer equipped with Varian 6 mm probes for solid state sample.

3.5.3 Thermal Behavior

The thermal behavior of the sample was performed on thermogravimetric analyzer (TGA/SDTA 851\(\text{e}\), Mettler Toledo, Switzerland). NR latex modified sample was dried and 0.011 g of sample was placed in an aluminum pan under a nitrogen atmosphere with the heating rate of 10°C min\(^{-1}\) and operated at 40 to 900°C.

3.5.4 Morphology Study

The morphology of particles was observed using a transmission electron microscope (TEM, JEM-2100, JEOL, Japan and TECNAI 20 TWIN, Philips, Netherlands) under an electron beam with an accelerating voltage of 120 kV. In addition, the morphology of meshes were characterized by scanning electron microscope equipped with energy-dispersive spectroscopy (SEM-EDS, JSM-5410 LV, JEOL, Japan) under low vacuum condition at an accelerating voltage of 20 kV and optical microscope (Olympus BX50, USA) with a MDPlan 10 objective lens that were captured by camera Olympus DP20. Atomic force microscope (AFM, NX10, Park System, Korea) equipped...
with NANOSENSORS™ PPP-NCHR probes (PointProbe® Plus Non-Contact/Tapping Mode - High Resonance Frequency - Reflex Coating). The AFM probe with nominal force constant $k = 42 \text{ N/m}$ and nominal frequency $f_0 = 330 \text{ kHz}$ was used. The typical radius of these tips is $<10 \text{ nm}$. All AFM procedures were conducted at room temperature ($25^\circ \text{C}$).

For the characterization of mesh surface by Atomic Force Microscope (AFM), it uses two dimension matrix that each $(x_i, y_j)$ array has a height of $h(x_i, y_j)$. It can be estimated a large number of points and statistical analyses of surfaces. The average height $\langle h(i,j) \rangle$ of surface is described by Equation 3.1

$$\langle h(i, j) \rangle = \frac{1}{n^2} \sum_{i=1}^{n} \sum_{j=1}^{n} h(i, j)$$  \hspace{1cm} (Equation 3.1)

where $n$ is the number of point and $h(i, j)$ is the height of $i^{th}$ and $j^{th}$ point.

The main parameter of statistical studied is root-mean-square (RMS or $R_q$) roughness as the standard deviation of the surface from the mean plane within the sampling area that it is described by Equation 3.2

$$R_q = \sqrt{\frac{1}{n^2} \sum_{i=1}^{n} \sum_{j=1}^{n} (h(i, j) - \langle h(i, j) \rangle)^2}$$  \hspace{1cm} (Equation 3.2)

The other important parameter for characterization asymmetry of the height distribution surface of mesh is skewness ($R_{sk}$). For the Gaussian distribution, the skewness is equal to zero. The skewness is defined as Equations 3.3.

$$R_{sk} = \frac{1}{nR_q^3} \sum_{i=1}^{n} (h(i, j) - \langle h(i, j) \rangle)^3$$  \hspace{1cm} (Equation 3.3)

As demonstrated, the sign of $R_{sk}$ is negative or positive, which it reveals proportionately below or above the mean surface level, respectively [57].
3.5.5 Contact Angle Measurement

The hydrophobicity of the mesh was characterized and presented as contact angle (CA) and surface free energy (SFE) of oil and water and surface energy using standard contact angle goniometer (TL100, Theta Lite, Finland). A drop of liquid was placed onto the mesh surface by 6 µL with microsyringe. The image of a liquid droplet was recorded by a CCD camera and analyzed the contact angle by the OneAttension software version 2.2.

The contact angle measurements were used to calculate the surface free energy (SFE) of the mesh. Contact angles (θ) on the surfaces were measured with a goniometer (TL100, Theta Lite, Finland). Several approaches for the surface energy calculation were proposed by Harmonic-mean equation. The SFE is composed of two components, the Lifshitz-van der Waals component (dispersive contribution, \( \gamma^d \)) and Lewis acid-base component (polar contribution, \( \gamma^p \)).

The harmonic mean can be used to calculate the dispersive and polar contribution of the surface energy by measuring the angles of two liquids, water (A) and dodecane (B).

The two equations are then:

\[
W_{SL(A)} = \gamma_{LV(A)} (1 + \cos \theta_A) = \frac{4\gamma_{LV(A)}^d \gamma_{SV}^d}{\gamma_{LV(A)}^d + \gamma_{SV}^d} + \frac{4\gamma_{LV(A)}^p \gamma_{SV}^p}{\gamma_{LV(A)}^p + \gamma_{SV}^p} \quad \text{(Equation 3.4)}
\]

\[
W_{SL(B)} = \gamma_{LV(B)} (1 + \cos \theta_B) = \frac{4\gamma_{LV(B)}^d \gamma_{SV}^d}{\gamma_{LV(B)}^d + \gamma_{SV}^d} + \frac{4\gamma_{LV(B)}^p \gamma_{SV}^p}{\gamma_{LV(B)}^p + \gamma_{SV}^p} \quad \text{(Equation 3.5)}
\]

where \( W_{SL}, \gamma_{LV} \) and \( \gamma_{SV} \) are work of adhesion between solid-liquid phase, liquid-vapour interfaces and solid-vapour interfaces. The superscripts d and p refer to the dispersive and polar contribution to the surface free energy of material and the subscripts A and B refer to water and dodecane, respectively.

Moreover, the harmonic mean is used also for the polar components. The justification of this assumption is not necessarily solid, but is necessary here to obtain an analytical solution. This set of equations may be converted to two second degree equations as given below.
where the constants are

\[ a^d (\gamma_{SV}^d)^2 + b^d \gamma_{SV}^d + c^d = 0 \quad \text{(Equation 3.6)} \]

\[ a^p (\gamma_{SV}^p)^2 + b^p \gamma_{SV}^p + c^p = 0 \quad \text{(Equation 3.7)} \]

and

\[ a^d = A_B B_A - A_A B_B \quad \text{(Equation 3.8)} \]

\[ b^d = C_B B_A - C_A B_B - D_A A_B + D_B A_A \quad \text{(Equation 3.9)} \]

\[ c^d = D_B C_A - D_A C_B \quad \text{(Equation 3.10)} \]

\[ a^p = A_B C_A - A_A C_B \quad \text{(Equation 3.11)} \]

\[ b^p = B_B C_A - B_A C_B - D_A A_B + D_B A_A \quad \text{(Equation 3.12)} \]

\[ c^p = D_B B_A - D_A B_B \quad \text{(Equation 3.13)} \]

for \( i \) is \( A(\text{water}) \) and \( B(\text{dodecane}) \), respectively and \( \gamma \) is the surface free energy. The superscripts \( p \) and \( d \) refer to the polar and dispersive contribution to the surface free energy of a given material and the subscripts \( \text{LV} \) refer to the liquid–vapor surfaces.

The roots of the second degree equations are found in the usual way and obtain the positive roots.

The selected test liquids were water and dodecane with analytical-reagent quality whose dispersive and polar components of the SFE that are shown in Table 3.1.
Table 3.1 Surface tension ($\gamma$) of components (mN/m) for selected contact angle test liquids at 25°C [58]

<table>
<thead>
<tr>
<th>Component</th>
<th>Total surface free energy ($\gamma_{LV}$) (mN/m)</th>
<th>Dispersion component ($\gamma_{LV}^d$) (mN/m)</th>
<th>Polar component ($\gamma_{LV}^p$) (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
<td>21.8</td>
<td>51.0</td>
</tr>
<tr>
<td>Dodecane</td>
<td>25.4</td>
<td>25.4</td>
<td>0</td>
</tr>
</tbody>
</table>

3.5.6 Surface Modification of Mesh Treated with the NR/SiO$_2$ Modified with Fluoroalkylsilane

The stainless steel mesh (#150) was cleaned in an ultrasonic bath with acetone for 30 min and DI water for 30 min to remove surface impurities. The mesh was dip-coated in latex system at room temperature, left for 3 min and dried at 70°C. The mesh was dip-coated with NR/SiO$_2$ modified FAS named as NR/SiO$_2$ modified FAS-3 coated mesh and NR/SiO$_2$ modified FAS-17 coated mesh and the mesh without FAS named as NR/SiO$_2$ coated mesh. The mesh was dip-coated with NR latex 2.5% DRC named as NR coated mesh and the pristine mesh named as uncoated mesh.

3.6.7 Oil/Water Separation Experiment

The various types of non-polar liquid as the representative of oil were selected for oil/water separation test. The viscosities and surface tensions of liquid using in experiment are listed in Table 3.2.
Table 3.2 Viscosity of liquid used in oil/water separation test

<table>
<thead>
<tr>
<th>Type of liquid</th>
<th>Viscosity at 40°C (cSt)</th>
<th>Surface Tension (mN m⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>0.27</td>
<td>16.5</td>
<td>[59] and [60]</td>
</tr>
<tr>
<td>Dodecane</td>
<td>1.1</td>
<td>24.1</td>
<td>[59] and [61]</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.55</td>
<td>27.0</td>
<td>[62]</td>
</tr>
<tr>
<td>Gasohol*</td>
<td>0.49</td>
<td>20.4</td>
<td>[62]</td>
</tr>
<tr>
<td>Diesel</td>
<td>3</td>
<td>27.3</td>
<td>[62]</td>
</tr>
<tr>
<td>De-ionized water</td>
<td>1</td>
<td>71.5</td>
<td>[62]</td>
</tr>
</tbody>
</table>

*Gasohol is a mixture of gasoline and ethanol with 95% of gasoline and 5% of ethanol.

Five types of non-polar liquids included hexane, dodecane, toluene, gasohol and diesel were selected to investigate the oil/water separation of the mesh. Hexane, dodecane and toluene were selected as representatives of short, long and aromatic hydrocarbon, respectively that are very important for petrochemical raw materials. Gasohol and diesel were selected as representatives of low-viscosity oil and high-viscosity oil, respectively. All tests were performed at 30°C.

The equipment consists of two tubes, which are 100 mm and 100 mm in length, respectively, and 25 mm in diameter (Figure 3.3). The hydrophobic nature of the coatings was tested with oil/water separation experiment. The mesh was cut circle shape (30 mm in diameter) and fixed between two tubes by four screws. The oil/water mixtures (75%, 50% and 25% v/v) of various types of oil were poured onto the mesh, and then the separation was proceeded by gravity. The oil/water separation efficiency was used to quantitatively describe the oil/water separation ability of the as-prepared stainless steel mesh. The collected oil was then weighed and the water content in the collected oil was measured based on a titration method according to the reference [8]. The oil/water separation efficiency ($\eta$, expressed as a percentage) was determined with the following equation:
\[ \eta (%) = \left( \frac{m_{\text{collected}} - m_{\text{water}}}{m_{\text{collected}}} \right) \times 100 \]  

(Equation 3.18)

where \( m_{\text{water}} \) and \( m_{\text{collected}} \) are the water content (g) determined by the titration method and the weight (g) of the collected oil after separation process, respectively.

**Figure 3.3** Separation equipment.

**Determination of the Water Content**

For the determination of the water content of the oil collected from the separation process (Figure 3.4), a typical procedure is presented as follow. Before the separation process, 0.01 M of NaOH aqueous solution (12.5% v/v to 37.5% v/v) was added in water (12.5% v/v to 37.5% v/v). Then, oil (25% v/v to 75% v/v) was added to make the oil/water mixture. After the separation process ended, the collected oil
was weighted and then titrated with 0.01 M HCl aqueous solution in the presence of bromothymol blue indicator. Water content in the collected oil was determined by the following equation:

\[ m_{\text{water}} = V_{\text{HCl}} \times \rho_{\text{water}} \]  

(Equation 3.19)

where \( V_{\text{HCl}} \) is the volume (mL) of the consumed HCl aqueous solution, \( \rho_{\text{water}} \) is the density (g/mL) of water at 30°C (0.996 g/mL) [63].

Figure 3.4 Determination of the water content process.
3.6.8 Reusability Test

The reusability process was repeated 30 cycles of oil/water separation experiment. The oil/water mixtures (75%, 50% and 25% v/v) of various types of oil were poured onto the mesh, and then the separation was proceeded by gravity.

The reusability of mesh was determined from oil/water separation efficiency ($\eta$, expressed as a percentage) of each cycle. Figure 3.5 shows the NR/SiO$_2$ modified with FAS process and application.

![Figure 3.5 Schematic formation of the NR/SiO$_2$ modified fluoroalkylsilanes process and application.](image)

Ref. code: 2565589040016HJX
CHAPTER 4
RESULTS AND DISCUSSION

The objective of this research was improved the property of natural rubber (NR) latex by modified with silica and fluoroalkylsilane (FAS) group and used as an coating materials for oil/water separation. Firstly, the NR was encapsulated with silica shell using tetraethyl orthosilicate (TEOS) as a silica precursor. Secondly, the process was integrated between NR/SiO$_2$ and FAS group. Then, the stainless steel mesh was dip-coated by NR/SiO$_2$ modified with FAS (FAS-3 or FAS-17).

Characterization the chemical structure of modified NR was determined by Fourier transform infrared (FTIR) spectroscopy, a real-time in situ mid-infrared measurements and $^{29}$Si solid-state NMR spectroscopy. The morphology and thermal property of modified NR were observed by transmission electron microscope (TEM) and thermogravimetric analysis (TGA), respectively. The particles size of unmodified and modified NR latex was determined.

The morphology of modified mesh was observed by optical microscope (OM), atomic force microscope (AFM) and scanning electron microscope equipped with energy-dispersive spectroscopy (SEM-EDS). The hydrophobicity and oleophilicity of uncoated and coated mesh were determined by oil and water contact angle. The oil/water separation efficiency and reusability of coated mesh were investigated.
4.1 Characterization of Natural Rubber-Encapsulated Silica (NR/SiO₂)

4.1.1 Preparation and Properties of NR/SiO₂

The natural rubber (NR) was prepared with the sol-gel reaction under alkaline conditions to provide the natural rubber-encapsulated silica (NR/SiO₂). Table 4.1 shows the latex stability and particle size of NR/SiO₂ synthesized with various types of surfactants, temperature, reaction time, concentration and flow rate of TEOS.

Table 4.1 Latex stability and particle size of NR/SiO₂ synthesized

<table>
<thead>
<tr>
<th>Run</th>
<th>Surfactant nature&lt;sup&gt;a&lt;/sup&gt;</th>
<th>TEOS:NR weight ratio</th>
<th>Temperature (°C)</th>
<th>Reaction time (min)</th>
<th>Flow rate (mL/min)</th>
<th>Stability of latex&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Size of particles (µm) ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cationic</td>
<td>1:50</td>
<td>27</td>
<td>20</td>
<td>1.0</td>
<td>C</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>Anionic</td>
<td>1:50</td>
<td>27</td>
<td>20</td>
<td>1.0</td>
<td>M</td>
<td>0.753 ± 0.338</td>
</tr>
<tr>
<td>3</td>
<td>Nonionic</td>
<td>1:50</td>
<td>27</td>
<td>20</td>
<td>1.0</td>
<td>M</td>
<td>0.708 ± 0.426</td>
</tr>
<tr>
<td>4</td>
<td>Nonionic</td>
<td>1:50</td>
<td>27</td>
<td>240</td>
<td>1.0</td>
<td>M</td>
<td>1.030 ± 0.499</td>
</tr>
<tr>
<td>5</td>
<td>Nonionic</td>
<td>1:50</td>
<td>50</td>
<td>20</td>
<td>1.0</td>
<td>M</td>
<td>0.707 ± 0.540</td>
</tr>
<tr>
<td>6</td>
<td>Nonionic</td>
<td>1:50</td>
<td>6</td>
<td>20</td>
<td>1.0</td>
<td>M</td>
<td>0.681 ± 0.276</td>
</tr>
<tr>
<td>7</td>
<td>Nonionic</td>
<td>4:50</td>
<td>27</td>
<td>20</td>
<td>1.0</td>
<td>C</td>
<td>N/A</td>
</tr>
<tr>
<td>8</td>
<td>Nonionic</td>
<td>1:50</td>
<td>27</td>
<td>20</td>
<td>4.0</td>
<td>C</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<sup>a</sup> Surfactant; cationic (CTAB), anionic (SDS), nonionic (Triton™ X-100)

<sup>b</sup> Stability of latex during a sol-gel reaction. M, milky fluid; C, coagulate

N/A = not applicable

Figure 4.1 illustrates the mechanistic expectancy of NR encapsulation within the silica shell by hydrolysis and condensation of TEOS via a sol-gel route under alkaline conditions. This research presents a simple one-pot procedure. The NR latex was dispersed in an emulsion system containing different types of surfactant; cationic surfactant (CTAB), anionic surfactant (SDS) or nonionic surfactant (Triton™ X-100), which
resulted in a stable emulsion. It can be seen from Table 4.1 that the latex stability of cationic surfactant has been coagulated. In addition, the morphology of encapsulated particles that used cationic and anionic surfactant was not fully encapsulated by silica. The commercial source of NR latex comprises about 36% of rubber fraction, 5% of non-rubbers components such as protein, lipid, and sugar with water accounting for the remaining 59% [64]. Therefore, the surface surrounding the NR particle contains both positive and negative charges. The negative charges are attributed to ionization of adsorbed carboxylic group on phospholipid molecules and the positive charges are generated from certain amino groups of the adsorbed proteins. During this stage, cationic and anionic surfactant are not suitable conditions for stabilization in the present system, which observes from the stability of latex during a sol-gel reaction and TEM image.

Figure 4.1 Preparation of the natural rubber-encapsulated silica (NR/SiO₂) via a sol-gel process and proposed mechanism.
When the TEOS solution was added into the emulsion containing micelles, these silica precursors possibly attracted onto surfaces of the micelles through a hydrogen-bonding (H-bond) interaction between the silanol groups (Si-OH) of silica shell and hydrophilic segments of the surfactant. The silica particles with various morphologies, such as raspberry-like [65], daisy-shaped, multipod-like [66], snowman-like [67], raisin bun-like [68], organic (core)-silica (shell) [69] and silica (core)-organic material (shell) [70], have been produced by different methods. The dispersion of silica in the matrix is confronted by the lipophobic properties of the silica particles. The silica particles have negative surface charge, due to the existence of the silanol-type hydroxyl groups on their surface. The surface charge of the silica particle makes them highly hydrophilic, which causes their agglomeration during mixing [71]. The high-rate of silica addition induced self-assembly during mixing. Thus, adding TEOS with rate of 1 mL/min and continuous stirred was suitable condition. To drop TEOS of high-content into latex, the latex tended to coagulate, due to the different polarity between the TEOS and NR. The effect of various synthetic parameters on the reaction time between NR and surfactant was significantly controlled in the size distribution of NR/SiO$_2$ (Table 4.1). Therefore, the NR/SiO$_2$ synthesized with long reaction time had a wider size distribution (1.030 ± 0.499 nm) because the surfactant with NR interaction had time to self-agglomerate. In addition, low temperature of reaction may be not only slow down TEOS hydrolysis and condensation reaction, but also reduces vibration of oligomer that it may avoid aggregation among oligomers.

Hence, the suitable conditions of synthesized NR/SiO$_2$ are when use nonionic surfactant (Triton-X), 1:50 weight ratio (TEOS to NR) addition of 1 mL/min and reacted at 6°C for 20 min.
4.1.2 FTIR Analysis

The structure of functional shell was analyzed using FTIR. Figure 4.2 shows the FTIR spectra of the neat NR, neat silica, and the NR/SiO$_2$ synthesized. In the spectrum of neat NR, it illustrated strong absorption peaks of asymmetric and symmetric stretching of C-H groups -C-CH$_3$ and -CH$_2$ (2961-2853 cm$^{-1}$), -CH$_2$ (1433 cm$^{-1}$), and -CH- (1376 cm$^{-1}$) hydrocarbon backbone of cis-1,4-polyisoprene structure. The neat silica spectra showed absorption peaks of Si–O–Si stretching (1054 and 963 cm$^{-1}$) and Si-OH group (3382 cm$^{-1}$ and 792 cm$^{-1}$). The band around 3382 cm$^{-1}$ could be attributed to H-bonded of silanol (Si-OH) group [72-74]. It was found that the spectra of the NR/SiO$_2$ was quite similar, in which the peaks at 3289 and 1097 cm$^{-1}$ were attributed to Si-OH stretching and Si–O–Si stretching vibrations, respectively of the silica shell. The peak appeared at around 2961 to 2851, 1436, and 1376 cm$^{-1}$ that referred to the C-H stretching, -CH$_2$-, and -CH- hydrocarbon backbone of NR compound, respectively. Thereby, the FTIR spectra can confirm a structure of natural rubber-encapsulated silica (NR/SiO$_2$).

![Figure 4.2 FTIR spectra of (a) NR/SiO$_2$, (b) Neat silica, and (c) Neat NR.](image-url)
4.1.3 $^{29}$Si Solid-State NMR Analysis

The NR/SiO$_2$ sample was prepared when used nonionic surfactant (Triton-X), 1:50 weight ratio (TEOS to NR) addition of 1 mL/min and reacted at 4-8°C for 20 min. The range of $^{29}$Si chemical shifts are variously from −60 ppm to −129 ppm for the three-dimensional cross-linked framework ($Q^4 \approx -98$ to −129 ppm), chain branching sites ($Q^3 \approx -88$ to −98 ppm), middle groups in chains ($Q^2 \approx -82$ to −88 ppm), disilicates and chain end groups ($Q^1 \approx -76$ to −82 ppm) and monosilicates ($Q^0 \approx -68$ to −76 ppm) according to an ascending sequence [75-78]. The silicon atom is referred to as $Q^n$ group ($n = 1$ to 4), where $n$ defines the number of neighboring silicon atoms.

The NMR spectra is reported in Figure 4.3. In the NR/SiO$_2$ spectrum, a peak at -95.28 ppm and -105.10 ppm were attributed to (Si-O)$_3$Si-OH (call $Q^3$, single silanol) and Si(Si-O)(call $Q^4$, siloxane bridges), respectively. The $Q^0$ group corresponds to a tetraethylorthosilicate that all four oxygen atoms are bound to other silicon atoms. In the meanwhile, the silicon atom of $Q^3$ is linked to three another silicon and corresponded to one silanol group (-Si-OH), which can be reacted with FAS group. The intensity of the signal is low due to low weight ratio (1:50) of TEOS to NR. Consequently, the $^{29}$Si NMR can confirm the silica shell of encapsulated particles.

![Figure 4.3 $^{29}$Si solid-state NMR spectrum of NR/SiO$_2$ sample.](image)
4.1.4 Real Time *In situ* FTIR for NR/SiO$_2$ System

Preparation the natural rubber-encapsulated silica (NR/SiO$_2$) and mechanism were studied through the real-time *in situ* Fourier transform infrared (FTIR) spectra measurements, which the corresponding results were listed in Figure 4.4. The latex system compound was analyzed by Mettler-Toledo ReactIR 15 instrument. The probes began scanning after Triton X-100 mixing with DI water addition and spectra was obtained every 50 seconds. It could be seen from the Figure 4.4(a) that the bands emerged at 1454, 1376, 1104, 1044 and 828 cm$^{-1}$. These bands were selected as marker to monitor of reaction proceed. The bands at 1454, 1376 and 828 cm$^{-1}$ were related to the -CH$_2$, -CH- of hydrocarbon backbone and CH out-of-plane bending vibrations respectively, indicating the formation of cis-1,4-polyisoprene structure, which were confirm by FTIR spectra of NR as presented in Figure 4.5(a). The 1104 and 1044 cm$^{-1}$ bands were ascribed to the Si-O-Si bonds, which were confirm by FTIR spectra of TEOS in Figure 4.5(b).

It could be seen from the Figure 4.4(a) that the peak intensity at 1454, 1376 and 828 cm$^{-1}$ increased markedly from a point to b point, indicating from adding NR and then remained stable from b point to d point. After adding TEOS at c point, the peak intensity at 1104 and 1044 cm$^{-1}$ increased and remained stable from c point to d point. Then, the sharp decreasing of absorption peak from d point to e point indicated that the NR and TEOS converted to encapsulation particles. The NR core was covered by silica shell that was generated from hydrolysis and condensation reaction of TEOS as following from Figure 4.1.

The intensity of band after 01:08:15 hour (point e) was weak and kept steadily (point e to point f) after that time as presented in Figure 4.4(a).

As shown in Figure 4.4(b), the intensity of the NR band was strong at the beginning and became weaker after 01:05:15 hour. However, the intensity of the NR/SiO$_2$ band became stronger after 01:05:15 h and then the both of peaks kept steadily.

The FTIR spectra of NR/SiO$_2$ is shown in Figure 4.5(c). The absorption band at 1091 cm$^{-1}$ and 1047 cm$^{-1}$ were respectively assigned to asymmetric Si-O-Si stretching.
vibration of silica shell. The peaks at 1675, 1452 and 1376 cm\(^{-1}\) were respectively attributed to C=C stretching, CH\(_2\)_-, and -CH- hydrocarbon backbone of cis-1,4-polyisoprene structure. It is noteworthy that the characteristic peak of NR/SiO\(_2\) can be distinguished in the spectra of the encapsulation particles.

![Graph showing FTIR spectra and kinetic profile](image)

**Figure 4.4** (a) Real time *in situ* FTIR spectra for preparation of NR/SiO\(_2\) system and (b) kinetic profile (peak height vs. time) of 15% DRC NR latex and NR/SiO\(_2\). The reaction was monitored from 0 min to 130 min. Point a; start scanning after triton X-100 mixing with DI water addition (00:00:00), point b; addition of 15% DRC NR latex (00:02:12), point c; addition of TEOS (00:14:56), point d; the point at 01:05:15, point e; the point at 01:08:15 and point f; the point at 02:10:00.
Figure 4.5 FTIR spectra of (a) 15% DRC NR latex, (b) TEOS solution and (c) NR/SiO$_2$ latex.
4.1.5 Morphological Studies

4.1.5.1 Transmission Electron Microscopy (TEM)

Figure 4.6(c)-(h) show the effects of surfactants, reaction time and temperature of reaction on the morphology of NR/SiO₂ synthesized as illustrated by TEM images. Figure 4.6(a) showed TEM image of neat NR that was stained by phosphotungstic acid (PTA). The morphology of neat silica, which was prepared from TEOS solution was obtained without staining as presented in Figure 4.6(b). The average diameter of neat silica and neat NR were 400 nm and 250 nm, respectively. The size of the silica particles is almost twice the NR particles due to self-assembly of silica particles.

The result of stability of latex (Table 4.1), using anionic and nonionic surfactant were not coagulating. Thus, the TEM image is used to study various types of surfactants including anionic and nonionic as shown in Figure 4.6(c) and 4.6(d), respectively. The core is natural rubber and silica as the shell. The average diameter of NR/SiO₂ was 0.8 µm, which was confirmed by particle size measurements and TEM image. The nonionic surfactant is more suitable than anionic surfactant because the NR particle is fully encapsulated with silica.

Figure 4.6(f)-(h) show the TEM image of various temperature (50, 27 and 6°C). The silica fully encapsulated the rubber particles when prepared at 6°C because of kinetic of silica. At low temperature, the TEOS hydrolysis and condensation reactions can slow down therefore NR is slowly encapsulated with silica [79]. The effect of various synthetic parameters on the reaction time between NR and surfactant is illustrated in Figure 4.6(d) (20 min) and Figure 4.6(e) (240 min). The particle size and TEM results showed that the emulsion-based allow to agglomerate at 240 min. The reaction time induces significant change in the particles size and size distribution of NR/SiO₂. The NR/SiO₂ synthesized at 240 min had a wider size distribution (1.030 ± 0.499 nm) with more than the other conditions. Moreover, the NR particle is not fully encapsulated with silica and silica allows to agglomerate also. As the result, the suitable conditions of synthesized NR/SiO₂ are when use nonionic surfactant (Triton-X) at 6°C for 20 min.
Figure 4.6 TEM images of (a) neat NR (scale bar, 0.5 μm) was stained by phosphotungstic acid (PTA), (b) neat silica (scale bar, 100 nm) was obtained without staining. Preparation of NR/SiO$_2$ under different parameters (c) anionic surfactant, (d) nonionic surfactant, (e) 240 min of reaction, temperature at (f) 50°C, (g) 27°C, and (h) 6°C.
4.1.5.2 Scanning Electron Microscopy (SEM)

The effect of various percent dry rubber content (%DRC) of NR latex (3.5% DRC and 2.5% DRC) was studied. The coated mesh with NR latex of 3.5% DRC and 2.5% DRC was observed by SEM image. As seen in Figure 4.7, the uncoated mesh as showed in Figure 4.7(a) had the opening diameter of about 110 μm while its wire thickness was 61 μm. For the 2.5% DRC NR coated mesh (Figure 4.7(b)) and 3.5% DRC NR coated mesh (Figure 4.7(c)), these had the opening diameter of about 83 μm and 99 μm, respectively and the wire thickness of 91 μm, 74 μm, respectively (All of them were obtained from the Images J software). Therefore, the 2.5% DRC NR coated mesh and 3.5% DRC NR coated mesh were coated on the stainless steel mesh with the coating thickness of around 12 and 29 μm, respectively. These results support the conclusion that the percent dry rubber content (%DRC) significantly affect the pore size of mesh. Hence, 2.5% DRC was more suitable condition. Because the large film of NR has an impact of contact angle (CA) values and oil/water separation process. If the wire of mesh was covered by large film, the oil or water could not pass through the mesh or be hard to pass through.

![Figure 4.7 SEM images of (a) uncoated mesh, (b) 2.5% DRC NR coated mesh and (c) 3.5% DRC NR coated mesh.](image)
4.1.6 Thermal Analysis

The thermal stability of the natural rubber-encapsulated silica (NR/SiO₂) was investigated by thermogravimetric analyses, which presented the mass loss of samples and corresponding temperature over the temperature range of 40-900°C with the heating rate of 10°C min⁻¹. Figure 4.8 shows the degradation behavior of NR/SiO₂ and the result from TGA-DTG curve of neat NR and NR/SiO₂ are summarized in Table 4.2.

The NR/SiO₂ exhibited one-stage decomposition temperature range of 280-490°C (Figure 4.8). The differential thermogravimetric (DTG) curve of NR/SiO₂ also showed one-stage decomposition due to the decomposition of NR segments. The small peak of TGA-DTG curve of NR/SiO₂ at 490 to 600°C was possibly due to the decomposition of inorganic curing agents. After complete decomposition, the residual silica compounds are remained. The onset temperature of decomposition (T₀) and maximum temperature of decomposition (Tₘₐₓ) values of NR/SiO₂ were 300.0°C and 403.9°C, respectively. While, the T₀ and Tₘₐₓ values of NR were 200.9°C and 391.0°C, respectively. From the result, the NR/SiO₂ curve shows higher T₀ and Tₘₐₓ values than the NR curve that it is attributed to the effect of the silica shell. Therefore, the silica shell increased the thermal properties of NR core.

![Figure 4.8 TGA-DTG curve of the (a) natural rubber (NR) and (b) natural rubber-encapsulated silica (NR/SiO₂).](image-url)
<table>
<thead>
<tr>
<th>Thermal properties</th>
<th>NR</th>
<th>NR/SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{\text{id}} ) ( ^{\text{a}} ) (°C)</td>
<td>200.9</td>
<td>300.0</td>
</tr>
<tr>
<td>( T_{\text{max}} ) ( ^{\text{b}} ) (°C)</td>
<td>391.0</td>
<td>403.9</td>
</tr>
</tbody>
</table>

\( ^{\text{a}} \) Onset temperature of decomposition.

\( ^{\text{b}} \) Maximum temperature of decomposition.

4.2 Characterization of NR/SiO₂ Modified Fluoroalkylsilane (FAS)

4.2.1 Preparation and Properties of NR/SiO₂ Modified FAS

The NR/SiO₂ modified with fluoroalkylsilane (FAS) was prepared through the chemical reaction between the hydroxyl groups and silanol group in NR/SiO₂ under alkaline condition. As shown in Figure 4.9, the first reaction was hydrolysis of FAS and TEOS and the second reaction was condensation of hydrolyzed TEOS and FAS. Then the condensation could proceed with NR/SiO₂ particles.

![Figure 4.9 Reaction scheme of NR/SiO₂ modified FAS.](image)

Ref. code: 25605809040016HJX
Table 4.3 showed the effect of various FAS types (FAS-3 and FAS-17) and FAS concentration were studied. From the result, water contact angle (WCA) is affected by the FAS concentration and type of FAS. The effect of various FAS concentration (0.105, 0.157, 0.209 and 0.262 mmol) was studied in part of preparation NR/SiO₂ modified FAS-3. The OCA and WCA of uncoated mesh are 15.6° and 77.5°, respectively. Moreover, the WCA of NR/SiO₂ modified FAS-3 coated mesh with concentration of 0.105, 0.157 and 0.209 mmol increased to 106.9°, 121.0° and 138.0°, respectively (Figure 4.10). An oil droplet with a low surface tension quickly spreads on surface of NR/SiO₂ modified FAS-3 coated mesh and permeates through it, exhibiting a superoleophilic property (OCA of 0°) (Figure 4.10). In the meanwhile, at FAS-3 concentration of 0.262 mmol the latex suspension suddenly coagulates because of the different polarity between the NR/SiO₂, TEOS and FAS. In addition, the WCA of NR/SiO₂ modified FAS-3 coated mesh and NR/SiO₂ modified FAS-17 coated mesh were 138.0° and 153.9°, respectively. Consequently, the FAS concentration of 0.209 mmol is suitable content for this system. A trend is observed where the WCA of NR/SiO₂ modified FAS-3 coated mesh is increased with increasing FAS concentration and fluoroalkyl chain-length. The mesh was dip-coated with NR/SiO₂ modified FAS-3 latex and NR/SiO₂ modified FAS-17 latex that exhibited hydrophobicity and superhydrophobicity, respectively.

### Table 4.3 Preparation of NR/SiO₂ modified FAS

<table>
<thead>
<tr>
<th>run</th>
<th>Type of FAS</th>
<th>FAS concentration (mmol)</th>
<th>Stability of latexa</th>
<th>Size of particles (μm) ± SD</th>
<th>WCA (°)</th>
<th>OCA (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FAS-3</td>
<td>0.105</td>
<td>M</td>
<td>0.714 ± 0.281</td>
<td>106.9</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>FAS-3</td>
<td>0.157</td>
<td>M</td>
<td>0.798 ± 0.105</td>
<td>121.0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>FAS-3</td>
<td>0.209</td>
<td>M</td>
<td>0.776 ± 0.117</td>
<td>138.0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>FAS-3</td>
<td>0.262</td>
<td>C</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>5</td>
<td>FAS-17</td>
<td>0.209</td>
<td>M</td>
<td>0.776 ± 0.114</td>
<td>153.9</td>
<td>0</td>
</tr>
</tbody>
</table>

a Stability of latex during reaction. M, milky fluid; C, coagulate

N/A = not applicable
Figure 4.10 The contact angle (°) values of studied FAS-3 concentration and types FAS. The insets are photographs of the water droplet on various substrates.

4.3 Characterization of the Mesh

4.3.1 Preparation and Properties of Dip-Coated Mesh

To determine the effect of coating cycle number for dip-coated on mesh, water droplet and oil droplet on the NR/SiO$_2$ modified FAS-17 surface was measured (Figure 4.11). The OCA and WCA of uncoated mesh were 15.6° and 77.5°, respectively. Furthermore, the water contact angle (WCA) of coated cycle number with one, two and three cycle were 153.9°, 152.0° and 153.7°, respectively. However, the oil contact angle (OCA) of two and three coated cycle were 0°, 38.7° and 56.1°, respectively. Because the pore of mesh is covered by natural rubber (NR) film, the oil droplet of thrice mesh is not easily passed through the pore. If the cycle number of dip-coating was increased, the OCA would be increased also. Therefore, the once times for dip-coated of NR/SiO$_2$ modified FAS is suitable condition for this experiment.
Figure 4.11 The contact angle (°) values of studied the effect of coating cycle number with one, two and three cycle for dip-coated of NR/SiO$_2$ modified FAS-17. The insets are photographs of the water droplet on various substrates.

4.3.2 The Morphology of Mesh

4.3.2.1 Scanning Electron Microscopy (SEM)

To realize the controllable oil permeation, a substrate is necessary. In this work, stainless steel mesh substrates are chosen because of wide application in industrial production, anti-chemical erosion and low cost [7, 47].

Figure 4.12 shows the typical scanning electron microscopy (SEM) image of various substrates. The diameter of one wire and the size of one square pore can be estimated to be 75 $\mu$m and 125 $\mu$m, respectively. The uncoated stainless steel mesh (Figure 4.12(a)) and NR coated mesh (Figure 4.12(b)) showed a smooth surface. As shown in Figure 4.12(c), the surface of NR/SiO$_2$ can be seen some small particles from silica shell. Figure 4.12(d) and 4.12(e) show the SEM images of NR/SiO$_2$ modified FAS-3 coated mesh and NR/SiO$_2$ modified FAS-17 coated mesh, respectively. Both of meshes are provided surface roughness. It can be seen that the NR/SiO$_2$ modified FAS coated meshes have been completely covered by encapsulation particles. Therefore, the morphology of the stainless steel mesh is greatly influenced by FAS mixing with silica.
Figure 4.12 SEM image of (a) uncoated mesh, (b) NR coated mesh, (c) NR/SiO$_2$ coated mesh, (d) NR/SiO$_2$ modified FAS-3 coated mesh and (e) NR/SiO$_2$ modified FAS-17 coated mesh. The insets show high-magnification images of the corresponding mesh.
SEM-EDS image of uncoated mesh as presented in Figure 4.13(a) showed slightly oxygen mapping from chromium oxide (Cr$_2$O$_3$) [77-78], which was anti-corrosion coating of stainless steel mesh. As shown in Figure 4.13(b), oxygen and carbon mapping of NR coated mesh distributed uniformly on mesh. The carbon compound is the main component of natural rubber (NR). Moreover, NR latex is composed of non-rubber such as protein, lipid and sugar also. Hence, the SEM-EDS image of NR coated mesh could be displayed element of oxygen from non-rubber (protein, lipid and sugar). In the meanwhile, carbon mapping of NR/SiO$_2$ coated mesh as presented in Figure 4.13(c) was not distributed uniformly on mesh because NR was encapsulated with silica shell. Element mapping of silicon (Si), fluorine (F), carbon (C) and oxygen (O) of NR/SiO$_2$ modified FAS-3 and NR/SiO$_2$ modified FAS-17 coated mesh were shown in Figure 4.13(d) and 4.13(e), respectively. Si, F and O as the main component of encapsulation particles were distributed uniformly on the stainless steel mesh. It was noticed that the NR/SiO$_2$ modified FAS was coated on the stainless steel mesh evenly. However, the F mapping of NR/SiO$_2$ modified FAS-17 signal was lower than NR/SiO$_2$ modified FAS-3 signal because of effect of fluoroalkyl chain length.
Figure 4.13 SEM images (I) and SEM-EDS elemental maps of Si (II), F (III), C (IV) and O (V) of (a) uncoated mesh, (b) NR coated mesh, (c) NR/SiO$_2$ coated mesh, (d) NR/SiO$_2$ modified FAS-3 coated mesh and (e) NR/SiO$_2$ modified FAS-17 coated mesh.
4.3.2.2 Atomic Force Microscopy (AFM)

For the characterization of mesh surface by AFM, the AFM images of mesh are shown in Figure 4.14. The images with 30 μm × 30 μm scan area were taken from some randomly selected areas of mesh. Figure 4.14 (a)-(e) show the uncoated coated mesh, NR coated mesh, NR/SiO₂ coated mesh, NR/SiO₂ modified FAS-3 coated mesh and NR/SiO₂ modified FAS-17 coated mesh, respectively; in addition, left-hand side and right-hand side are 3D and 2D AFM images, respectively. The AFM image of NR/SiO₂ coated mesh shows the micro-nanoscale hierarchical structures of silica particles. It can be seen that the surface roughness and actual height of NR/SiO₂ modified FAS-3 coated mesh and NR/SiO₂ modified FAS-17 coated mesh increase with micro-nanostructure that is formed from NR/SiO₂ modified with FAS.

The root-mean-square roughness ($R_q$) values and skewness ($R_{sk}$) values are shown in Table 4.4. The root-mean-square roughness of NR coated mesh (162.029 nm), NR/SiO₂ modified FAS-3 coated mesh (181.667 nm) and NR/SiO₂ modified FAS-17 coated mesh (163.509 nm) increased when these values compared with $R_q$ value of uncoated mesh (144.376 nm); however, $R_q$ values of NR/SiO₂ decreased. Because the $R_q$ values have effect from using stainless steel mesh with commercial grade and mesh surface is not smooth. Accordingly, this research cannot control roughness valley ($R_v$) and roughness peak ($R_p$) at surface of commercial mesh.

Consequently, skewness ($R_{sk}$) values are more suitable values for observation. Because it is a measure of how strongly a profile, which is biased above or below the mean value. The high values of roughness indicate surface with more deviation from the norm [82-83]. Skewness values of uncoated mesh, NR coated mesh, NR/SiO₂ coated mesh, NR/SiO₂ modified FAS-3 coated mesh and NR/SiO₂ modified FAS-17 coated mesh were 0.084, 0.212, -0.491, 0.886 and 0.809, respectively. More valley and more peak on the surfaces of mesh can be defined by more negative or positive $R_{sk}$ values. The negative $R_{sk}$ values show valleys with a tail extending out toward more negative height. In contrast, the positive $R_{sk}$ values indicate a distribution of peaks with an asymmetric tail extending out toward more positive height. The $R_{sk}$ values of NR coated mesh increase from NR film on stainless steel mesh and the $R_{sk}$ values of NR/SiO₂ coated...
mesh went up from natural rubber-encapsulated silica particle. Furthermore, the $R_{sk}$ values of NR/SiO$_2$ modified FAS coated mesh are a high value. The $R_{sk}$ value of NR/SiO$_2$ modified FAS-3 coated mesh and NR/SiO$_2$ modified FAS-17 coated mesh are an increased from that NR/SiO$_2$ particles modifies with TEOS and FAS. The 3D AFM images, 2D AFM images and surface profiles of NR/SiO$_2$ modified FAS coated mesh clearly show the increasing root-mean-square roughness ($R_q$) and skewness ($R_{sk}$) values. Hence, the mesh is dip-coated with NR/SiO$_2$ modified FAS become rougher, as expected and the surface roughness possess hydrophobic or superhydrophobic behaviors.

Table 4.4 Root-mean-square roughness ($R_q$) and skewness ($R_{sk}$) of test mesh from the AFM characterization

<table>
<thead>
<tr>
<th>Sample Mesh</th>
<th>$R_q$ (nm)</th>
<th>$R_{sk}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncoated coated mesh</td>
<td>144.376</td>
<td>0.084</td>
</tr>
<tr>
<td>NR coated mesh</td>
<td>162.029</td>
<td>0.212</td>
</tr>
<tr>
<td>NR/SiO$_2$ coated mesh</td>
<td>115.002</td>
<td>-0.491</td>
</tr>
<tr>
<td>NR/SiO$_2$ modified FAS-3 coated mesh</td>
<td>181.667</td>
<td>0.886</td>
</tr>
<tr>
<td>NR/SiO$_2$ modified FAS-17 coated mesh</td>
<td>163.509</td>
<td>0.809</td>
</tr>
</tbody>
</table>
Figure 4.14 AFM topographic images (30 µm × 30 µm) of (a) uncoated mesh, (b) NR coated mesh, (c) NR/SiO$_2$ coated mesh, (d) NR/SiO$_2$ modified FAS-3 coated mesh and (e) NR/SiO$_2$ modified FAS-17 coated mesh with (1) 3-D AFM images and (2) 2-D AFM images.
4.3.2.3 Optical Microscopy (OM)

The optical microscopy (OM) images of uncoated mesh as presented in Figure 4.15(a), NR/SiO$_2$ modified FAS-3 coated mesh and FAS-3 coated mesh are shown in Figure 4.15. The stainless steel mesh was dip-coated with NR/SiO$_2$ modified FAS-3 latex as presented in Figure 4.15(b). In the meanwhile, the FAS-3 coated mesh was prepared by dip-coated method of stainless steel mesh in solution, which included the mixing of methanol, FAS-3 and TEOS solution without NR/SiO$_2$ latex. As shown in Figure 4.15(c), a wire of mesh was covered by composite that it was formed by chemical reaction between FAS-3 and TEOS. The composite has effect on contact angle (CA) and oil/water separation process. In the meanwhile, the wettability and efficiency separation of NR/SiO$_2$ modified FAS coated mesh depend on both surfaces chemical and topographical microscopic properties. Therefore, stainless steel mesh that was dip-coated included natural rubber polymer was the choice for oil/water separation materials with environment-friendly and increasing homogenous film coating.

Figure 4.15 The morphology of (a) uncoated mesh, (b) NR/SiO$_2$ modified FAS-3 coated mesh and (c) FAS-3 coated mesh.
4.3.3 Surface Free Energy

The harmonic mean prefers for low surface energy such as polymers, water, organic liquids and organic pigments and often provides more reliable values than the geometric mean. The average contact angle (CA) is gathered in Table 4.5 for all the selected experimental condition.

**Table 4.5** Average contact angle values (°) measured for drop of water and dodecane formed on the uncoated coated mesh, NR coated mesh, NR/SiO₂ coated mesh, NR/SiO₂ modified FAS-3 coated mesh and NR/SiO₂ modified FAS-17 coated mesh

<table>
<thead>
<tr>
<th>Surface</th>
<th>Water (°)</th>
<th>Dodecane (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncoated mesh</td>
<td>77.5</td>
<td>15.6</td>
</tr>
<tr>
<td>NR coated mesh</td>
<td>85.2</td>
<td>20.1</td>
</tr>
<tr>
<td>NR/SiO₂ coated mesh</td>
<td>0</td>
<td>23.4</td>
</tr>
<tr>
<td>NR/SiO₂ modified FAS-3 coated mesh</td>
<td>138.0</td>
<td>0</td>
</tr>
<tr>
<td>NR/SiO₂ modified FAS-17 coated mesh</td>
<td>153.9</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table 4.6** Apparent surface energy (mN/m) of the uncoated mesh, NR coated mesh, NR/SiO₂ coated mesh, NR/SiO₂ modified FAS-3 coated mesh and NR/SiO₂ modified FAS-17 coated mesh

<table>
<thead>
<tr>
<th>Mesh</th>
<th>Total surface free energy (γ)</th>
<th>Dispersion component (γd)</th>
<th>Polar component (γp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated mesh</td>
<td>37.87</td>
<td>24.48</td>
<td>13.39</td>
</tr>
<tr>
<td>NR coated mesh</td>
<td>33.84</td>
<td>23.90</td>
<td>9.95</td>
</tr>
<tr>
<td>NR/SiO₂ coated mesh</td>
<td>72.88</td>
<td>23.39</td>
<td>49.49</td>
</tr>
<tr>
<td>NR/SiO₂ modified FAS-3 coated mesh</td>
<td>5.95</td>
<td>5.95</td>
<td>0</td>
</tr>
<tr>
<td>NR/SiO₂ modified FAS-17 coated mesh</td>
<td>2.03</td>
<td>2.03</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 4.6 shows the resulting surface free energy for the tested mesh. The surface free energy is a measure of intermolecular forces due to the difference in energy between molecules at the surface and molecules in the bulk material. It allows one to determine parameters such as wetting, adsorption and adhesion, as well as the nature and extent of the interphase region. The dispersion contribution (London) of the surface energy is due to electron motion, however the polar contribution (Keesom) is due to permanent dipole moments [84].

The total surface free energy of the tested mesh provides an indication of the degree of wetting. The NR/SiO$_2$ coated mesh is the highest total surface free energy of 72.88 mN/m and the highest polar contribution of 49.49 mN/m from all the tested mesh. Hence, NR/SiO$_2$ coated mesh has a very polar from the polar components of a silica (silanol group).

In the meanwhile, the total surface free energy of NR/SiO$_2$ modified FAS-3 coated mesh and NR/SiO$_2$ modified FAS-17 coated mesh are 5.95 mN/m and 2.03 mN/m, respectively. For dodecane droplet on NR/SiO$_2$ modified FAS-3 coated mesh and NR/SiO$_2$ modified FAS-17 coated mesh, the contact angle values were 0°. The fact that the CA was 0° indicated a complete wetting of the surface. Therefore, the mesh modified with FAS exhibits hydrophobic/oleophilic characteristic due to complete wetting of polar contribution.

### 4.3.4 Contact Angle

It is well-known that wettability of solid interfaces bases on their surface roughness and surface energy, in which surface roughness dependents on micro-nanoscale hierarchical structures, while surface energy mainly relies the surface components [85].

In this work, FAS is hydrophobic as traditional of fluoro-compound. After the micro-nanostructure is formed from NR/SiO$_2$ modified with FAS particles, the mesh achieves its hydrophobic or superhydrophobic property. The SEM characterization (Figure 4.12(d) and 4.12(e)) showed that the micro-nanostructures were created with
low-surface-energy materials that these were successfully prepared on the surface of stainless steel mesh through this method. The NR/SiO$_2$ modified FAS coated mesh had a large amount of micro-nanostructure, which could capture a large amount of air. The surface wettability is evaluated by contact angle (CA) measurement. The modification with FAS and silica changes the surface wettability of mesh. The oil/water mixture can penetrate the uncoated mesh as presented in Figure 4.19(b) suggesting mesh without selectivity. Figure 4.16 shows the contact angle (CA) values of uncoated mesh, NR coated mesh, NR/SiO$_2$ coated mesh, NR/SiO$_2$ modified FAS-3 coated mesh and NR/SiO$_2$ modified FAS-17 coated mesh. Moreover, Figure 4.17 shows the photographs of WCA and OCA. The water contact angle (WCA) and oil contact angle (OCA) of uncoated mesh were measured to be 77.5° and 15.6°, respectively. The WCA and OCA of NR coated mesh were 85.2° and 20.1°, respectively. However, the NR/SiO$_2$ coated mesh exhibited superhydrophilic property (WCA of 0°). For the meshes after dip-coated with NR/SiO$_2$ modified FAS-3 and NR/SiO$_2$ modified FAS-17, the WCAs were 138° and 153.9°, respectively, as shown in Figure 4.17. In contrast, an oil droplet (dodecane) with a low surface tension quickly spread on surface of NR/SiO$_2$ modified with FAS coated mesh and permeated through it, exhibited a superoleophilic property (OCA of 0°). Its WCA approaches 153.9°, indicating that the surface is superhydrophobicity. A trend is observed where the WCA of as-prepared stainless steel mesh increased with longer fluoroalkyl chain length, resulting in transition of the wetting state from hydrophobic to superhydrophobic. In summary, the hydrophobic and superhydrophobic property of mesh are contributed by both the micro-nanostructure and the hydrophobic of FAS. For this kind of system, the WCA could be expressed by the Wenzel model and the Cassie model. As Figure 4.18 shows the models to explain the Wenzel and the Cassie model. Both of them demonstrate the CA in function of the Young contact angle (θ) that is measured for a flat surface. For Wenzel model, the water droplet is easily to penetrate into the grooves of rough surface. For Cassis model, the water droplet is considered to contact with solid-liquid surface and some air or vapor trap below the liquid drop [86].
Figure 4.16 WCA and OCA of uncoated mesh, NR coated mesh, NR/SiO$_2$ coated mesh, NR/SiO$_2$ modified FAS-3 coated mesh, and NR/SiO$_2$ modified FAS-17 coated mesh. The insets are photographs of the water droplet on various substrates.
Figure 4.17 (a) Water contact angle and (b) oil contact angle of (1) uncoated mesh, (2) NR coated mesh, (3) NR/SiO$_2$ coated mesh, (4) NR/SiO$_2$ modified FAS-3 coated mesh and (5) NR/SiO$_2$ modified FAS-17 coated mesh.
Figure 4.18 The detailed of (a) Young model, (b) Wenzel model and (c) Cassie models. ($\gamma_{SG}$, $\gamma_{SL}$, $\gamma_{LG}$: the interfacial free energies per unit area of solid-gas, solid-liquid and liquid-gas interfaces, respectively, $r$: roughness factor and $f$: area fraction of solid surface) [86].
4.4 Application for Oil/Water Separation

A combination of superhydrophobicity and superoleophilicity, the NR/SiO$_2$ modified FAS-3 and NR/SiO$_2$ modified FAS-17 have great potential to be applied to oil/water separations. The oil/water separation experiment is performed as shown in Figure 4.19. The tested mesh was fixed between two tubes. In order to ensure the sealing performance, there has sealing rings in the junction of the two tubes. This experiment studies the separation efficiency of three meshes include uncoated mesh, NR/SiO$_2$ modified FAS-3 coated mesh and NR/SiO$_2$ modified FAS-17 coated mesh. As shown in Figure 4.19, the mixture of oil (dyed with Oil Red O) and blue-colored aqueous solution (50% v/v) was poured into the tube, the oil penetrated the NR/SiO$_2$ modified FAS coated mesh and flowed down the beaker underneath, while the water was retained in the upper tube. However, the mixture of oil and water (50% v/v) could easily penetrate the uncoated stainless steel mesh. During the oil/water separation process, no artificial external force was employed, indicating its easy operation and low energy costs.

Oil/water separation efficiency is used to quantitatively describe the oil/water separation ability of the NR/SiO$_2$ modified FAS coated mesh. Because the hydrophobic layer is robust, the NR/SiO$_2$ modified FAS coated mesh can be reused. Therefore, we investigate the suitability of mesh for the separation of oil from water. The recycling ability is also investigated by taking the oil/water mixture as an example. We measured the separation efficiency of the NR/SiO$_2$ modified FAS-3 coated mesh and NR/SiO$_2$ modified FAS-17 coated mesh with different types of organic solvents and oil, such as hexane, dodecane, toluene, gasohol and diesel.
Figure 4.19 Oil/water separation device and process: (a) before separation (hexane and water), after separation of (b) uncoated mesh, (c) NR/SiO₂ modified FAS-3 coated mesh and (d) NR/SiO₂ modified FAS-17 coated mesh. Water was colored by copper (II) sulphate and oil was colored by Oil Red O.
The separation efficiency ($\eta$, expressed as a percentage) is determined with the following from Equation 3.18 (chapter 3). As shown in Figure 4.20, different types of organic solvents and oil such as hexane, dodecane, toluene, gasohol and diesel oil, are successfully separated from the mixtures by using NR/SiO$_2$ modified FAS-3 coated mesh and NR/SiO$_2$ modified FAS-17 coated mesh. The separation efficiency of organic solvents and oil are presented as Figure 4.20. The efficiency of NR/SiO$_2$ modified FAS-17 coated mesh ($>99.84\%$) is slightly higher than NR/SiO$_2$ modified FAS-3 coated mesh ($>99.70\%$). For oil/water separation test with different organic solvents and oil, the separation efficiency values of NR/SiO$_2$ modified FAS with low viscosity oil (0.27-1.1 cSt) are slightly higher than high viscosity oil (3 cSt). Hence, the ability of NR/SiO$_2$ modified FAS coated mesh is not affected from viscosity of oil. The viscosity of oil will affect about separation time because the oil with low viscosity easily penetrates into the pore mesh while the oil with high viscosity slowly penetrates and requires longer time than low viscosity oil. Furthermore, different volumes of oil in water including 75%, 50% and 25% v/v were successfully separated from the hexane/water mixture. The separation efficiencies of NR/SiO$_2$ modified FAS-3 coated mesh for 75%, 50% and 25% v/v of oil content were 99.87%, 99.92% and 99.87%, respectively.

Figure 4.20 The separation efficiencies of different organic liquids and oil.
In addition, the hexane/water mixture is observed to be separated by NR/SiO$_2$ modified FAS-3 coated mesh and NR/SiO$_2$ modified FAS-17 coated mesh, which performs a separation efficiency around 99.78% and 99.86%, respectively, even after 30 cycles (Figure 4.21). The comparison of CA, separation efficiency and reusability of several oil substrate materials, which are reported in previous literature are summarized in Table 4.7. The WCA of NR/SiO$_2$ modified FAS coated mesh is lower than copper modified with lauric acid mesh, ZnO mesh, polyester fabric, PE film and CuCl$_2$ mesh. However, the NR/SiO$_2$ modified FAS performs higher separation efficiency and reusability than FeCl$_3$ with n-octadecylthiol mesh, copper modified with lauric acid mesh, PE film and CuCl$_2$ mesh. In addition, separation material produces from NR that is biorenewable polymer possibly compete with separation materials from other component for oil/water separation.

![Figure 4.21](image_url) The separation efficiencies versus the cycle numbers by taking hexane/water mixture as an example.
Table 4.7 Comparison of separating materials

<table>
<thead>
<tr>
<th>Type of substrate</th>
<th>Detail</th>
<th>Separation substance</th>
<th>WCA (*)</th>
<th>OCA (*)</th>
<th>η (%)</th>
<th>Cycle number</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel mesh</td>
<td>NR modified with FAS</td>
<td>hexane, dodecane, toluene, gasohol or diesel mixing water</td>
<td>153.9</td>
<td>0</td>
<td>&gt;99.86</td>
<td>30</td>
<td>This study</td>
</tr>
<tr>
<td>Copper mesh</td>
<td>Modification with lauric acid</td>
<td>petroleum, toluene, hexane, gasoline or diesel mixing water</td>
<td>155.5</td>
<td>0</td>
<td>&gt;93</td>
<td>10</td>
<td>[7]</td>
</tr>
<tr>
<td>Stainless Steel mesh</td>
<td>FeCl₃ solution and n-octadecylthiol</td>
<td>gasoline, diesel oil, engine oil, hexane or liquid paraffin mixing water</td>
<td>145.0</td>
<td>0</td>
<td>&gt;99</td>
<td>10</td>
<td>[8]</td>
</tr>
<tr>
<td>Stainless Steel Mesh</td>
<td>ZnO Microstructured</td>
<td>toluene in water</td>
<td>160.0</td>
<td>0</td>
<td>-</td>
<td>15</td>
<td>[46]</td>
</tr>
<tr>
<td>Stainless steel mesh</td>
<td>Modification with CuCl₂ and HCl</td>
<td>hexane, hexadecane, motor oil or heavy mineral oil mixing water</td>
<td>160.0</td>
<td>0</td>
<td>92.9</td>
<td>58</td>
<td>[47]</td>
</tr>
<tr>
<td>Material</td>
<td>Treatment</td>
<td>Contact Angle (°)</td>
<td>pH</td>
<td>OCA (%)</td>
<td>SEM (%)</td>
<td>Ref.</td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------------------------------------------</td>
<td>-------------------</td>
<td>----</td>
<td>---------</td>
<td>---------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>Stainless Steel mesh</td>
<td>Silica nanoparticles modified with PETMP and TMTVi</td>
<td>&gt;150</td>
<td>0</td>
<td>99.85</td>
<td>-</td>
<td>[52]</td>
<td></td>
</tr>
<tr>
<td>Polyethylene (PE) membrane</td>
<td>Scratching and pricking film</td>
<td>154.3</td>
<td>0</td>
<td>&gt;99.5</td>
<td>30</td>
<td>[48]</td>
<td></td>
</tr>
<tr>
<td>Polyester fabric</td>
<td>PFDTS and SiO$_2$ nanoparticles modified with PFOTS</td>
<td>154.6</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>[55]</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The modified stainless steel mesh with excellent oil/water separation efficiency was successfully prepared via simple and environmentally friendly method by dip-coated with NR/SiO$_2$ modified FAS-3 or NR/SiO$_2$ modified FAS-17. The natural rubber-encapsulated silica (NR/SiO$_2$) can undergo the chemical reaction with fluoroalkylsilane (FAS) under alkaline conditions at 6°C to provide the NR/SiO$_2$ modified FAS. Firstly, the natural rubber was encapsulated with inorganic silica shell using tetraethyl orthosilicate (TEOS) as a silica precursor. Secondly, the process was integrated between NR/SiO$_2$ and fluoroalkylsilane group including FAS-3 or FAS-17. Fourier transform infrared (FTIR) spectra, $^{29}$Si solid-state NMR spectra, the real time in situ FTIR spectra and kinetic profile confirmed that the silica shell was successfully fabricated onto the surface of natural rubber core. The $^{29}$Si solid-state NMR spectra of NR/SiO$_2$ resonance at -95.28 ppm and -105.10 ppm were attributed to Q$^3$ and Q$^4$ signal, respectively. The morphology of the encapsulated particles was investigated by transmission electron microscopy (TEM) and particle size can be determined by dynamic light scattering (DLS) technique. The thermal behavior of surface modified natural rubber was characterized by thermogravimetric analysis (TGA). The results showed the thermal stability enhancement of natural rubber after encapsulated with silica shell. The morphology of NR/SiO$_2$ revealed rubber core covered by silica shell. The silica fully encapsulated the rubber particles when used nonionic surfactant (Triton-X), 1:50 weight ratio (TEOS to NR) addition of 1 mL/min and reacted at 6°C for 20 min.

The NR/SiO$_2$ modified with fluoroalkylsilan (FAS) was prepared through the chemical reaction between the hydroxyl groups and silanol group in NR/SiO$_2$ under alkaline condition. The NR/SiO$_2$ was successfully modified with FAS when used 0.209 mmol of FAS-3 or 0.209 mmol of FAS-17. The wettability and surface morphology were characterized by water contact angle (WCA) measurements, scanning electron
microscopy (SEM) and atomic force microscopy (AFM). The stainless steel meshes, which were dip-coated with NR/SiO$_2$ modified FAS-3 and NR/SiO$_2$ modified FAS-17 exhibited hydrophobicity (WCA of 138°) and superhydrophobicity (WCA of 153.9°), respectively and superoleophilicity (OCA of 0°) of both modified meshed. In addition, the NR/SiO$_2$ modified FAS showed excellence oil/water separation efficiency including hexane/water, dodecane/water, toluene/water, gasohol 95/water and diesel oil/water mixture. The separation efficiency of NR/SiO$_2$ modified FAS-17 coated mesh (>99.84%) was slightly higher than NR/SiO$_2$ modified FAS-3 coated mesh (> 99.70%). For oil/water separation test with different organic solvents and oil, the separation efficiency values of NR/SiO$_2$ modified FAS with low viscosity oil (0.27-1.10 cSt) were slightly higher than high viscosity oil (3 cSt). For reusability, the separation efficiency of NR/SiO$_2$ modified FAS coated mesh can be reused over 30 cycles. Therefore, this research provided coating material, which can be applied a wide range of oil types with excellence oil/water separation efficiency, high reusability. Moreover, it has potential application in industrial oil/water mixture and oil spill accident.

5.2 Recommendations

The future investigation of this work should be carried out with the following aspect:

1. The effect of H$_2$O/TEOS ratio of reaction should be further studied for silica encapsulated natural rubber.

2. The confirmation of the present of fluoroalkylsilane segments and silica on the surface of natural rubber particles should be measured the surface elemental composition by X-ray photoelectron spectroscopy (XPS) using ion etching.
REFERENCES


[10] L. Wu, L. Li, B. Li, J. Zhang, A. Wang, Magnetic, Durable, and Superhydrophobic Polyurethane@Fe₃O₄@SiO₂@Fluoropolymer Sponges for Selective Oil Absorption and Oil/Water Separation, ACS Appl. Mater. Interfaces 7 (8) (2015) 4936–4946.


Figure A1 Oil/water separation process of (a) orange-colored gasohol 95/water mixture, (b) yellow-colored diesel/water mixture, (c) dodecane dyed/water mixture, (d) toluene dyed/water mixture for (1) oil/water mixture, (2) uncoated mesh, (3) NR/SiO$_2$ modified FAS-3 coated mesh and (4) NR/SiO$_2$ modified FAS-17 coated mesh. Water was colored by copper (II) sulphate.
APPENDIX B
Calculation the surface free energy (SFE)

Several approaches for the surface energy ($\gamma_{SV}$) calculation are proposed by Harmonic-mean equation. The SFE is composed of two components, the Lifshitz-van der Waals component (dispersive contribution, $\gamma_{SV}^d$) and Lewis acid-base component (polar contribution, $\gamma_{SV}^p$).

The harmonic mean can be used to calculate the dispersive and polar contribution of the surface energy by measuring the angles of two liquids, water(A) and dodecane(B).

This set of equations can be converted to two second degree equations as given below.

$$a^d(\gamma_{SV}^d)^2 + b^d\gamma_{SV}^d + c^d = 0 \quad \text{(Equation 3.6)}$$
$$a^p(\gamma_{SV}^p)^2 + b^p\gamma_{SV}^p + c^p = 0 \quad \text{(Equation 3.7)}$$

where the constants are

$$a^d = A_BB_A - A_AB_B \quad \text{(Equation 3.8)}$$
$$b^d = C_BB_A - C_AB_B - D_AA_B + D_AB_A \quad \text{(Equation 3.9)}$$
$$c^d = D_BC_A - D_AC_B \quad \text{(Equation 3.10)}$$
$$a^p = A_BC_A - A_AC_B \quad \text{(Equation 3.11)}$$
$$b^p = B_BC_A - B_AC_B - D_AA_B + D_AB_A \quad \text{(Equation 3.12)}$$
$$c^p = D_BB_A - A_BB_B \quad \text{(Equation 3.13)}$$

and

$$A_i = \gamma_{LV_i}(3 - \cos\theta)/4 \quad \text{(Equation 3.14)}$$
$$B_i = \gamma_{LV_i}^p[\gamma_{LV_i}^d - \gamma_{LV_i}(1 + \cos\theta_i)/4] \quad \text{(Equation 3.15)}$$
$$C_i = \gamma_{LV_i}^p[\gamma_{LV_i}^p - \gamma_{LV_i}(1 + \cos\theta_i)/4] \quad \text{(Equation 3.16)}$$
$$D_i = \gamma_{LV_i}^d\gamma_{LV_i}^p\gamma_{LV_i}[(1 + \cos\theta_i)/4] \quad \text{(Equation 3.17)}$$
for i is A(water) and B(dodecane), respectively and \( \gamma \) is the surface free energy. The superscripts p and d refer to the polar and dispersive contribution to the surface free energy of a given material and the subscripts LV refer to the liquid–vapor surfaces.

**Table data for calculation**

**Table 3.1** Surface tension (\( \gamma \)) of components (mN/m) for selected contact angle test liquids at 25°C [58]

<table>
<thead>
<tr>
<th></th>
<th>Total surface free energy (( \gamma_{LV} )) (mN/m)</th>
<th>Dispersion component (( \gamma_{LV}^d )) (mN/m)</th>
<th>Polar component (( \gamma_{LV}^p )) (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (A)</td>
<td>72.8</td>
<td>21.8</td>
<td>51.0</td>
</tr>
<tr>
<td>Dodecane (B)</td>
<td>25.4</td>
<td>25.4</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table 4.5** Average contact angle values (°) measured for drop of water and dodecane formed on the uncoated coated mesh, NR coated mesh, NR/SiO\(_2\) coated mesh, NR/SiO\(_2\) modified FAS-3 coated mesh and NR/SiO\(_2\) modified FAS-17 coated mesh

<table>
<thead>
<tr>
<th>Surface</th>
<th>Test liquids</th>
<th>Water (°)</th>
<th>Dodecane (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncoated mesh</td>
<td></td>
<td>77.5</td>
<td>15.6</td>
</tr>
<tr>
<td>NR coated mesh</td>
<td></td>
<td>85.2</td>
<td>20.1</td>
</tr>
<tr>
<td>NR/SiO(_2) coated mesh</td>
<td></td>
<td>0</td>
<td>23.4</td>
</tr>
<tr>
<td>NR/SiO(_2) modified FAS-3 coated mesh</td>
<td></td>
<td>138.0</td>
<td>0</td>
</tr>
<tr>
<td>NR/SiO(_2) modified FAS-17 coated mesh</td>
<td></td>
<td>153.9</td>
<td>0</td>
</tr>
</tbody>
</table>

**Example of calculation:**

- Surface free energy (\( \gamma_{SV} \)) of NR/SiO\(_2\) modified FAS-3 coated mesh of water(A) contact angle is determined with Equation 3.6 - Equation 3.17.

\[
A_i = \frac{\gamma_{LV}(3 - \cos \theta)}{4} \quad \text{(Equation 3.14)}
\]

\[
B_i = \gamma_{LV}^p \left[ \gamma_{LV}^d - \gamma_{LV}(1 + \cos \theta)/4 \right] \quad \text{(Equation 3.15)}
\]
\( C_i = \gamma_{LV_i}^d \left[ \gamma_{LV_i}^p - \gamma_{LV_i}(1 + \cos \theta_i)/4 \right] \)  
(Equation 3.16)

\( D_i = \gamma_{LV_i}^d \gamma_{LV_i} \gamma_{LV_i}(1 + \cos \theta_i)/4 \)  
(Equation 3.17)

\( \gamma_{LV_A} = 72.8 \text{ mN/m} \)
\( \cos \theta_A = 138^\circ \)
\( \gamma_{LV_A}^p = 51.0 \text{ mN/m} \)
\( \gamma_{LV_A}^d = 21.8 \text{ mN/m} \)

\[ A_A = (72.8 \text{ mN/m} \times (3 - \cos(138))/4 = 68.13 \text{ mN/m} \]
\[ B_A = (51.0 \text{ mN/m} \times (21.8 \text{ mN/m}) - (72.8 \text{ mN/m} \times (1 + \cos(138))/4 = 873.39 \text{ mN/m} \]
\[ C_A = (21.8 \text{ mN/m} \times (51.0 \text{ mN/m}) - (72.8 \text{ mN/m} \times (1 + \cos(138))/4 = 1009.90 \text{ mN/m} \]
\[ D_A = (21.8 \text{ mN/m} \times (51.0 \text{ mN/m}) \times (72.8 \text{ mN/m}) \times (1 + \cos(138))/4 = 5197.40 \text{ mN/m} \]

Hence, \( A_A \), \( B_A \), \( C_A \) and \( D_A \) are 68.13, 873.39, 1009.90 and 5197.40 mN/m, respectively.

\[ a^d = A_B A_A - A_A B_B \]  
(Equation 3.8)

\[ b^d = C_B A_A - C_A B_B - D_A A_B + D_B A_A \]  
(Equation 3.9)

\[ c^d = D_B C_A - D_A C_B \]  
(Equation 3.10)

\[ a^p = A_B C_A - A_A C_B \]  
(Equation 3.11)

\[ b^p = B_B C_A - B_A C_B - D_A A_B + D_B A_A \]  
(Equation 3.12)

\[ c^p = D_B B_B - D_A B_B \]  
(Equation 3.13)

\( A_A = 68.13 \text{ mN/m} \)
\( B_A = 873.39 \text{ mN/m} \)
\( C_A = 1009.90 \text{ mN/m} \)
\( D_A = 5197.40 \text{ mN/m} \)
\( A_B = 12.70 \text{ mN/m} \)
\( B_B = 0.0 \text{ mN/m} \)
\( C_B = -322.58 \text{ mN/m} \)
\( D_B = 0.0 \text{ mN/m} \)
\[ a^d = (12.70 \text{ mN/m})(873.39 \text{ mN/m}) - (68.13 \text{ mN/m})(0.0 \text{ mN/m}) = 11092.02 \text{ mN/m} \]
\[ b^d = (-322.58 \text{ mN/m})(873.39 \text{ mN/m}) - (1009.90 \text{ mN/m})(0.0 \text{ mN/m}) -
(5197.40 \text{ mN/m})(12.70 \text{ mN/m}) + (0.0 \text{ mN/m})(68.13 \text{ mN/m}) = -347744.20 \text{ mN/m} \]
\[ c^d = (0.0 \text{ mN/m})(1009.90 \text{ mN/m}) - (5197.40 \text{ mN/m})(-322.58 \text{ mN/m}) = 1676578.20 \text{ mN/m} \]
\[ a^p = (12.70 \text{ mN/m})(1009.90 \text{ mN/m}) - (68.13 \text{ mN/m})(-322.58 \text{ mN/m}) = 34801.44 \text{ mN/m} \]
\[ b^p = (0.0 \text{ mN/m})(1009.90 \text{ mN/m}) - (873.39 \text{ mN/m})(-322.58 \text{ mN/m}) -
(5197.40 \text{ mN/m})(12.70 \text{ mN/m}) + (0.0 \text{ mN/m})(68.13 \text{ mN/m}) = 215730.17 \text{ mN/m} \]
\[ c^p = (0.0 \text{ mN/m})(873.39 \text{ mN/m}) - (5197.40 \text{ mN/m})(0.0 \text{ mN/m}) = 0.0 \text{ mN/m} \]

Therefore, \(a^d, b^d, c^d, a^p, b^p\) and \(c^p\) are 11092.02, 347744.20, 1676578.20, 34801.44, 215730.17 and 0.0 mN/m, respectively.

\[
\begin{align*}
  a^d(y_{SV}^d)^2 + b^d y_{SV}^d + c^d & = 0 \quad \text{(Equation 3.6)} \\
  a^p(y_{SV}^p)^2 + b^p y_{SV}^p + c^p & = 0 \quad \text{(Equation 3.7)}
\end{align*}
\]

\[
\begin{align*}
  (11092.02 \text{ mN/m})(y_{SV}^d)^2 + (347744.20 \text{ mN/m})(y_{SV}^d)^2 + (1676578.20 \text{ mN/m}) & = 0 \quad \text{(Equation 3.6)} \\
  (34801.44 \text{ mN/m})(y_{SV}^p)^2 + (215730.17 \text{ mN/m})(y_{SV}^p)^2 + (0.0 \text{ mN/m}) & = 0 \quad \text{(Equation 3.7)}
\end{align*}
\]

The solution to the second degree equation is given by the quadratic formula:

\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad \text{(Equation A1)}
\]
Example in term of polar contribution ($\gamma_{SV}^p$)

\[ a^p = 34801.44 \text{ mN/m} \]
\[ b^p = 215730.17 \text{ mN/m} \]
\[ c^p = 0.0 \text{ mN/m} \]

\[
\therefore x = \frac{(-34801.44 \text{ mN/m}) \pm \sqrt{(34801.44 \text{ mN/m})^2 - 4(215730.17 \text{ mN/m})(0.0 \text{ mN/m})}}{2(34801.44 \text{ mN/m})}
\]

\[ = -6.20 \text{ and } 0.0 \text{ mN/m} \]

Thus, the polar contribution ($\gamma_{SV}^p$) of NR/SiO$_2$ modified FAS-3 coated mesh is 0 mN/m because the roots of the second degree equations are found in the positive roots.

Furthermore, the dispersive contribution ($\gamma_{SV}^d$) of NR/SiO$_2$ modified FAS-3 coated mesh is 5.95 mN/m, which is calculated as above (Example in term of polar contribution ($\gamma_{SV}^p$)). The surface free energy is composed of two components, therefore the surface free energy ($\gamma_{SV}$) of NR/SiO$_2$ modified FAS-3 coated mesh is 5.95 mN/m.
APPENDIX C

Calculation the oil/water separation efficiency (\( \eta \))

The oil/water separation efficiency (\( \eta \), expressed as a percentage) is determined with the following equation:

\[
\eta \, (\%) = \left( \frac{m_{\text{collected}} - m_{\text{water}}}{m_{\text{collected}}} \right) \times 100
\]  
(Equation 3.18)

where \( m_{\text{collected}} \) is the weight (g) of the collected oil after separation process and

\( m_{\text{water}} \) is the water content (g) determined by the titration method, respectively.

Furthermore, the water content in the collected oil is determined by following equation:

\[ m_{\text{water}} = V_{\text{HCl}} \times \rho_{\text{water}} \]  
(Equation 3.19)

where \( V_{\text{HCl}} \) is the volume (mL) of the consumed HCl aqueous solution and

\( \rho_{\text{water}} \) is the density (g/mL) of water at 30°C (0.996 g/mL).

The reusability of mesh is determined from oil/water separation efficiency (\( \eta \), expressed as a percentage) of each cycle.

Example of calculation:

- The oil/water separation efficiency (\( \eta \)) of NR/SiO\(_2\) modified FAS-3 coated mesh with hexane is determined with Equation 3.18 and Equation 3.19.

\[
V_{\text{HCl}} = 1.0 \text{ mL}
\]

\[
\rho_{\text{water}} = 0.996 \text{ g/mL}
\]

\[
\therefore m_{\text{water}} = (1.0 \text{ mL})(0.996 \text{ g/mL})
\]

\[
= 0.996 \text{ g}
\]

Thus, the water content (g) determined by the titration method (\( m_{\text{water}} \)) is 0.996 g
\[ m_{\text{collected}} = 20.0 \text{ g} \]
\[ m_{\text{water}} = 0.996 \text{ g} \]
\[
\therefore \eta(\%) = \left(\frac{20 \text{ g} - 0.996 \text{ g}}{20.0 \text{ g}}\right) \times 100% \\
= 95.02 \%
\]

Therefore, the oil/water separation efficiency (\(\eta\)) of \(\text{NR/SiO}_2\) modified FAS-3 coated mesh with hexane is 95.02%.
**BIOGRAPHY**

<table>
<thead>
<tr>
<th>Name</th>
<th>Miss Jitraporn Saengkaew</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date of Birth</td>
<td>September 8, 1992</td>
</tr>
</tbody>
</table>
| Educational Attainment| 2008: Secondary school at Sarakhampittayakhom Mahasarakham  
                           2011: High school at Sarakhampittayakhom Mahasarakham  
                           2015: Bachelor of Science (Chemistry) at Thammasat University |
| Scholarship           | 2015: Scholarship for Talent Student, Faculty of science and technology, Thammasat University  
                           2017: Scholarship for Master Student of STEM (Science, Technology, Engineering, Mathematics) Workforce 2560, National Science and Technology Development Agency : NSTDA  
                           2017: Scholarship for exchange student 2017 from Faculty of science and technology, Thammasat University |
| Work Experiences      | Visiting student for 2 months (July 31, 2017 to October 1, 2017) at Department of Frontier Materials Chemistry, Hirosaki University, Japan.  
                           2017: Oral Presentation in title “Fabrication of Hydrophobic Mesh by NR/ SiO$_2$-encapsulated Fluoroalkylsilane Coating for Oil/Water Separation” at The International Conference on |
Surfaces, Coatings and Interfaces (SurfCoat Korea 2017), March 29-31, Incheon, Rep. of Korea

2016: Poster Presentation in title “Encapsulation of Natural Rubber by Silica via One-Pot Procedure” at International Polymer Conference of Thailand, June 30-July 1, Pathumwan Princess Hotel, Bangkok, Thailand