MODIFICATION OF CALCIUM CARBONATE SURFACE BY POLYISOPRENE FOR IMPROVED COMPATIBILITY WITH NATURAL RUBBER

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Thesis
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ABSTRACT

Calcium carbonate ($CaCO_3$) is a low-cost inorganic filler commonly used in manufacturing of natural rubber latex products. However, the main problem of $CaCO_3$ is the incompatibility with and low dispersibility in hydrophobic natural rubber, resulting in a decrease of mechanical properties of $CaCO_3$-filled natural rubber products. This problem may be solved by modification of the $CaCO_3$ surface to reduce its polarity and, hence, to improve its affinity with non-polar rubbers. In this study, the surface of $CaCO_3$ was modified with polyisoprene using admicellar polymerization. The parameters which influence admicellar polymerization of isoprene on the surface of $CaCO_3$ were examined. The results of FTIR and TGA testing showed that polyisoprene was successfully formed as an ultra-thin layer on the $CaCO_3$ surface. The modified $CaCO_3$ particles also showed increased hydrophobicity. Incorporation of the modified $CaCO_3$ into natural rubber latex gave dried rubber film with improved mechanical properties. In addition, a lower amount of modified $CaCO_3$ was required to achieve similar properties compared with the unmodified $CaCO_3$.

KEY WORDS: ADMICELLAR POLYMERIZATION / NATURAL RUBBER / CALCIUM CARBONATE / POLYISOPRENE

78 pages

การดัดแปรผิวแคลเซียมคาร์บอเนตด้วยพอลิไอโซพรีน เพื่อปรับปรุงการเข้ากันได้กับยางธรรมชาติ

MODIFICATION OF CALCIUM CARBONATE SURFACE BY POLYISOPRENE FOR IMPROVED COMPATIBILITY WITH NATURAL RUBBER

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บทคัดย่อ

แคลเซียมคาร์บอเนตเป็นสารตัวเติมที่นิยมใช้กันอย่างแพร่หลายในอุตสาหกรรมผลิตภัณฑ์จากน้ำยางธรรมชาติ อย่างไรก็ตาม ปัญหาส่วนใหญ่ที่พบคือการแยกชั้นและการกระจายตัวต่ำของแคลเซียมคาร์บอเนต เมื่อใช้ในยางธรรมชาติ ซึ่งส่งผลให้คุณสมบัติเชิงกลของผลิตภัณฑ์จากยางธรรมชาติลดลง ปัจจุบัน ปัญหาการใช้สารตัวเติมแคลเซียมคาร์บอเนตสามารถแก้ไขได้โดยการปรับปรุงสภาพพื้นผิวของแคลเซียมคาร์บอเนตเพื่อลดความมีขั้ว ซึ่งส่งผลให้สารตัวเติมแคลเซียมคาร์บอเนตนี้สามารถเข้ากันได้ดีกับยางธรรมชาติมากขึ้น ในงานวิจัยนี้ ได้ศึกษาการปรับปรุงพื้นผิวของแคลเซียมคาร์บอเนต โดยการเคลือบผิวด้วยพอลีไอโซพรีน ผ่านกระบวนการที่เรียกว่า แอดไมเซลลาร์ พอลีเมอไรเซชั่น โดยทำการศึกษาปัจจัยต่างๆที่มีผลต่อกระบวนการนี้ด้วย จากผลของ FTIR และ TGA พบว่า กระบวนการแอดไมเซลลาร์ พอลีเมอไรเซชั่น สามารถสังเคราะห์พอลีไอโซพรีนเคลือบผิวของสารตัวเติมแคลเซียมคาร์บอเนตได้ โดยแคลเซียมคาร์บอเนตหลังการปรับปรุงพื้นผิวนี้ มีความไม่ชอบน้ำเพิ่มขึ้นและกระจายตัวได้ดีในสารลดแรงตึงผิวอีกด้วย และเมื่อนำแคลเซียมคาร์บอเนตหลังการปรับปรุงพื้นผิว ใส่ลงไปในน้ำยางธรรมชาติ พบว่า สมบัติเชิงกลของยางธรรมชาติดีขึ้น ยิ่งไปกว่านั้น การใส่แคลเซียมคาร์บอเนตหลังการปรับปรุงพื้นผิวนี้ จะใช้ในปริมาณที่น้อยกว่า แต่ให้คุณสมบัติเชิงกลที่คล้ายคลึงกัน เมื่อเปรียบเทียบกับแคลเซียมคาร์บอเนตที่ไม่มีการปรับปรุงพื้นผิว

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LIST OF ABBREVIATIONS

NRL **=** **Natural rubber latex**
$CaCO_3$ = Calcium carbonate
GCC = Ground calcium carbonate
PCC = Precipitated calcium carbonate
hmc = Hemimicelles concentration
SDS = Sodium dodecyl sulfate
PZC = Point of zero charge
cac = Critical admicelles concentration
CMC = Critical micelle concentration
NaCl = Sodium chloride
HCl = Hydrochloric acid
NaOH = Sodium hydroxide
KOH = Potassium hydroxide
ZnO = Zinc oxide
ZDEC = Zinc diethyl dithiocarbamate
S = Sulphur
TGA = ThermogravimetricAnalyser
FTIR = Fourier Transform Infared Spectrometer
GPC = Gel Permeation Chromatography
DMA = Dynamic Mechanical Analyser
M_n = Number-average molecular weight
M_w = Molecular weights
PDI = Polydispersity
WCA = Water contact angle
E’ = Storage modulus

CHAPTER I
INTRODUCTION

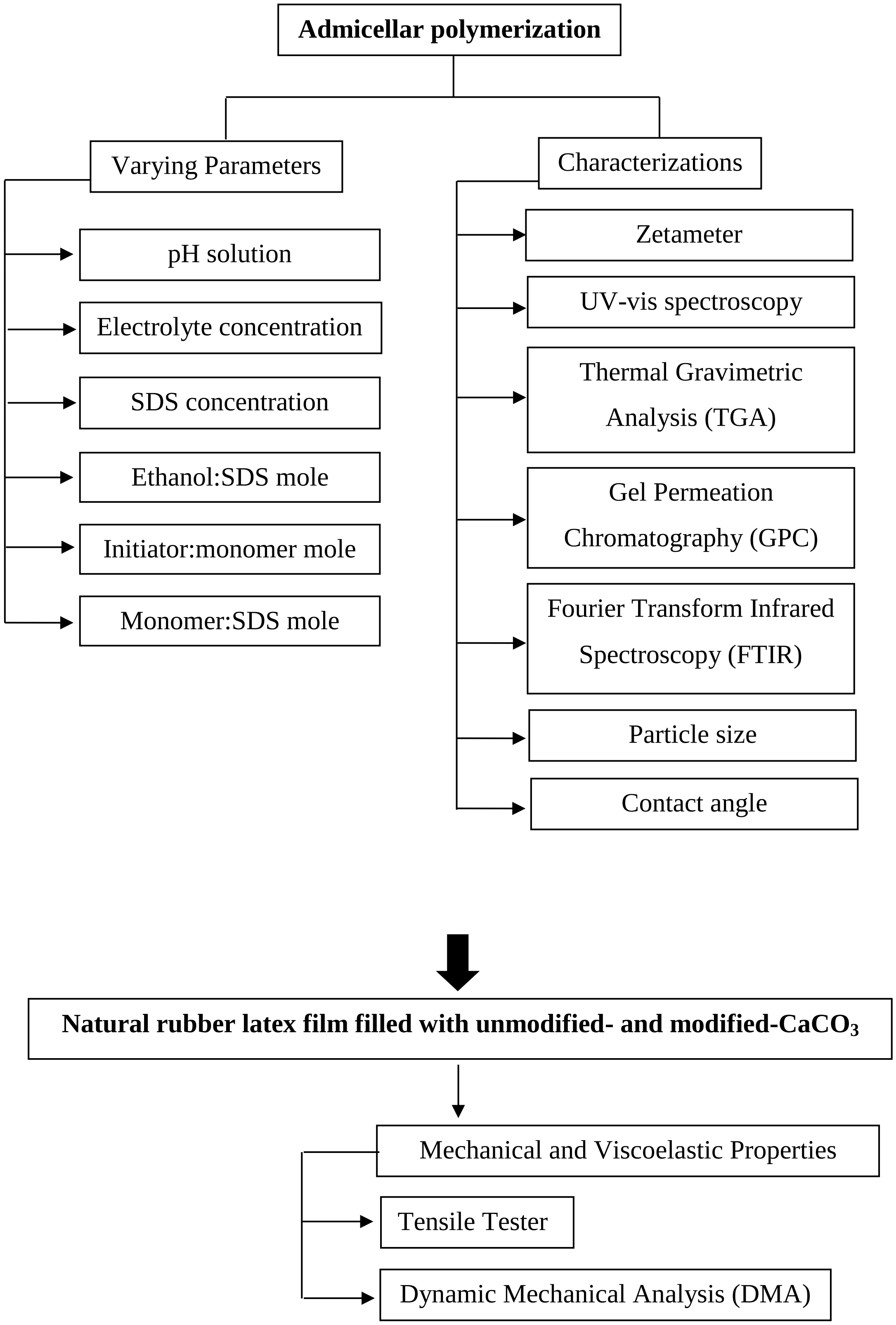
1.1. Background

Natural rubber (NR) has been an essential commodity in Thailand for a long time. Even though there are many synthetic rubbers, for example, styrene-butadiene rubber (SBR), butadiene rubber (BR), nitrile rubber (NBR), and isoprene rubber (IR), etc., that have attracted interest, NR remains use in various industrial applications such as automotives, adhesives and textiles due to its higher strain induce-crystallization than synthetic rubbers. Therefore, special properties such as high elasticity, low heat build-up and good abrasion resistance, are obtained in finished products that compose of NR as a main component. Natural rubber latex (NRL) is a milky fluid colloid, which mainly consists of *cis*-1,4-polyisoprene. It is a biosynthesized polymer which is mostly obtained from Heavea brasilliensis. NRL is used in wide range of applications such as latex gloves, condom, glue, medical products and coating. Fillers and pigments, for example, carbon black, silica, clay, and calcium carbonate have been applied in NRL products to obtain desired properties and colors. $CaCO_3$ is one of the most common mineral fillers used in various manufactories such as paper, rubber, paint and plastic, in order to reduce cost, discolor and stiffen the finished products. The major advantages of $CaCO_3$ are whiteness, brightness (about to 94%), non-toxic and high chemical stability. Generally, $CaCO_3$ can be classified into two types based on processing technique which are ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC). However, the main problem in the use of $CaCO_3$ is the incompatibility with hydrophobic polymer, which is directly affected on quality of final products. Therefore, to solve this problem, modified $CaCO_3$ surface by admicellar polymerization was considered. Admicellar polymerization is a technique to provide an ultra-thin polymeric film onto a solid substrate [1-4]. This method has an efficiency to enhance compatibility and increase dispersion of the filler in polymeric matrices. Several authors used the admicellar polymerization to improve dispersion of silica, aluminum pigment and $CaCO_3$. Generally, admicellar polymerization is carried out in four-steps; (1) The surfactant is first dissolved in water and then, adsorbs onto solid substrate in the form of bilayers (Admicelles) formation; (2) The monomers are absorbed into the interior admicelles; (3) The initiators are added to activate polymerization reaction within admicelle; and (4) The surface-modified $CaCO_3$ particles are washed by water to remove the excess surfactant and thus, an ultra-thin polymeric film is exposed. The adsorbed surfactants on solid surface are strongly relied on several parameters, such as nature of substrate surface, chemical structure of surfactant, and especially pH of the solution [1-2,5]. The surface charge on $CaCO_3$ can be either positive or negative charge depending on pH of the modified solution. This can be determined in terms of the point of zero charge (PZC), which is the pH at which a net charge on substrate is zero. When pH exceeds PZC, the surface of substrate is negatively charged. In contrast, the surface-charge of substrate is positively when pH values below PZC. Therefore, a study of pH ranges by PZC can be utilized to select a proper surfactant. The other factors influencing on the admicellar polymerization including SDS concentration, electrolyte concentration, ethanol content, and the amount of initiator and monomer, were also reported. We characterized the polyisoprene coated on the $CaCO_3$ surface and studied the mechanical properties of NRL filled with modified-$CaCO_3$.

1.2 Objective

The main purpose of this present work is to modify surfaces of $CaCO_3$ particles by polyisoprene using admicellar polymerization. The influence of unmodified- and modified-$CaCO_3$ on properties of natural rubber latex are also examined and compare with the commercial grade $CaCO_3$.

1.3 Scope of this work



CHAPTER II
LITERATURE REVIEW

This chapter consists of seven parts to explain the theory and the previous work which are related to our study including natural rubber latex, calcium carbonate, admicellar polymerization, surfactant, adsorption isotherm and its parameters, polymerization method and monomer, and natural rubber latex film.

2.1 Natural rubber latex (NRL)

Natural rubber latex (NRL) is a milk-like liquid, which is majority obtained from Hevea brasilliensis tree. NRL is categorized in a complex colloid system containing rubber particles, *cis*-1,4-polyisoprene (Figure 2.1), dispersed in water medium. The latex particles have negative charges on their surface. This is because the concentrated NRL still contains some protein and other non-rubber components which generate the negative charges to stabilize the latex particles. Consequently, the NRL particles are negatively charged at alkaline pH and the surface charge increases with increasing pH [3].

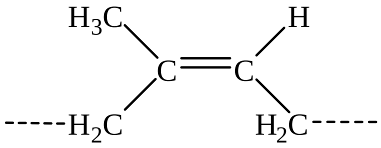


Figure 2.1 *cis*-1,4-polyisoprene.

The field latex contains about 95% rubber and 5% non-rubber contents such as protein, resin, ash and carbohydrate [3]. The general composition of the latex is given in Table 2.1.

Table 2.1 Chemical composition of the field latex [27].

Composition	Percentage by weight
Rubber (*cis*-1,4-polyisoprene)	33
Proteineous substances	1.0 - 1.5
Resinous substances	1.0 - 2.5
Ash	up to 1
Sugars/polysaccharides	1.0
Water	ca 60

NRL is used in numerous of rubber dipped goods manufacture such as gloves, condom, balloon and rubber shoes because it provides excellent elasticity, flexibility, antivirus permeation and biodegradability [20]. However, it is impossible to achieve the proper quality products for any applications without addition of fillers. Consequently, latex or rubber are often filled with fillers or pigments such as carbon blacks, calcium carbonate, talc, clays, silica, and others to ensure that the properties are good enough for desired applications or to produce new materials of the rubber composites [2,28,40].

2.2 Calcium carbonate ($CaCO_3$)

The mineral fillers (i.e., carbon blacks, silica, mica, calcium carbonate and clays) have been widely used in latex industries for decades in which of to stiffen products, to reduce cost or to color products [5,29]. In addition to these, the mineral fillers are extensively used to reinforce rubber products, resulting in the greater mechanical properties (i.e., tensile strength, tear strength and abrasion resistance) [29,40]. The effect of fillers on mechanical and other properties of the polymer composites depends strongly on its shape, particle size, aggregate size, surface characteristics and degree of dispersion [2,39]. Filler are classified fillers into four types based on their average particles size (nm), as shown in Figure 2.2.

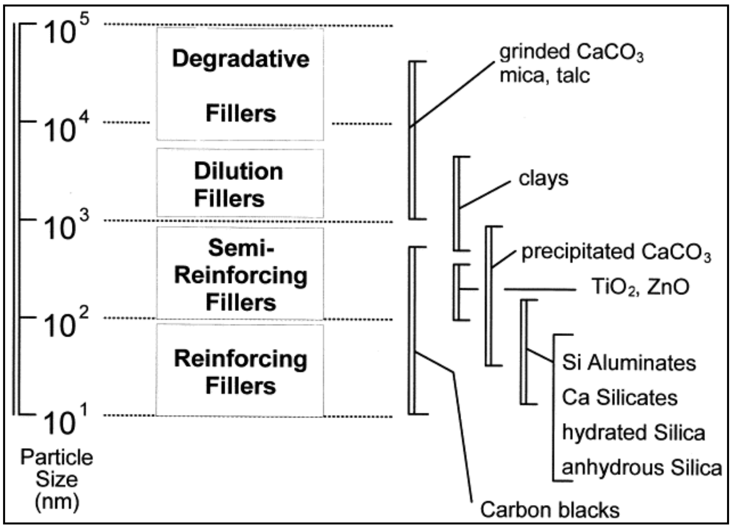


Figure 2.2 Classification of fillers based on their particle size [6].

In latex dipped goods, one of various mineral fillers that is $CaCO_3$ has been interested from rubber industry due to its low cost and various available forms [1-2,15].

$CaCO_3$ can be classified into two types which are ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) [1,5]. The general properties of both types of $CaCO_3$ are shown in Table 2.2.

Table 2.2 The general properties of $CaCO_3$ [5].

Properties	Information
Density (g/cm^3)	2.7-2.9
Mohs hardness	3-4
Decomposition temperature (°C)	1150
Water solubility (%)	0.99×10^{-8}
Water suspension pH	9-9.5
Refractive index	1.48- 1.70
Whiteness (%)	80-98
Brightness (%)	82-94
Color	white to gray
Particle size (µm)	0.02-30 (GCC), 0.02-0.4 (PCC)

GCC is produced by grinding the mineral $CaCO_3$ such as limestone, marble, chalk, and calcite. The particle size of particulate GCC is relatively large. The standardized compositions of GCC family should be more than 94 and 95 % $CaCO_3$ contents and brightness, respectively [5].

PCC is derived from re-crystallization of mineral $CaCO_3$. The crystalline form can be manipulated upon request. PCC is differentiated from GCC by higher whiteness, brightness, and smaller particles size [5].

According to the classification of fillers (Figure. 3), smaller particle size e.g., silica, carbon black and PCC, is able to reinforce products providing excellent mechanical properties, whereas larger size particles e.g., mica, talc and GCC act as extender to dilute or to reduce product cost. As the results, PCC grade is more suitable to improve performance of finished products than GCC grade.

2.2.1 Previous works

Many researchers attempted to improve the mechanical properties of polymer products by the addition of $CaCO_3$, as follow;

Cai and co-workers [35] reported that the modulus increased with increasing $CaCO_3$ contents ranging from 0 to 30 wt%, whereas elongation tended to decrease. The tensile and tear strength of natural rubber latex film improved when an ultrafine $CaCO_3$ content was added up to 15 wt% and, then, they are decreased. In this work, the optimum value for reinforcing latex film with nano-$CaCO_3$ is 15 wt%.

Jin and Park [36] reported that the thermal stability of butadiene rubber was significantly enhanced by adding nano-$CaCO_3$. The mechanical properties e.g., tensile strength increased with increasing nano-$CaCO_3$ content. The elongation at break of the composites increased by adding nano-$CaCO_3$ to 10 wt%, after that it kept a constant.

Manroshan and Baharin [37] studied the effect of $CaCO_3$ content on the mechanical properties of NRL films. They reported that 300 %modulus of latex film increased with the increase in nano-$CaCO_3$ content. The tensile strength and elongation at break tended to increase with the increase in nano-$CaCO_3$ up to 10 phr before decreasing.

Based on the aforementioned works, the limitation of $CaCO_3$ contents has been found. This is due to the incompatibility and low dispersibility of $CaCO_3$ in rubber matrix. Accordingly, modification of $CaCO_3$ surface would help to incorporate higher $CaCO_3$ loading into rubber matrix, resulting in the enhancement of mechanical properties of rubber.

2.3 Admicellar polymerization

Admicellar polymerization is one of the modification methods, which creates an ultra-thin polymeric film coating on solid substrate through a physical adsorption of surfactant template [1-2,7-11,57]. As previously discussed, the surface of $CaCO_3$ should be modified to enhance mechanical properties of rubber materials. There are many methods to modify surface of solid powder such as grafting, coupling and acid treating [41-43]. However, the advantages of admicellar polymerization method beside compatibility improvement are environmentally friendly, relatively precise, versatile and adaptability for different applications [8]. The admicellar polymerization process involves four basic steps, as illustrated in Figure 2.3.

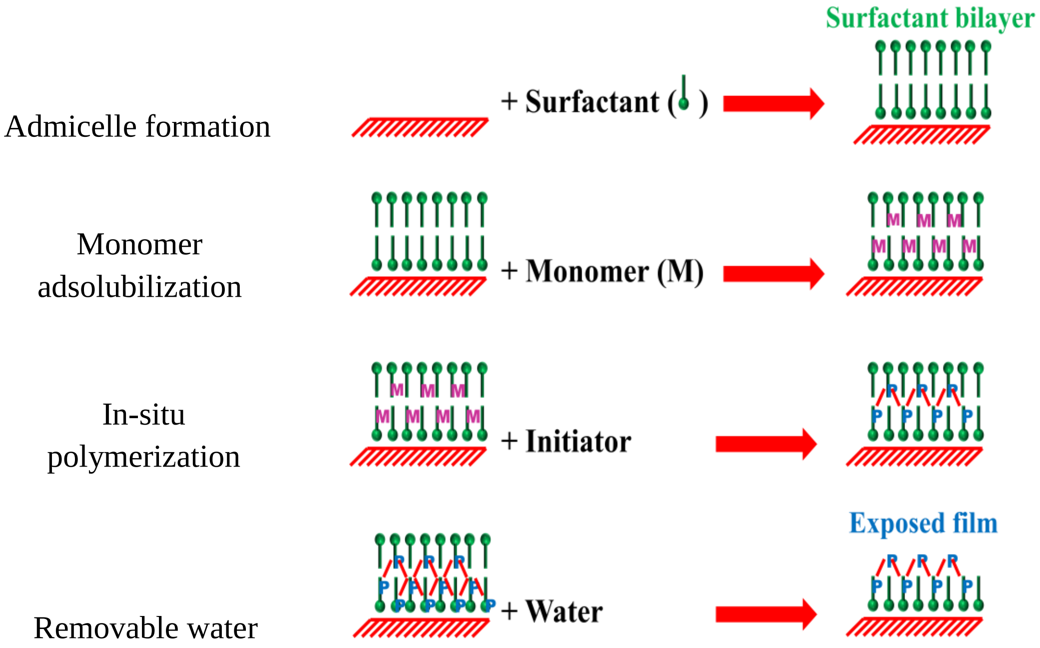


Figure 2.3 Admicellar polymerization [1-2,7,9].

Step 1. Admicellar formation. The surfactant molecules were priority dissolved in water to form admicelles or bilayers adsorbed on solid substrate [9,11,22]. The formation of this surfactant aggregates can be achieved through coulombic attraction (electrostatic force) between surfactant hydrophilic moieties and the mineral surface and the surfactant tail to tail interaction (hydrophobic effect) [13,17,24]. In this step, the selection of surfactant types is relied on the charge of solid surface, the chemical nature of the polymer formation, and the initiator system [9].

Step 2. Monomer adsolubilization. This process is an adsolubilization of hydrophobic monomers into the admicelle formation from step 1 [9,11,22]. The adsolubilization is defined as the partition of organic solutes into the interior of adsorbed surfactant aggregates [18].

Step 3. In situ polymerization. The initiator was added to activate polymerization reaction within the admicelles. In this study, the thermal initiator, potassium persulphate ($K_2S_2O_8$), was used [9,11,22].

Step 4. Water removal. To expose an ultra-thin polymeric film coated on the solid surface, the outer surfactant layer is removed by water as much as possible until no bubble occurred [9,11,22].

2.3.1 Previous works

Several authors have been proposed the using of admicellar polymerization to modify various solid surfaces, as follows:

Rungruang and co-workers [2] used admicellar polymerization to modify calcium carbonate particles before applying in isotactic polypropylene (iPP). They produced a thin layer of polypropylene (PP) on the calcium carbonate surface using sodium dodecyl sulphate (SDS) as the surfactant template, and sodium persulphate as the thermal initiator. From SEM, it was found that iPP filled with either acid-coated or admicellar-treated $CaCO_3$ exhibited a better distribution with a lower degree of agglomerate as compared with the untreated one. Furthermore, they observed that iPP filled with admicellar-treated $CaCO_3$ particles had greater impact strength than that of the untreated-$CaCO_3$.

Wang and co-workers [8] modified alumina surface in order to enhance its hydrophobicity by admicellar polymerization. They studied an ultra-thin film of polystyrene (PS) cross-linked with divinylbenzene (DVB) coated on the surface of alumina by admilcellar polymerization. Sodium dodecyl sulphate (SDS) and azobisisobutyronitrile (AIBN) were used as the surfactant template and the initiator, respectively. The results showed that the alumina particles became more hydrophobic with the presence of PS coating, although styrene is replaced with 10 %DVB. It is demonstrated that the surface-treated alumina by admicellar polymerization process could improve the wetting resistance of the materials.

Nontasorn and co-workers [21] examined the modification of precipitated silica by using admicellar polymerization in order to improve rubber-filler interaction in rubber compound process. In their work, cetryltriammonium bromide (CTAB), AIBN and comonomers of styrene and isoprene were selected to synthesize polymeric film coating on silica surface. They observed that rubber compound filled with modified-silica showed significantly improvement of its physical properties as compared to unmodified-silica. It was clear that the compatibility of silica particles with rubber matrix can be improved by using admicellar polymerization.

O’Haver and co-workers [22] studied the formation of copolymer on precipitated silica by using admicellar polymerization to reduce the cure times and to improve physical properties of rubber compound. The decrease of cure times was observed in rubber compound containing treated-precipitated silica, while the mechanical properties, e.g. tear strength, elongation at break, and cut growth resistance were increased as compared to these of the untreated one.

Somnuk, U. and co-workers [23] used the admicellar polymerization to modify milled glass fiber by coating a thin polyethylene film. The results showed that tensile, flexural, and impact strength of HDPE was increased by adding treated-glass fiber.

2.3.2 Monomer adsolubilization [1,16,18]

The differences between solubilization and adsolubilization can be described, as shown in Figure 2.4. Adsolubilization is the incorporation of compounds into the surfactant aggregates, whereas the solubilization is the partitioning of the compound into the micelles.

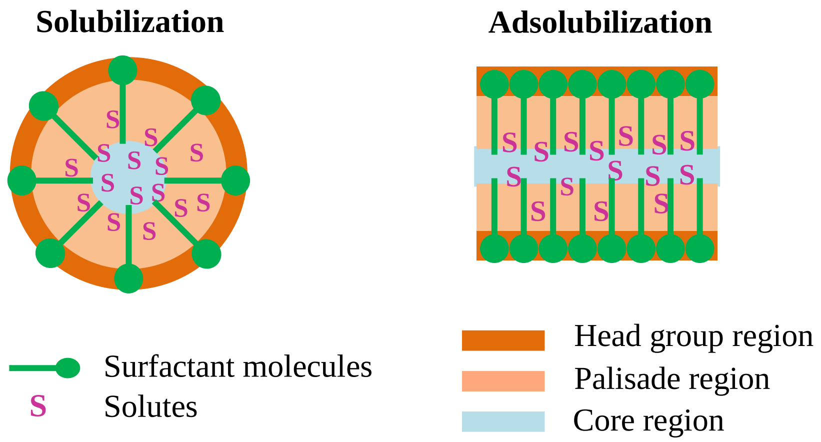


Figure 2.4 Phenomena of solubilization and adsolubilization**.**

2.3.3 The aid of ethanol on the monomer adsolubilization

Many authors attempted to explain the aid of ethanol on monomer adsolubilization. It was believed that an increased solubility of the monomer molecules within the surfactant template can be observed by adding ethanol or other constituents without affecting the adsorbed surfactant onto the solid particles [39,56]. For example, Wu and co-workers [39] described that the isoprene monomer was impossible to participate into the surfactant bilayer formation without ethanol content, due to the low solubility in water. Harwell and co-worker [56] reported that the solubility of styrene in SDS-alumina system may be increased by adding ethanol. Similar result was observed and reported by Wu and co-workers [10]. Sakhalkar and co-workers [7] studied the admicellar polymerization of polystyrene on the glass fiber. They found that the solubility of water-insoluble styrene in the surfactant solution can be enhanced by adding ethanol. Furthermore, some researcher reported the ethanol content influencing on surfactant adsorption isotherm, which was further described in section 2.5.1.

2.4 Surfactants

Surfactants are amphiphilic molecules composing of two proportions (Figure 2.5). The first is hydrophilic head group (water-like). This portion includes positive and/or negative charged depending on surfactant types. The other is hydrophobic tail (oil-like). The hydrophobic part composes of hydrocarbon substance (non-polar) and interacts very weakly with the water molecules [1,12-14].

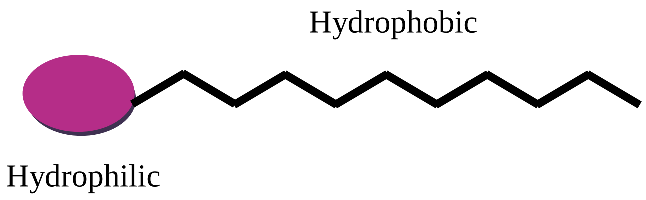


Figure 2.5 Schematic illustrations of surfactant molecule.

Surfactants can be generally classified into four classes based on the nature of head-groups [12-14], which are:

1. Anionic surfactant, compose of the negative charge on its hydrophilic head.
2. Cationic surfactant, consist of positive charge on its head group.
3. Non-ionic surfactant, no charge occurs in the head-group.
4. Amphoteric surfactant or Zwitterionics, contain at least one negative and one positive charge in molecule at the same time.

The role of surfactant is to reduce interfacial energy between immiscible bulk phases such as liquid/air, liquid/liquid, and solid/liquid leading to control foaming, or dissolution of oil in water. Moreover, the aid of surfactant for solid/liquid interfaces is to stabilize or improve dispersibility of solid particles [12-14] (i.e., carbon nanotubes [46-47], carbon black [48-49], alumina [50-52], and silica [53-55]) suspended in aqueous solution. By using surfactant, the homogeneous dispersion of solid particles should be observed.

2.5 Adsorption isotherm

It is important to discuss the adsorption process because the degree of dispersion can be improved by the adsorption of surfactant at the solid-liquid interface. The interaction of the adsorbent species to the interface can be either physical (e.g., van der Waals and electrostatic forces) or chemical (e.g., covalent bonding) adsorption [13]. But this present work, the adsorption of surfactant onto solid substrate is achieved through electrostatic forces, as was mentioned in section 2.3 step 1. Surfactant adsorption is characterized by adsorption isotherm [11,16-19,59]. The adsorption density that is the amount of adsorbed surfactant can be calculated in equation 1 [59].

$$\Gamma = (C_f - C_i)\frac{V}{W} \quad (1)$$

where Γ is the adsorption density in mol/g, C_f and C_i are the final and initial of the adsorbate concentration in mol/L, respectively, V is the volume of solution in liters, and W is the weight of the adsorbent in grams [13]. The adsorption isotherm of ionic surfactant onto oppositely charged of solid surface is typically an S'-shaped curve which can be divided into four regions, as shown in Figure 2.7.

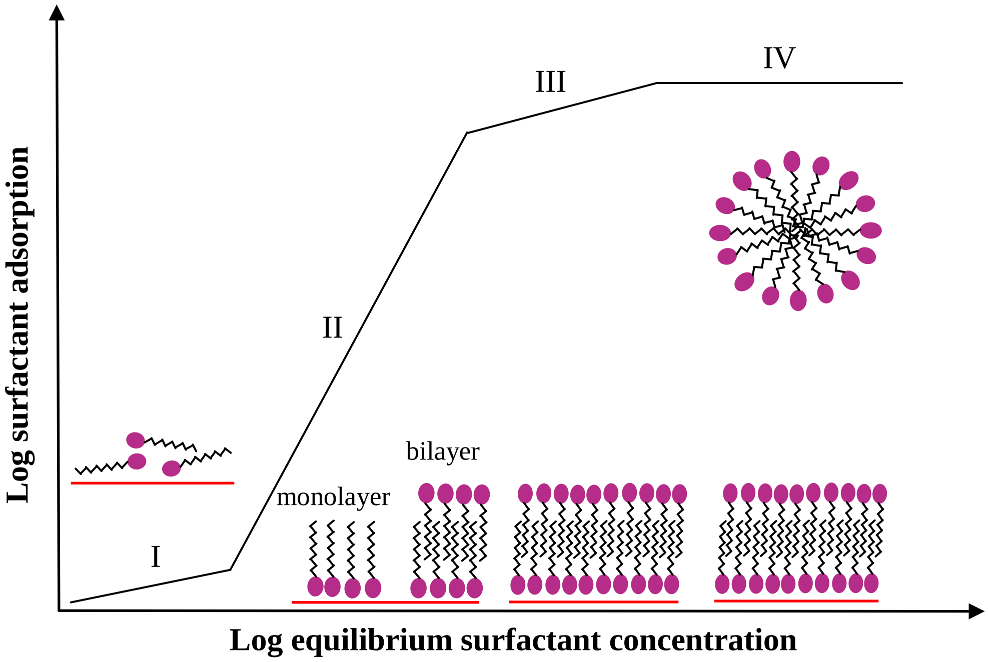


Figure 2.6 Schematic of adsorption isotherms [11,13,16-18,59].

Figure 2.6 represents the adsorption isotherm when plotted the log-log scale of adsorbed surfactant as a function of equilibrium surfactant concentration. **Region I** displays a negligible surfactant adsorption on solid substrate at low surfactant concentration resulting in a slightly increased of isotherm slope. Because the surfactant molecules are independently adsorbing onto the solid surface and not forming any aggregates, this region is commonly referred to as a Henry's Law region [16,18,59]. **Region II** shows a sharp increase of isotherm slope as compared to region I, owing to the formation of surfactant aggregates adsorption on the solid surface [16-18]. This region consists of two aggregates which are hemimicelles and admicelles, depending on their formed structures [18]. The hemimicelles is formed as a local monolayer onto the solid surface in which the hydrophilic head group adsorbed onto solid surface and the hydrophobic tail expanded to the solution. In contrast to these, the admicelle is considered to be a local bilayer surfactant formation by which the head group of lower layer adsorbed onto the solid surface and the upper layer of head group oriented toward the solution [16,18]. The transition point from region I to region II is called the hemimicelles concentration (hmc) or the critical admicelles concentration (cac) [16]. **Region III** corresponds to the decrease of isotherm slope with increasing surfactant concentration. This reduction is due to electrostatic repulsion among of surfactant head groups adsorbing on the solid surface and/or to the beginning of admicelle formation on lower energy surface patches [16,18,59]. It should be noted that the surfactant concentration in region III is suitable for modification solid surface by admicellar polymerization, due to an absence micelles formation to avoid emulsion polymerization [11]. **Region IV** is the plateau adsorption isotherm [18]. The transition point from region III to region IV is critical micelle concentration (CMC) [16-18,59], suggesting that the micelles formation should be observed at the surfactant concentration over CMC. In this transition point, it can be also reported that the solid surface was completely coverage by surfactant bilayer formation [17-18].

2.5.1 Parameters influencing on adsorption process

There are several parameters affecting on surfactant adsorption, including 1) the nature of solid surface, 2) The structure of surfactant molecule, 3) The characterization of aqueous phase including pH solution, electrolyte concentration, and ethanol content [11,16,18,58].

2.5.1.1 pH effect

Among of these factors, pH solution is necessary to be controlled because it strongly influences on surface-charge of solid substrate, related to the types of surfactant molecule to be used. The surface of solid particles can be provided either positive or negative charge by adjusting pH which can be determined by electrophoretic mobility [2,11]. The point of zero charge (PZC) is the pH value at which exhibits a net zero charged on solid surface [7,11]. At pH below PZC, the surface substrate is positively charged, whereas the negative charge is obtained at pH above PZC [2,7,9,11,16]. However, it can be negatively charged at lower pH value upon the structure of solid surface. For example, a greater adsorption of anionic surfactant on oppositely charged solid substrate is observed at below PZC for strong electrostatic interaction.

2.5.1.2 Electrolyte content

The effect of electrolyte concentrations on surfactant adsorption is also considered. The role of counter ions is to reduce the electrostatic repulsion between surfactant head-groups, leading to greater surfactant adsorption capacity [2,11,17,58,60].

2.5.1.3 Ethanol content

Many researchers studied the ethanol content influencing on the adsorption isotherm [8, 10, 56, 61]. The CMC of adsorption isotherm was decreased with the presence of alcohol. However, it is not clear how ethanol could reduce CMC of surfactant.

2.5.2 Previous work

Many researchers investigated the effect of pH solution, electrolyte conctration and ethanol content on the adsorption isotherm, as follows;

Rungruang and co-workers [2] reported types of charges on $CaCO_3$ surface with various pH. The effect of an electrolyte concentration on surfactant adsorption was also investigated. In Figure 2.7, it is obvious that the surface charge of $CaCO_3$ can be manipulated by changing pH of the solution. The PZC value of $CaCO_3$ substrate was found at pH about 11.4. According to SDS used as a surfactant template, the pH of 8 is an optimal condition to reach a strong adsorption of SDS on $CaCO_3$ surface.

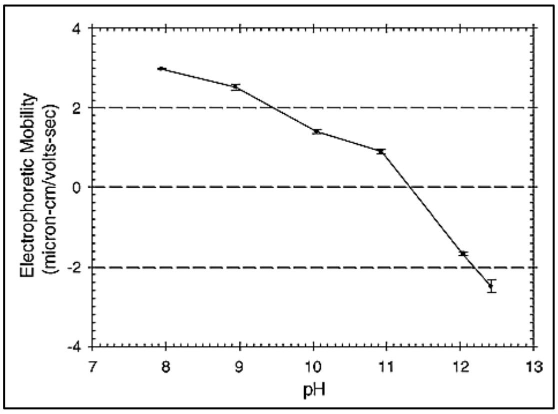


Figure 2.7 Effect of pH solution on surface charge of $CaCO_3$ by electrophoretic mobility determination [2].

Figure 2.8 presents the amount of SDS adsorbing on $CaCO_3$ surface with varying electrolyte concentrations. They found that SDS adsorption increased with increasing NaCl concentrations up to 0.3 M and, then, it was constant. This result supported that the aid of Na^+ counterions is to reduce the electrostatic repulsion between surfactant head-groups, leading to greater SDS adsorption capacity.

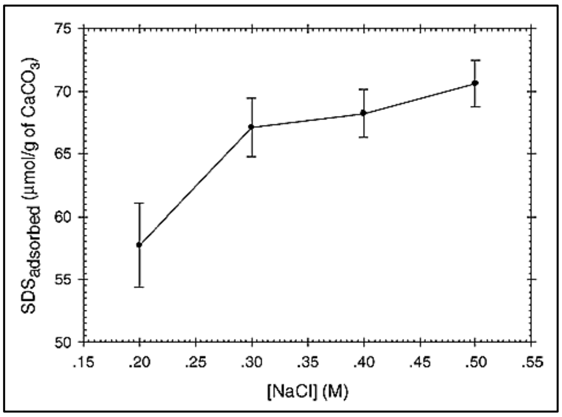


Figure 2.8 The amount of SDS adsorption on $CaCO_3$ surface at various electrolyte concentrations [2].

Pongprayoon and co-workers [11] studied the parameters including pH and electrolyte concentrations that influenced on the adsorption of linear alkylbenzene sulfonate (LAS) on cotton. They observed that the LAS adsorption decreased with increasing pH, as shown in Figure 2.9.

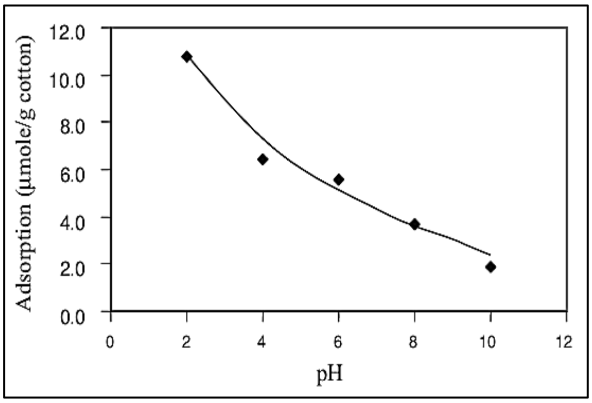


Figure 2.9 LAS adsorption at various pH values at 30 °C and initial LAS concentration of 5 mM [11].

The electrolyte concentrations were varied from 0.00-0.20 M at both pH 2 and 4 (Figure 2.10). It was found that the amount of LAS adsorption on cotton significantly increased with increasing NaCl concentration, ranging from 0.05-0.15 M, before a constant adsorption was observed.

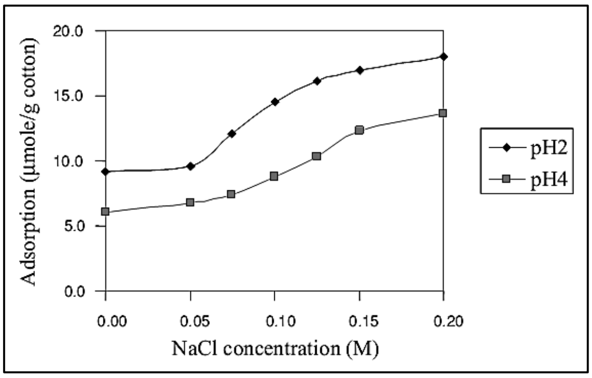


Figure 2.10 Effect of electrolyte concentration on LAS adsorption capacity at both pH 2 and 4 [11].

Bitting and Hawell [17] investigated the effect of electrolyte concentrations and pH solution on SDS adsorption at alumina surface. By varying pH of the solution, it was observed that PZC occurred at pH about 9.5 (Figure 2.11).

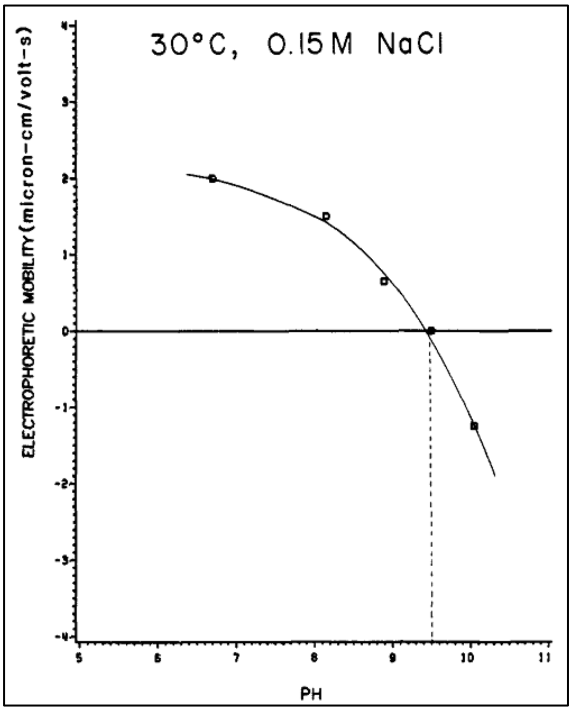


Figure 2.11 Surface charge of alumina particles at various pH at 30°C and 0.15 M NaCl [17].

The effect of electrolyte concentrations on SDS adsorption capacity is presented in Figure 2.12. The increase of NaCl concentrations to 0.15M tended to increase the amount of SDS adsorption. Furthermore, it was observed that the amount of SDS adsorption tended to decrease with increasing pH corresponded to surface charge of alumina particles. In addition, Figure 2.12 shows the effect of pH on SDS adsorption. It can be observed that the amount of SDS adsorption decreased with increasing pH values.

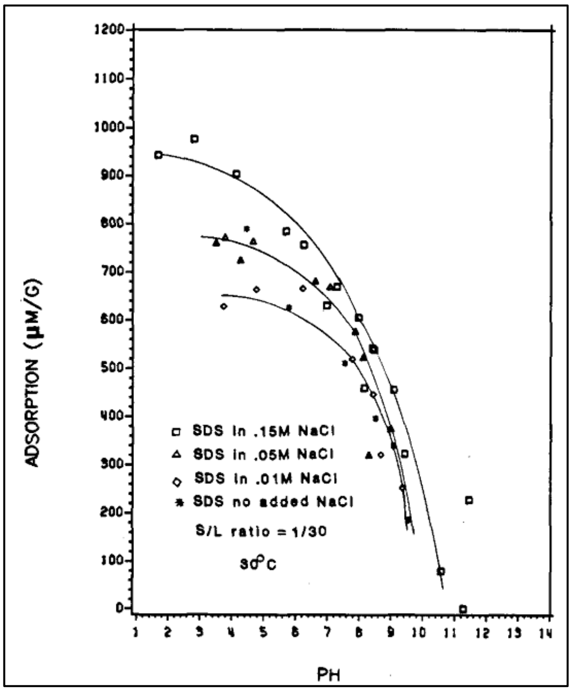


Figure 2.12 Effect of NaCl concentration on SDS adsorption at various pH at 30°C [17].

Førland and co-workers [30] reported the adsorption of SDS onto acid and basic alumina with different NaCl concentrations (Figure 2.13). The results showed that the adsorption isotherm of both alumina oxides surface increased with increasing the extent of salt due to the decrease of electrostatic repulsion between the surfactant head-groups. As a result, the closer packing of adsorbed molecules was obtained. Moreover, the adsorption isotherm of acidic alumina oxide reached the plateau region at SDS concentration lower than the basic one. This was due to the higher electrostatic interaction between SDS molecules and acidic alumina surface.

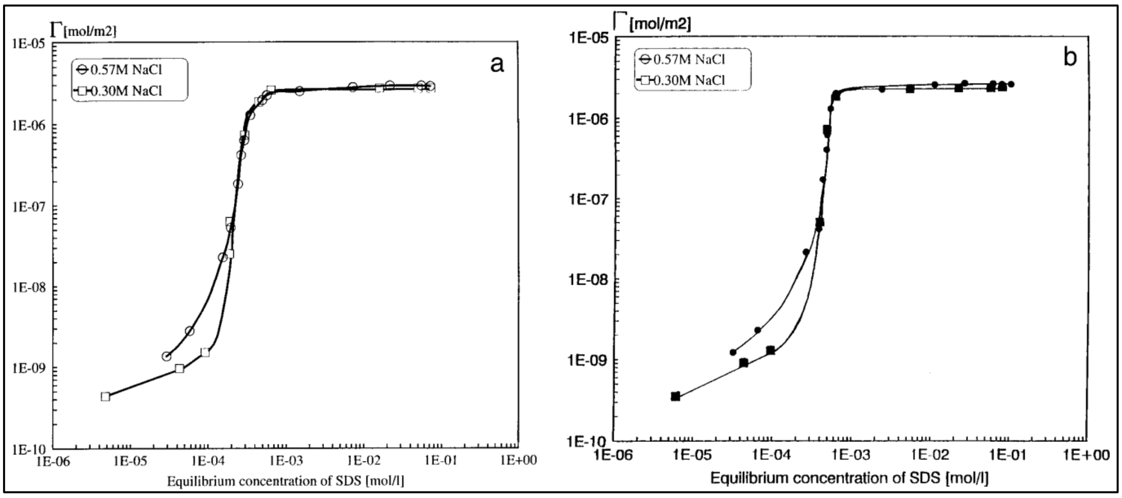


Figure 2.13 Representation of the adsorption isotherm of SDS on alumina surface with 0.3 and 0.57 M of NaCl; (a) acidic (pH of 5.7); and (b) basic (pH of 8.0) alumina oxide [30].

Wu and co-workers [10] reported the effect of ethanol content on the adsorption of SDS on alumina surface. Figure 2.14 shows the adsorption isotherm shifts to lower equilibrium SDS concentration with increasing the ethanol content, leading to CMC decreasing.

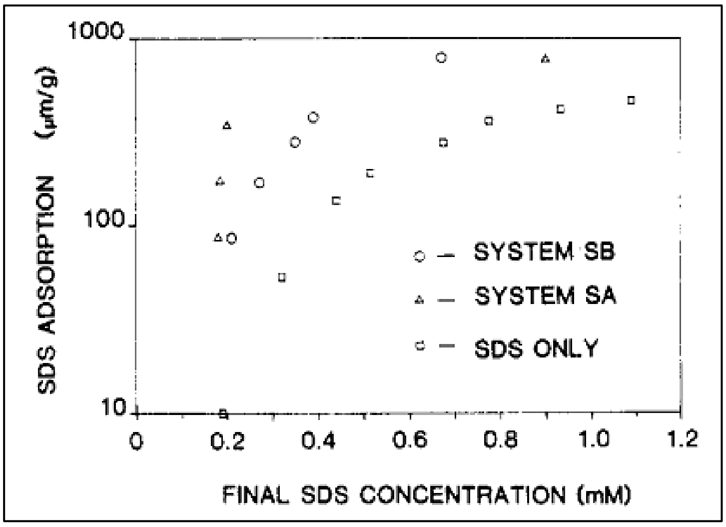


Figure 2.14 The SDS adsorption isotherm with and without ethanol content; SA 0.20 M of ethanol; and SB 0.50 M of ethanol [10].

Lai and co-workers [61] reported the adsorption isotherm of sodium perfluoroheptanoate (SPHN) shifts to lower SPHN equilibrium concentration with increasing the fluorocarbon alcohols content, as shown in Figure 2.15. Thus, the CMC is decreased when added hydrocarbon alcohols. Furthermore, the increase of fluorocarbon alcohols chain length tended to decrease the supernatant concentrations, which was dramatically affects in 0.05 fluorocarbon alcohols (Figure 2.15B). The chain length shows a little effect on the adsorption isotherm at 0.01M fluorocarbon alcohols (Figure 2.15B).

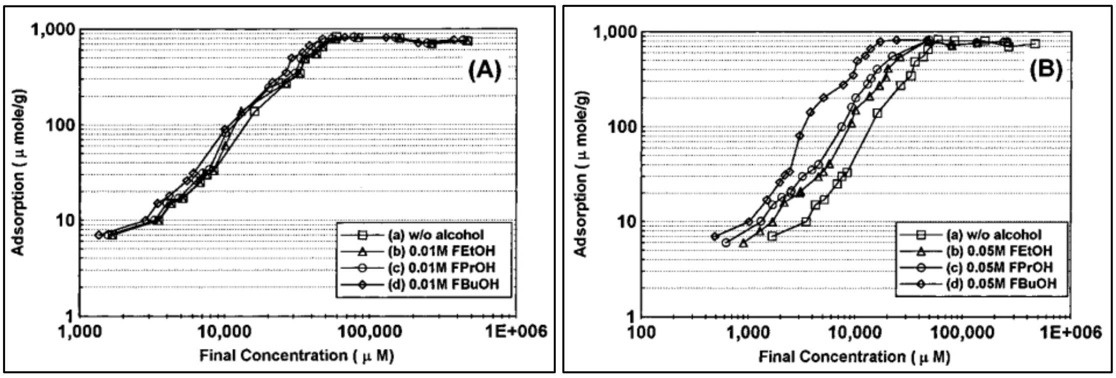


Figure 2.15 The adsorption isotherm of SPNH with and without fluorocarbon alcohols; (A) 0.01 M Fluorocarbon alcohols; and (B) 0.05 M Fluorocarbon alcohols [61].

Lee and co-workers [56] reported the effect of alcohol on SDS adsorption isotherm (Figure 2.16). They found that the equilibrium surfactant concentration reduced with increasing alcohol content, whereas the amount of SDS adsorbed was not significantly different. Similar results were observed by Wang and co-worker [8]. They reported that the CMC of SDS decreased form 8.1 mM to 6.5 mM when 0.5 M of ethanol was added.

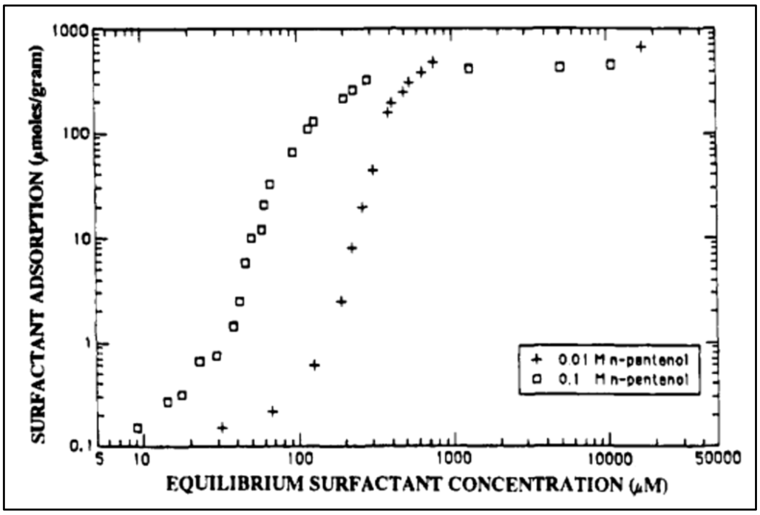


Figure 2.16 SDS adsorption isotherm in the presence of alcohol [56].

2.6 Polymerization

Polymerization is a method to convert monomer(s) to a polymer [34,38]. It can be classified into two terms based on their mechanism which are chain and stepwise polymerization. Chain polymerization or addition polymerization is the opening of double bond of unsaturated monomers without the presence of by product. The initiator is required to generate the reactive species R* on the monomer molecules. This reactive species may be free radical, cation, or anion. Meanwhile, stepwise polymerization, or condensation polymerization is formed from monomers having bifunctional and/or polyfunctional groups as reactive sites to form polymer molecules. The elimination of small molecules is present in this reaction. In this present work, an unsaturated isoprene monomer was selected to synthesize polymeric film coating on solid substrates. Therefore, chain polymerization in which of free radical polymerization only is described in this work.

2.6.1 Chain polymerization [34,38]

As mentioned above, chain polymerization is suitable for unsaturated monomers such as isoprene and butadiene. The most important type of chain polymerization is free radical polymerization [31]. This method is accomplished in three steps including initiation, propagation and termination, as described in Figure

2.17. First, initiation, this step involves two reactions. The first part is the production of free radicals by the dissociation of species I to a pair of radicals, $R^\bullet$. The second part of initiation step is the addition of these first radicals to monomer molecules. The radical $R^\bullet$ is often referred to as initiator radical or primary radical to produce chain-initiating monomer, $M^\bullet$. Second, propagation, the large number of monomer molecules are added to react with the initiating monomer from the first step. Each of addition creates the new radical and the increase of chain length is observed from this step. Third, termination, this reaction is carried out by bimolecular reaction between two radicals. It consists of two types for termination including combination and disproportionation. For combination (coupling), it occurs by the reaction between two radicals. By contrast, the disproportionation, a beta-hydrogen radical to one radical center is transferred to another radical center, resulting in the formation of two polymer molecules including one saturated and one unsaturated.

Initiation

$$I \longrightarrow 2R^\bullet$$

$$R^\bullet + M \longrightarrow M^\bullet_1$$

Propagation

$$M^\bullet_1 + M \longrightarrow M^\bullet_2$$

$$M^\bullet_2 + M \longrightarrow M^\bullet_3$$

or in general terms

$$M^\bullet_n + M \qquad M^\bullet_{n+1}$$

Termination

$$M^\bullet_n + M^\bullet_m \longrightarrow M_{n+m} \qquad \text{combination}$$

$$M^\bullet_n + M^\bullet_m \longrightarrow M_n + M_m \qquad \text{disproportionation}$$

Figure 2.17 Free radical polymerization mechanism; M as a monomer molecule and I as an initiator [38].

2.6.2 Initiator [38]

The initiators are composed of three types which are thermal, redox, and photochemical. For thermal initiator, it can be used at different temperature relying on their rate of decomposition, i.e., AIBN at 50-70 °C, acetyl peroxide at 70-90 °C, and benzoyl peroxide at 80-95 °C**.**

2.6.3 Isoprene monomer

It has two folds why we use isoprene monomer in this present work: 1) Isoprene monomer is in a liquid state at room temperature whereas butadiene monomer is in a gas state at room temperature. Consequently, isoprene monomer was easier to manipulate and adsolubilize into the admicelles formation, resulting in the greater percentage of carbon contents; and 2) It is an interest to apply the modified $CaCO_3$ into the NRL film which consist of polyisoprene in its back bone. Therefore, it should be better to modify the solid surface with the same polymer in NRL to obtain good dispersion and compatibility of the solid particles. The properties of isoprene monomer are shown in Table 2.3.

Table 2.3 Physical and Chemical properties of isoprene [33].

Properties	**Information**
Molecular weight	68.1 g $mole^{-1}$
Specific gravity	0.681 at 20 °C/4 °C
Melting point	-145.95 °C
Boiling point	34.07 °C at 760 mm Hg
Log K_{ow}	2.42
Water solubility	0.642 g/L at 25 °C
Vapor pressure	550 mm Hg at 25 °C
Vapor density relative to air	2.4

2.7 Latex film formation

As described in section 2.1, field latex consists of rubber and non-rubber parts which disperse in an aqueous phase. The centrifugation process is used to remove protein and non-rubber from this field latex and hence the percent weight of solid content increased from about 30 % to about 60 % in latex concentrate. However, this process cannot completely remove all of protein and non-rubber contents causing the residual of some protein and other non-rubbers still be found. The non-rubber contents i.e., carboxylic groups of adsorbed polypeptides, long chain fatty acid soaps and the protein, generates negative charge to stabilize the latex particles resulting in the negatively charged surface of NR latex particles. During centrifugation process, ammonia is used as a preservative to stabilize the latex particles. However, the latex particles changes with storage and hence ammonia (via pH), surfactants, or metals ions are used to manipulate the stability of latex particles [42].

2.7.1 Latex compounding

In latex compound, the additives e.g., dispersants, emulsifiers, wetters, cross-linking agents, accelerators, activators, antioxidants, pigments and viscosity modifiers, are added to aid compounding and processing, and providing desired products properties [27]. The roles of additives and formulation of latex compound are summarized in Table 3.4 and 3.5, respectively.

Table 2.4 The ingredients of latex compound and their functions [26].

Material	Function	Example
Stabilizer	To stabilize colloidal system during processing	Casein, SDS
Alkali	To protect destabilization of latex mix and control zinc oxide thickening	KOH
Antioxidant	To protect degradation of rubber chain by oxygen	Irganox 1330, Wingstay L.
Cross-linker	To crosslink rubber chains	Sulphur
Accelerator	To facilitate the vulcanization reaction	ZDEC
Activator	To facilitate the vulcanization reaction	ZnO
Pigment/filler	To reinforce or reduce products cost	Silica, Calcium carbonate

CHAPTER III
MATERIALS AND METHODS

3.1 Materials

Table 3.1 List of materials and chemicals.

Rubber	**Grade**	**Supplier**
Natural rubber latex	60 %DRC	THAI RUBBER LATEX CORP. CO., LTD
Calcium carbonate (CaCO$_3$)	Precipitated (PCC)	SAND AND SOIL INDUSTRY CO., LTD.
Sodium dodecyl sulphate (SDS)	AR (purity > 98%)	Sigma-Aldrich
Sodium chloride (NaCl)	AR (purity > 99.1%)	Carlo ErbaReagenti (Italy)
Hydrochloric acid (HCl)	AR (purity 37%)	RCI Labscan
Sodium hydroxide (NaOH)	AR (purity 99%)	BDHL
Ethanol	AR (purity 99.7%)	Sigma-Aldrich
Isoprene monomer	AR (purity 99%)	Sigma-Aldrich
10% KOH	-	Analytical Univar Reagent Ajax Finechem
50 %w/w ZnO dispersion	-	LUCKY FOUR CO., LTD.
50 %w/w ZDEC dispersion	-	LUCKY FOUR CO., LTD.
50 %w/w Sulphur dispersion	-	LUCKY FOUR CO., LTD.

3.2 Sample Preparation

3.2.1 Instrument

Table 3.2. List of apparatus used in this work.

Instrument	Trademark/supplier
Zetasizer Nano ZS	Marlvern Instruments
pH meter	Hanna instruments, pH 211
UV-Visible spectrophotometer	JASCO V-530
Matersizer 2000	MarlvernInstruments, Hydro 2000
ThermogravimetricAnalyser (TGA)	Perkin-Elmer, TGA 7
Fourier Transform Infared Spectrometer (FTIR)	Thermo Fisher Sciencetific, Nicolet 6700
Gel Permeation Chromatography (GPC)	Water2414 refractive index (RI) detector
Tensile Tester Machine	Instron 5566
Dynamic Mechanical Analyser (DMA)	Gabo Eplexor 25N, Germany

3.2.2 Experiments

3.2.2.1. Determination of the point of zero charge (PZC)

The electromobility was used to study the surface charge of $CaCO_3$ at various pH values. 1 g of $CaCO_3$ was diluted in 100 ml of DI water. The solution pH was adjusted by 0.1 M HCl/NaOH and, then, stirred at 350 rpm for 24 hours at room temperature. The Zetasizer Nano ZS (Marlvern) was used to determine PZC of the $CaCO_3$ particles.

3.2.2.2 Determination the effect of electrolyte concentration on SDS adsorption

NaCl concentration was varied from 0.1 to 0.3 M. A 40 ml of 35mM SDS was pipetted into the vial containing 1 g of $CaCO_3$. The solution pH was adjusted by 0.1 M HCl/NaOH. The sealed vial was then stirred at 350 rpm at room temperature for 24 hours. The effect of electrolyte concentration on SDS adsorption capacity was characterized by UV-spectrophotometer.

3.2.2.3 Determination of the SDS adsorption isotherm

1 g of $CaCO_3$ was weighted into 40 ml of varied SDS concentrations from 10 to 40 mM.The pH solution was adjusted to proper condition by using 0.1 M HCl/NaOH. Then, the vial was sealed and stirred at 350 rpm at room temperature for 24 hours. UV-Visible spectrophotometer was used to characterize the equilibrium SDS concentration compared with a calibration curve of pure SDS in water.

3.2.2.4 Determination the optimum mole ratios of $K_2S_2O_8$ to isoprene monomer

1 g of $CaCO_3$ was weighted and, then, added into the vials containing proper pH solution, NaCl and 40 ml of desired SDS concentration. The sealed vial was then stirred at 350 rpm for 24 hours before adding fixed mole ratio of isoprene monomer to SDS of 14:1. The mole ratios of $K_2S_2O_8$ initiator to isoprene monomer, varying from 0.050:1, 0.075:1, 0.10:1, 0.125:1, 0.150:1, 10.175:1, 0.200:1, and 0.250:1, were added in this step and, then, stirred for 24 hours at 350 rpm. The mixture was heated at 70 °C for 2 hours to initiate the polymerization reaction. The modified-$CaCO_3$ particles were filtrated and washed with distilled water until no bubble occurred. The modified $CaCO_3$ was dried at 60 °C for 1 day to remove water and residual monomer from the process. The amount of polymer coated on $CaCO_3$ surface with the different $K_2S_2O_8$ initiator contents was characterized by using Thermogravimetric Analysis (TGA). Furthermore, the optimum condition in term of molecular weight (M_W) of extracted polyisoprene with varying $K_2S_2O_8$ initiator content was determined by GPC using tetrahydrofuran (THF) as a solvent.

3.2.2.5 Determination the mole ratios of ethanol to SDS

1 g of $CaCO_3$ was added into the vial containing 40 ml of 24 mM SDS, proper solution pH and NaCl. The sealed vial was stirred at 350 rpm for 24 hours before adding the mole ratio of isoprene monomer to ethanol at 1:14. The mole ratios of ethanol to SDS was varied from 30:1, 35:1, 40:1, 45:1 and 50:1. The reaction mixture was stirred for 24 hours. The modified-$CaCO_3$ was washed with distilled

water and later dried in oven at 60ºC for 1 day. TGA was used to characterize the effect of ethanol on the partition of isoprene molecules into the bilayer surfactant formation.

3.2.2.6 Determination the optimum mole ratio of isoprene monomerto SDS

1 g of $CaCO_3$ and proper NaCl concentration were added into 40 ml of desired SDS concentration. This solution was adjusted to desired pH by using 0.1 M NaOH/HCl. The sealed vial was stirred at 350 rpm for 24 hours. After that, $K_2S_2O_8$, and various mole ratios of isoprene monomer to SDS were added in the vial. The reaction mixture was further stirred at 350 rpm for 24 hours. These solutions were heated at 70 °C for 2 hours to initiate polymerization reaction before being filtrated and washed with DI water until no bubble occurred. The modified-$CaCO_3$ was then dried in an oven at 60 °C for one day. The amount of polymer coated on $CaCO_3$ surface was determined by TGA. The samples were first dried in an oven at 60 °C for 1 day before characterization with TGA.

3.2.2.7 Preparation of polyisoprene admicellar polymerized on $CaCO_3$ surface

After obtaining the proper condition from part 3.2.2.1-3.2.2.6, the polyisoprene coating on $CaCO_3$ by means of admicellar polymerization was prepared, as shown in Figure 3.1.

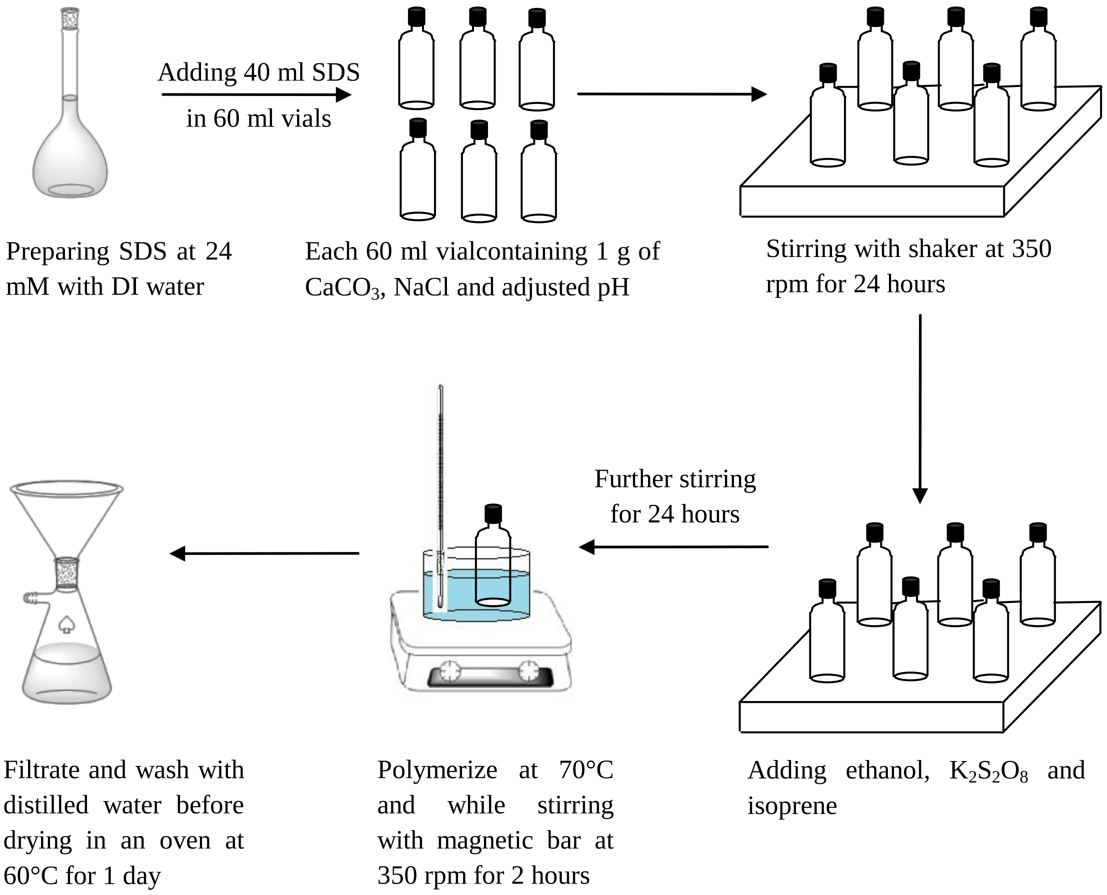


Figure 3.1. Experimental set up for preparation of admicellar polymerization.

3.2.2.8 Natural rubber latex compounding

The compounding of natural rubber latex was carried out at room temperature with the ingredients shown in Table 3.6.The mixture was stirred at about 250 rpm for 1 hour at room temperature to obtain the homogeneous mixture. After that, the mixture was matured to equilibrium for 1 day. The latex compound was placed on glass plate and dried at room temperature for 4 days. The vulcanization process of the latex film was carried out by drying at 70 °C in an oven for 90 minutes. The mechanical properties of the latex film with modified- and unmodified-$CaCO_3$ were characterized by universal tensile tester and DMA.

Table 3.3 Formulation of natural rubber latex compound [59].

Ingredient	Dry (phr)	Wet (grams)
60% HA NR latex	100	166.67
20% KOH	0.25	1.25
50% ZnO	0.50	1.00
50% ZDEC	0.50	1.00
50% Sulfur	1.00	2.00
50% Rulcanox	1.00	2.00
50% $CaCO_3$	5/10/15	10/20/30

3. 3 Characterizations

3.3.1 Characterization of polyisoprene coated on $CaCO_3$ particles though admicellar polymerization.

Four methods were used to characterize the polymeric coating. First, Fourier-transformed infared spectroscope (FTIR) was used to characterize the functional group of polyisoprene. Second, Gel permeation chromatography (GPC) was used to determine the molecular weight (MW) of polyisoprene which was removed from $CaCO_3$ surface by extraction withtetrahydrofuran (THF). Third, the amount of polyisoprene coating on the surface of $CaCO_3$ particles was determined by Thermogravimetric analysis (TGA). Lastly, the size of admicellar polymerization-modified $CaCO_3$ was characterized by using particle sizer in comparison with unmodified $CaCO_3$ particles.

3.3.1.1 Fourier-transformed infared spectroscopy (FTIR)

The formation of polyisoprene coating on $CaCO_3$ surface was determined by FTIR. The samples were grounded and mixed with KBr before the measurement. The spectra were collected in a range of 400-4000cm^{-1} with 32 scans. The characteristics peaks were observe to confirm the presence of polyisoprene coating on $CaCO_3$ surface.

3.3.1.2 Gel permeation chromatography (GPC)

The molecular weight of polyisoprene coating on $CaCO_3$ surface was investigated by GPC with Water 2414 refractive index (RI) detector and Styragel HR5E 7.8 x 300 mm column (molecular weight resolving range = 2,000-4,000,000 Dalton). The GPC column was eluted using tetrahydrofuran with a flow rate of 1.0 ml/min at 40 °C and calibrated with polystyrene standard.

3.3.1.3 Thermogravimetric analysis (TGA)

The amount of polyisoprene coating on $CaCO_3$ particles was determined by TGA. The decomposition temperature of polyisoprene was observed in a range of 350-400°C. The sample was weighted about 8-10 mg with a heating rate of 20 °C/ min under nitrogen gas. The temperature was varied from 40 to 600 °C.

3.3.1.4 Particles size

The particle size of modified- and unmodified-$CaCO_3$ was also investigated by paticle sizer. All of samples was dispersed in 0.5% SDS and stirred for 24 hours before testing. The particle size of the samples was measured in a wet mode using water dispersant and 1.572 refractive index of $CaCO_3$.

3.3.2 Properties of natural rubber latex film

The degree of polyisoprene modified-$CaCO_3$ dispersion in natural rubber latex film was characterized by using dynamic mechanical analysis (DMA). Furthermore, the mechanical properties of natural rubber latex films containing both modified- and unmodified-$CaCO_3$ were determined by tensile tester.

3.3.2.1 Tensile strength

Mechanical properties of natural rubber latex films filled with modified and unmodified-$CaCO_3$ surface including tensile strength, elongation at break, and 300% modulus were measured by an Instron mechanical tester (model 5566) according to ASTM D 412. The cross-head speed was fixed at 500 mm/min with 25 mm of a grip length. Five specimens were measured per samples and the average value was reported.

3.3.2.2 Dynamic mechanical analysis (DMA)

The viscoelastic properties of natural rubber latex films filled with modified and unmodified-$CaCO_3$ was carried out by DMA with strain sweep under tension mode. For strain sweep test, the frequency was fixed at 5 Hz under 10 % of static strain at room temperature.

CHAPTER IV
RESULTS AND DISCUSSION

This chapter consists of three parts. In the first part, the parameters affecting admicellar polymerization, including pH (referred to as a PZC), electrolyte concentration, and SDS concentration (referred to as an adsorption isotherm), were examined. In addition, the optimum mole ratios of initiator ($K_2S_2O_8$) and monomer (isoprene) for admicellar polymerization method was also reported. The second part reports on the characterization on polyisoprene coated on $CaCO_3$ particles by TGA and FTIR. The molecular weight (MW) of polyisoprene formed on $CaCO_3$ particles was also measured by GPC. For the third part, the effects of modified-$CaCO_3$ on mechanical properties of dipped latex film as measured by tensile tester and dynamic mechanical analyzer (DMA) and also the resulting morphology were studied.

4.1. The effect of pH on surface-charges of $CaCO_3$ particles and the amount of SDS adsorption

The effect of pH on surface-charge of solid particles is shown in Figure 4.1. The results show that the positive charges on $CaCO_3$ particles decreased with increasing pH. The point of zero charge (PZC) was observed at pH of about 10.55. The maximum positive charges were observed at pH of about 8. In the theory, the anionic surfactant tends to adsorb well at low pH. However, the decrease of positive charges on $CaCO_3$ surfaces was observed with decreasing pH value lower than 8. From UV-Vis spectroscopic results (measured at the wavelength of 224 nm), the amount of SDS tended to decrease with increasing pH. It is obvious that pH value was influenced by the amount of surfactant adsorption due to the presence of surface-charges on $CaCO_3$ particles. For strong SDS adsorption, the $CaCO_3$ surface should be positively charged. Similar results were observed in Section 2.5.1.1. However, it should be considered the other factor that is the equilibrium of $CaCO_3$. Martinez-

Luevanos et al. reported that the equilibrium reaction between $CaCO_3$ and protons was observed at pH of 8.3 [6]. Consequently, the pH of 8 was selected to give the best balance between the two factors.

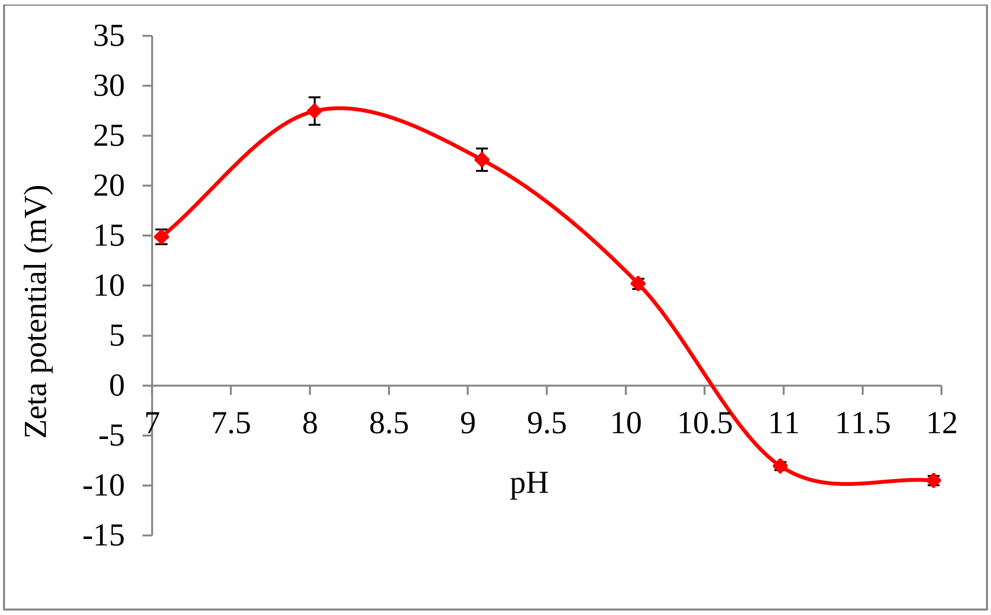


Figure 4.1 Zeta potential of SDS-adsorbed on $CaCO_3$ surface as a function of pH.

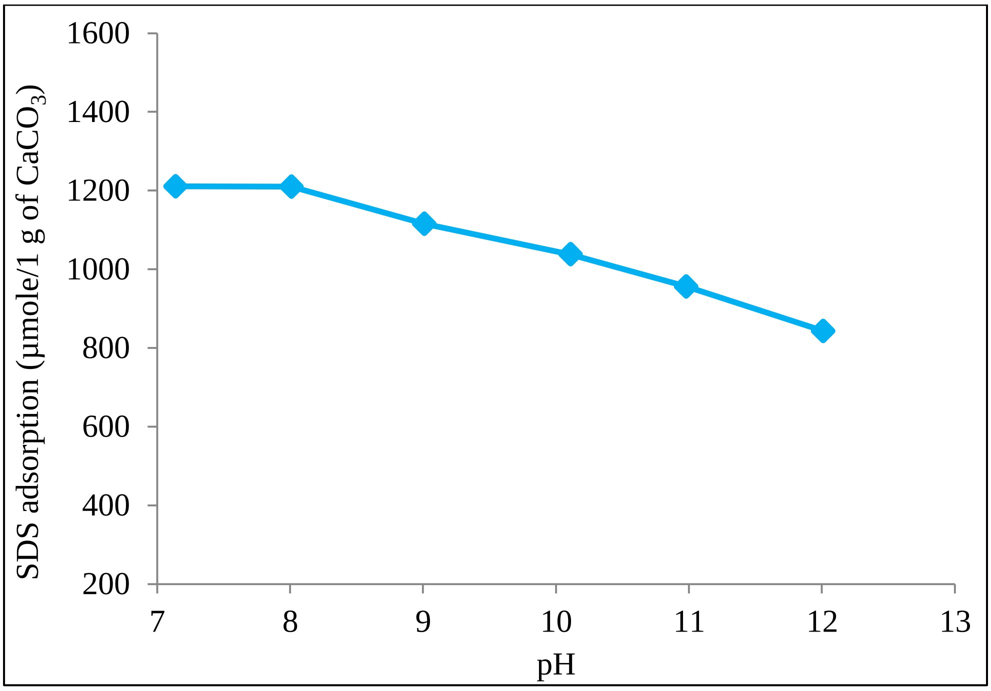


Figure 4.2 The amount of SDS adsorption with varying pH at fixed 35 mM initial SDS concentration measured by UV-Vis spectrophotometer at 224 nm.

4.2 The effect of electrolyte concentration on the amount of SDS adsorbed on $CaCO_3$

The influence of electrolyte concentration on SDS adsorption was determined by varying NaCl concentration at a fixed 35 mM of the initial SDS concentration and pH of 8 using UV-Vis spectrophotometer at 224 nm (shown in Figure 4.3). The samples showed a good repeatability of the experiment. The amount of surfactant adsorption increased with increasing NaCl concentration before being constant at 0.15 M, which corresponded to the amount of SDS adsorption of about 1200 µmole/ 1g $CaCO_3$. It is indicated that NaCl is able to reduce ionic repulsion among the surfactant head-groups and/or increasing positive charge density on the substrate surface, resulting in higher surfactant adsorption. Similar results were observed in Section 2.5.1.2.

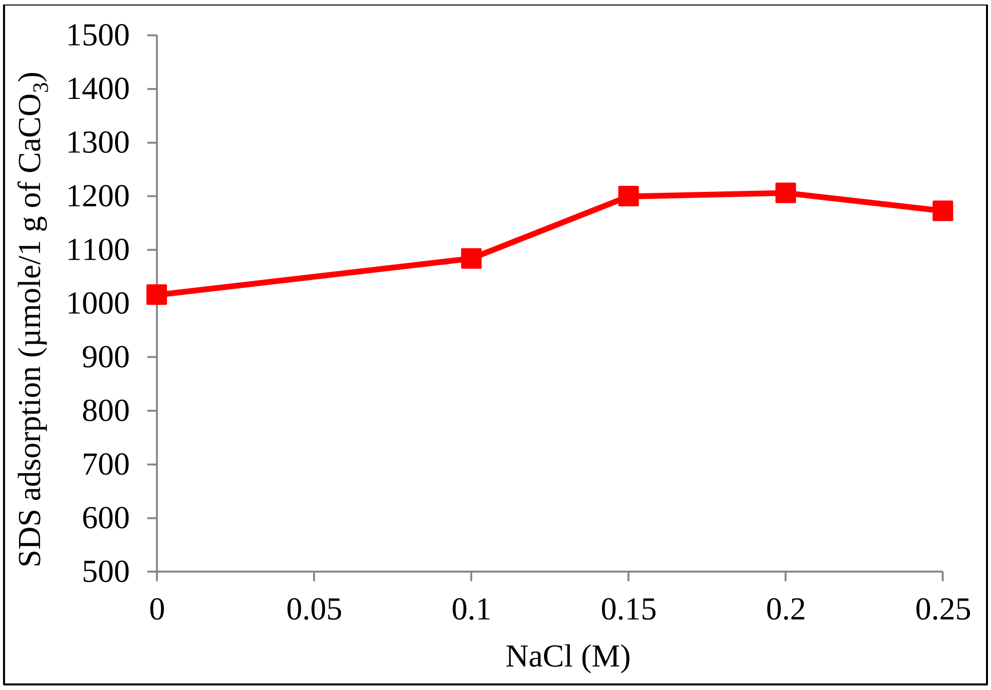


Figure 4.3 SDS adsorption on $CaCO_3$ particles at various electrolyte concentrations. The pH and the initial SDS concentration were fixed at 8 and 35 mM, respectively.

4.3 Adsorption isotherm

The adsorption isotherm of SDS adsorbed on $CaCO_3$ is shown in Figure 4.4, which showed good repeatability of the experiment. The S-shape curves of surfactant adsorption isotherm were observed as shown in the theory [Section 2.5, Chapter II]. The amount of SDS adsorbed on the surface of $CaCO_3$ particles reached a constant value when the equilibrium SDS concentration is over CMC, which was about 2 mM and corresponded to the amount of surfactant adsorption of about 900 µmole/ 1g of $CaCO_3$. It can be observed that the CMC value of SDS adsorbed onto $CaCO_3$ surface reduced when compared to the adsorption isotherm of pure SDS solution (8 mM). Similar results were obtained by Rungruan et. al [2], Wang et. al [8], and Rosen [57]. To avoid the emulsion polymerization, the equilibrium SDS concentration should be lower than CMC. The optimum value of equilibrium SDS molecule was found to be about 1.9 mM which is lower than CMC. This value corresponds to the amount of adsorbed SDS of about 850 µmole/ 1 g of $CaCO_3$.

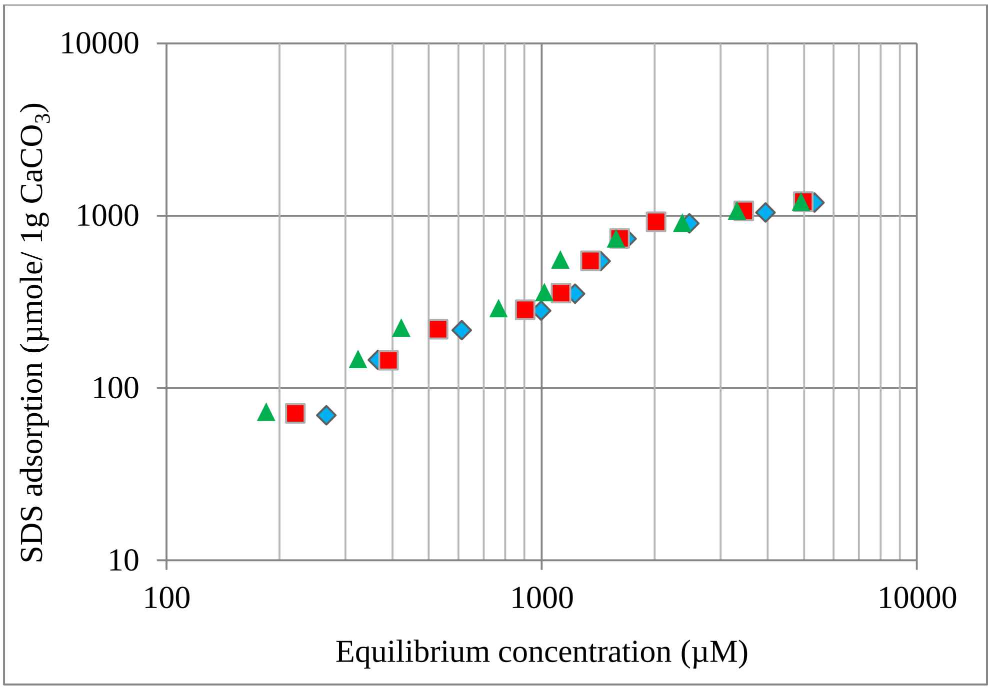


Figure 4.4 SDS adsorption versus equilibrium concentration at fixed pH of 8 and 0.15 M NaCl. (The experiments were repeated 3 times)

4.4 The effect of ethanol on the amount of polyisoprene coating on $CaCO_3$ surface

Many researchers have studied the effect of alcohol on monomer adsolubilization and the surfactant adsorption amount such as types and chain length of its [10,39]. They reported that the aid of ethanol is to increase the participation of monomer into the bilayer formation, leading to high polymer formation on the substrate. In the present work, the effect of ethanol contents on SDS adsorption isotherm and polymer formation was studied. As shown in Figure 4.5, the adsorption isotherm shifts to lower equilibrium SDS concentration. CMC value was also reduced from 2 mM to 1 mM in the presence of ethanol. However, the SDS adsorption was not significantly different, in agreement with the work reported by Wang and co-worker [8], Lee and co-worker [56], and Lai and co-workers [61].

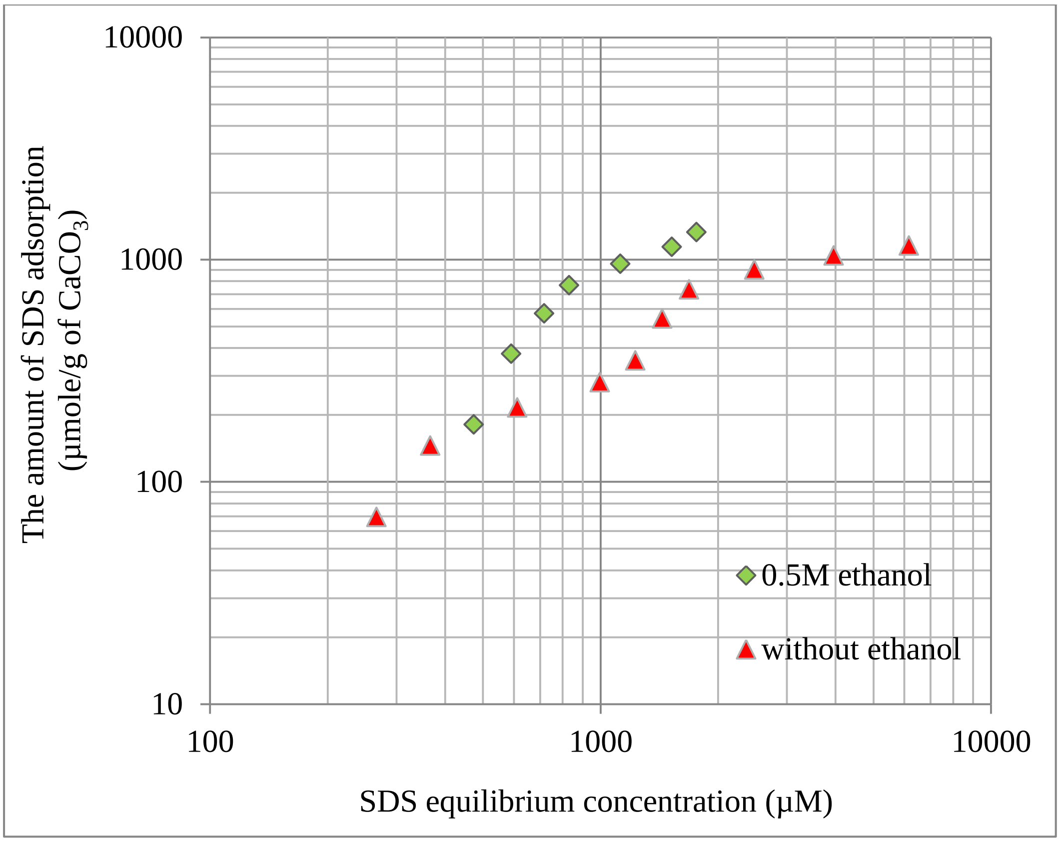


Figure 4.5 The adsorption isotherm with 0.5 M ethanol and without ethanol.

The effect of ethanol content on polyisoprene formation was characterized by TGA with varying ethanol to SDS mole ratios, ranging from 30:1 to 50:1, at fixed of 0.15:1 mole ratio of $K_2S_2O_8$ to isoprene monomer and 14:1 mole ratio of isoprene monomer to SDS, as shown in Figure 4.6. As a result of SDS adsorption with 0.5 M ethanol, the CMC of SDS adsorbed onto $CaCO_3$ surface was shifted to lower CMC causing by ethanol content. Consequently, the equilibrium SDS concentration should be different from that without ethanol. Therefore, 0.83 mM SDS was selected to be the equilibrium SDS concentration with ethanol content, which corresponded to the amount of surfactant adsorption of about 770 µmole/ 1 g of $CaCO_3$. The initial SDS concentration was about 20 mM. Whereas, 1.9 mM SDS was selected to be the equilibrium concentration, which corresponded to the amount of SDS adsorption of about 850 µmole/ 1g of $CaCO_3$ without ethanol (Section 4.3). The initial SDS concentration for the condition without ethanol was about 23 mM. It is obvious that the amount of polyisoprene increased with adding ethanol to SDS mole ratio to 30:1 before reaching a constant value.

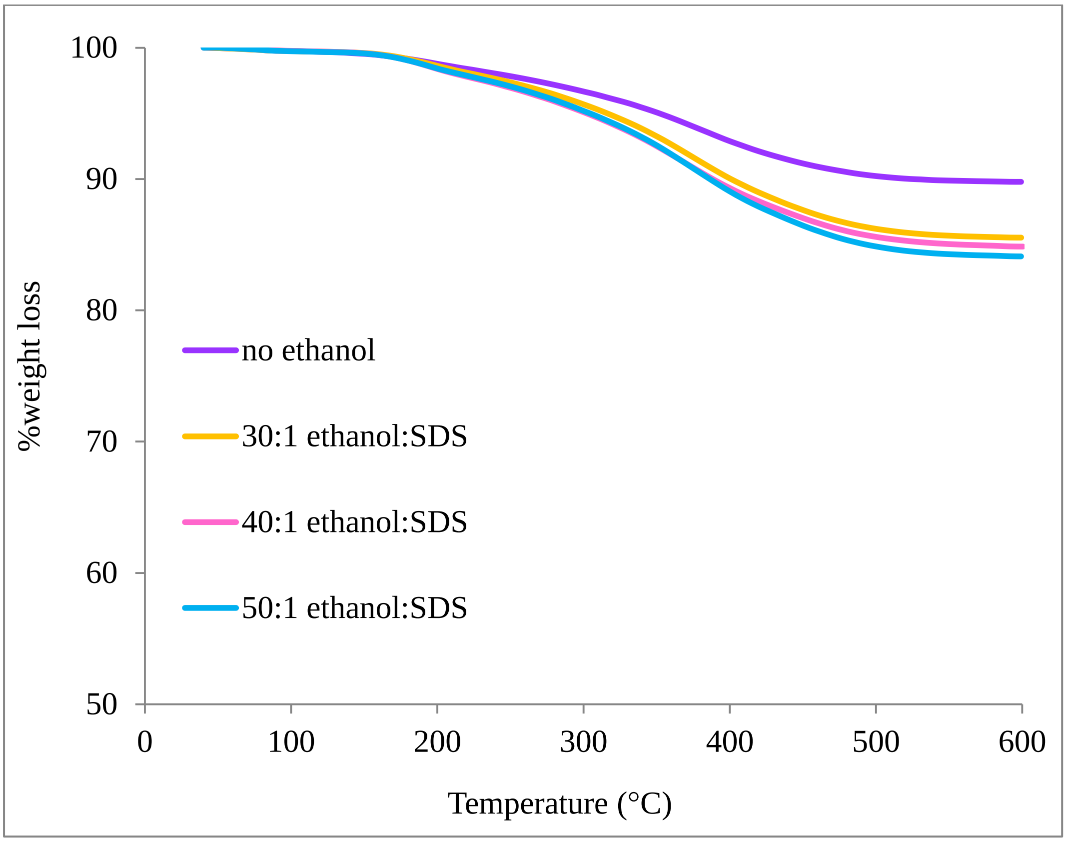


Figure 4.6 %weight loss (obtained by TGA measurement) of polyisoprene formed on $CaCO_3$ particles prepared by varying mole ratios of ethanol to SDS as a function of temperature. The samples were prepared at fixed pH, NaCl, initial SDS concentration, and KPS:isoprene monomer mole ratio at 8, 0.15 M, 20 mM, and 0.15:1, respectively.

However, when compared the result to the one that use 23 mM SDS initial concentration without ethanol (Table 4.1), it was found that the amount of polyisoprene was not significantly different. Therefore, it appeared that ethanol might not be necessary for admicellar polymerization of isoprene.

Table 4.1 Weight percentage of polyisoprene coated on $CaCO_3$ particles, calculated from the difference of %weight loss at 300 and 500 °C, with various mole ratios of ethanol to SDS, at fixed pH of 8, 0.15 M NaCl, 0.15:1 KPS:isoprene monomer, and 14:1 isoprene monomer:SDS. The initial SDS concentration, were fixed at 20 mM without ethanol**.**

Ethanol:SDS mole ratio	**Amount of polyisoprene (weight%)**
without ethanol with 20 mM SDS	7.25
30:1	10.7
40:1	10.8
50:1	11.7
without ethanol with 23 mM SDS	14.0

4.5 The optimum mole ratio of $K_2S_2O_8$ to isoprene monomer

Effect of initiator ($K_2S_2O_8$) on the amount of polyisoprene formed on $CaCO_3$ particles was studied by using TGA. The results are shown in Figure 4.5, at fixed pH of 8, 0.15 M NaCl, 23 mM of initial SDS concentration and 14:1 mole ratio of isoprene monomer to SDS. The initial weight% was observed in a range of 185-250 °C [1], which corresponded to the decomposition temperature of SDS. The second weight% occurred at a temperature range of 300-500 °C [1], referred to the decomposition temperature of polyisoprene. It was found that weight% of polyisoprene increased with increasing mole ratio of KPS to isoprene monomer. The %weight loss of polyisoprene reached a constant value when the mole ratio of $K_2S_2O_8$ to isoprene monomer was more than 0.15:1.

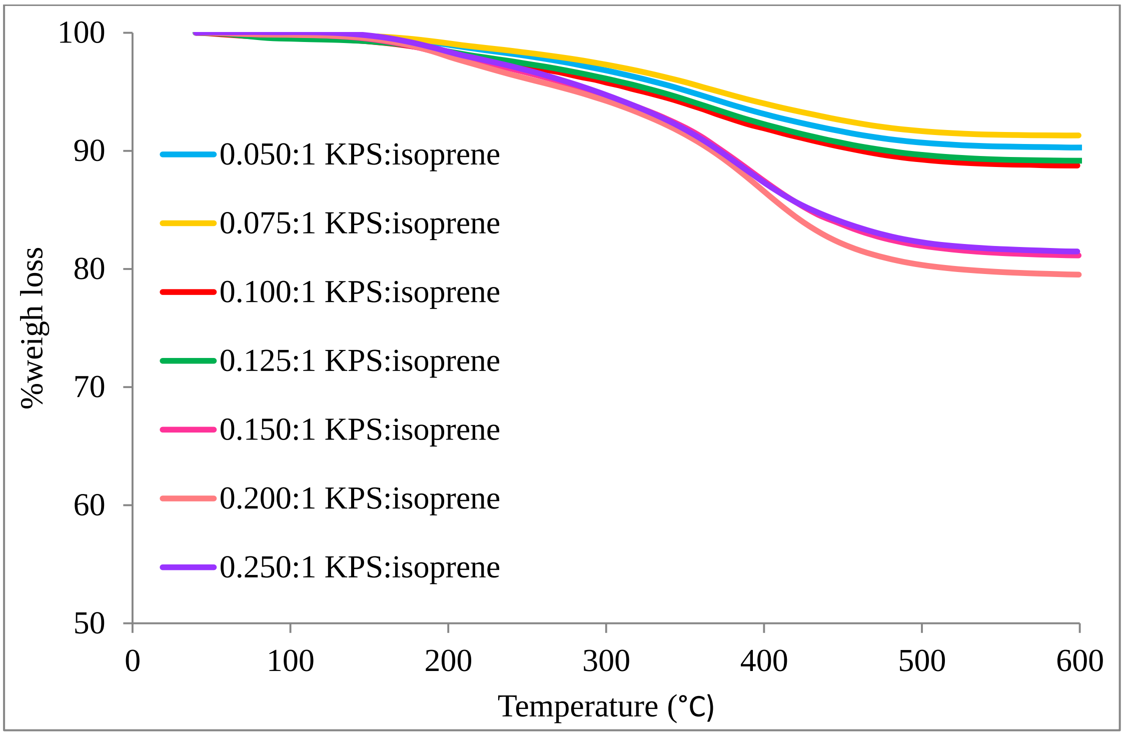


Figure 4.7 %weight loss (obtained by TGA measurement) of polyisoprene coated on $CaCO_3$ particles preparing by varying mole ratios of KPS to isoprene as a function of temperature. The samples were prepared at fixed pH, NaCl, and initial SDS concentration at 8, 0.15 M, and 23 mM, respectively.

The difference of weigh% at 300 and 500 °C was correlated to the amount of polyisoprene-formed on $CaCO_3$ particles as shown in Table 4.2. It was found that the amount of polyisoprene increased with increasing mole ratio of KPS to isoprene monomer from 0.05:1 to 0.15:1 before reaching the constant values at about 14.2%. The amount of polyisoprene in a range of 0.05:1-0.125:1 mole ratios of KPS to isoprene monomer decreased because the KPS content is insufficient to activate the isoprene monomer in the admicellar formation. Consequently, isoprene monomer remains in the solution and less polyisoprene formation was observed. The optimum ratio of KPS to isoprene monomer was 0.15:1 moles.

Table 4.2 Weight percentage of polyisoprene coated on $CaCO_3$ particles calculated from the difference of %weight loss at 300 and 500 °C with various mole ratios of

KPS to isoprene monomer, at fixed pH of 8, 0.15 M NaCl, 23,000μM initial SDS, and 14:1 isoprene monomer:SDS.

KPS: isoprene monomer mole ratios	**Amount of polyisoprene (weight%)**
0.050:1	6.85
0.075:1	6.31
0.100:1	7.38
0.125:1	7.29
0.150:1	14.0
0.200:1	14.9
0.250:1	13.8

In the polymerization process, the KPS-initiator decomposes into radicals and attack at the unsaturated bonds of isoprene monomer to initiate polymerization. Therefore, the amount of polyisoprene and its molecular weight are controlled by initiator to monomer mole ratio. GPC was used to characterize the molecular weight of polyisoprene including number-average molecular weight (M_n), weight-average molecular weights (M_w), and polydispersity index (PDI). The polyisoprene was extracted by THF before determining the MW by GPC. As shown in Table 4.3, the M_w increased with increasing KPS to isoprene monomer ratios and reaching the maximum at 0.15:1 mole ratio. With further increase mole ratios of initiator to monomer, M_w tended to decrease. This could be explained that as mole of KPS increase, higher number of radicals was generated in the solution, leading to formation of many short chains of polyisoprene molecules. Table 4.3 also shows PDI values which were in a range of 1.98 to 2.26, which agreed well with theory of chain growth polymerization.

Table 4.3 Molecular weight and PDI of polyisoprene extracted from $CaCO_3$ particles with various KPS:isoprene mole ratios.

KPS: isoprene monomer mole ratios	**M_n (Daltons)**	**M_w (Daltons)**	**PDI**
0.10:1	3064	6078	1.98
0.15:1	2966	6698	2.26
0.20:1	2846	6177	2.16
0.25:1	2758	6202	2.25

4.6. Particle sizes of polyisoprene-modified $CaCO_3$ particles

The amount of polyisoprene was calculated from the difference in %weight loss at 300-500 °C by TGA. In Figure 4.8 and Table 4.4., %weight loss tended to increase with increasing mole ratios of isoprene monomer to SDS before reaching a constant value of about 11 % at 8.0:1 mole ratio of isoprene monomer to SDS.

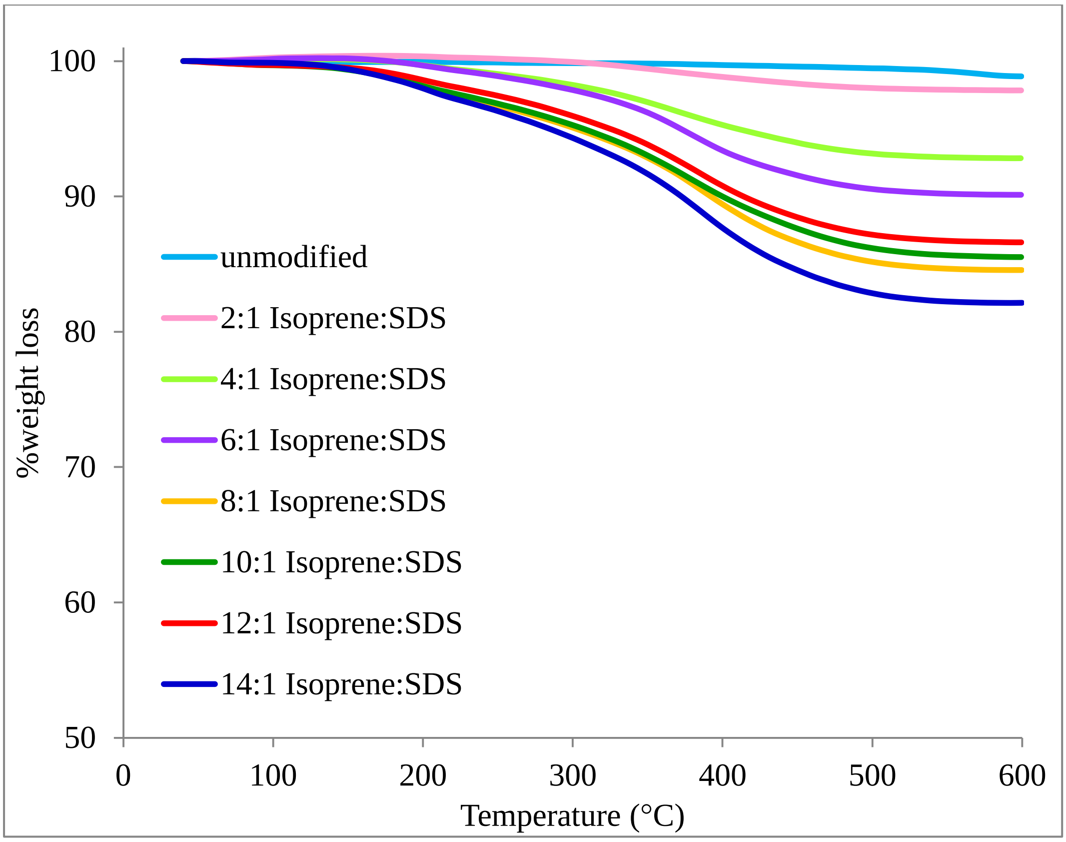


Figure 4.8 %weight loss (obtained by TGA measurement) of polyisoprene formed on $CaCO_3$ particles prepared by varying mole ratios of isoprene monomer to SDS as a function of temperature. The samples were prepared at fixed pH, NaCl, initial SDS concentration, and KPS:isoprene monomer mole ratios at 8, 0.15 M, 23 mM, and 0.15:1 respectively.

The particle sizes of polyisoprene-modified $CaCO_3$ by admicellar polymerization were also determined. The results are shown in Table 4.5. It could be seen that the particle size of polyisoprene-modified $CaCO_3$ tended to increase with increasing isoprene:SDS mole ratio but the extent of the increase were not great. However, the mole ratio of isoprene monomer to SDS of 8:1 was selected for admicellar polymerization of isoprene.

Table 4.4 Percentage weight loss of polyisoprene modified-$CaCO_3$ particles, calculated from the difference of weight% at 300 and 500 °C with various mole ratios of isoprene monomer to SDS, at fixed pH of 8, 0.15 M NaCl, 23,000 µM initial SDS concentration, and 0.15:1 KPS:isoprene monomer.

Isopenemonomer:SDS mole ratios	**Amount of polyisoprene (weight%)**
Unmodified-$CaCO_3$	0.00
2:1	2.18
4:1	5.68
6:1	8.08
8:1	11.0
10:1	11.7
12:1	10.7
14:1	12.8

Table 4.5 Particle size of $CaCO_3$ modified with various isoprene monomer to SDS mole ratios, at fixed 10 %w/w of $CaCO_3$ and dispersed in 0.5 %SDS solution.

Isopene monomer:SDS mole ratios	**Particle size (µm)**
Unmodified-$CaCO_3$	3.32
2:1	3.21
4:1	3.41
6:1	3.75
8:1	3.49
10:1	4.35
12:1	3.12

4.7 Characterization of polyisoprene coated onto $CaCO_3$ surface

The existence of polyisoprene layer on $CaCO_3$ particles was identified by ATR-FTIR, as shown in Figure 4.9. The main characteristics FT-IR peaks are given in Table.4.6. In Figure 4.9a, characteristic peak of SDS spectra appeared at 2955, 2917, and 2850 cm^{-1} assigned to asymmetrical $-CH_3$ and $-CH_2-$, and symmetrical $-CH_3$ stretching, respectively. Symmetrical S=O and C-C stretching of SDS represented at 1248 and 1084 cm^{-1}, respectively. The –OH stretching was assigned at about 3460 cm^{-1}. The unmodified $CaCO_3$ showed three strong characteristic peaks, as shown in Figure 4.9b. The band at 1439 and 878 cm^{-1} were attributed to C=O stretching. The peak at 713 cm^{-1} was assigned as the Calcite. Figure 4.9c, shows the modified $CaCO_3$ particles. The band at 1586 cm^{-1} was attributed to C=C stretching. However, the C=C was weak IR band because of M_w of polyisoprene as observed in Table 4.3. In addition, the main characteristic peak, 1248 and 1221 cm^{-1} of SDS did not clearly appeared on the modified $CaCO_3$ particles. Therefore, peaks around 2971 and 2875 cm^{-1} ($-CH_3$ stretching) should related to polyisoprene. The broad peak which is assigned to water in a range of 3200-3500 cm^{-1} was also observed. From the results, it was obvious that the admicellar polymerization was an efficient method to accomplish polymer coated on surface of solid particles.

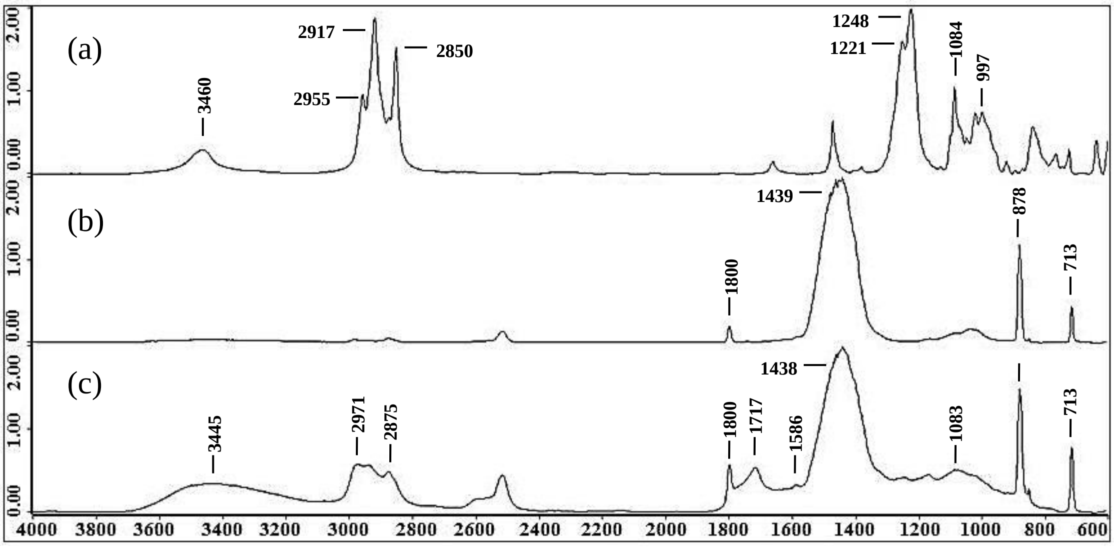


Figure 4.9 The FT-IR spectra; (a) pure SDS; (b) unmodified $CaCO_3$, and (c) polyisoprene-modified $CaCO_3$.

Table 4.6 FTIR peak assignment of polyisoprene coated on $CaCO_3$ [2,45,62,65].

Wavenumber /cm^{-1}	**Absorbing species**
3460,3445	Water and -OH stretching
2917	Asymmetrical -CH_2- stretching
2971, 2955	Asymmetrical -CH_3 stretching
2875	symmetrical -CH_3 stretching
1800	$\nu_1 + \nu_4$ symmetrical CO_3^{2-} vibration
1722-1717	C=O stretching region
1650-1450	C=C stretching region
1439	ν_3 asymmetrical CO_3^{2-}vibration
997	Asymmetrical C-O-S stretching
1248	Symmetrical S=O stretching
1221	SO_4^{2-} ion
1083	C-C stretching
878	ν_2 asymmetrical CO_3^{2-} stretching
713	ν_4 symmetrical CO_3^{2-}vibration

4.8 Contact angle of modified $CaCO_3$ surface

In the present work, the water contact angle (WCA) was used to determine wettability of modified $CaCO_3$ surface, as shown in Table 4.7. The sample was prepared by pressing the powder in order to flatten the sample. The unmodified $CaCO_3$ sample was prepared by the same manner but without the presence of SDS. The hydrophilic surface with 0° contact angle was observed in the unmodified $CaCO_3$, as shown in Figure 4.10a. Meanwhile, the amount of polyisoprene of about 11.0% formed on $CaCO_3$ surfaces showed increase of water contact angle from none to 70.71° (Figure 4.10b), which agreed well with the results obtained by Wang, and co-workers [63]. They reported that the hydrophobicity of cellulose-graft-polyisoprene copolymer increases because of the existence of grafted polyisoprene. As a result, it can be confirmed that the surface of $CaCO_3$ particles was coated by polyisoprene through admicellar polymerization.

Table 4.7 Water contact angle (WCA) of unmodified and modified $CaCO_3$.

Sample	Amount of polyisoprene coating (wt. %)	WCA (°)
Unmodified $CaCO_3$	0.00	0.00
Modified $CaCO_3$	11.03	70.71±0.12

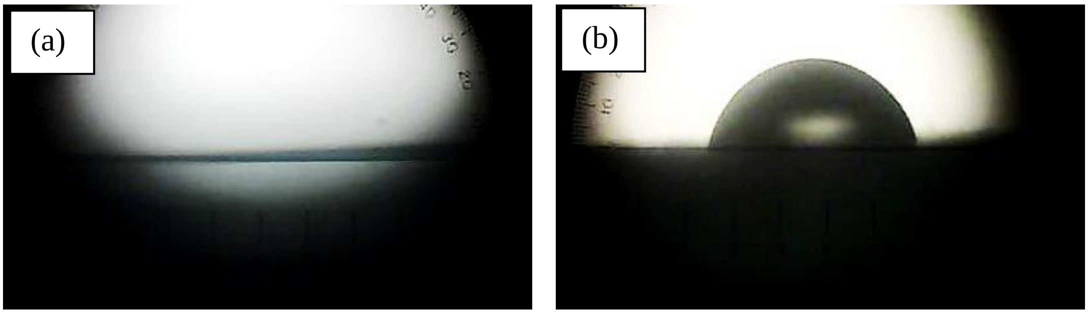


Figure 4.10 Water contact angle of $CaCO_3$ particles; (a) unmodified $CaCO_3$ and (b) polyisoprene-modified $CaCO_3$.

4.9 Water dispersion of $CaCO_3$

In order to prepare aqueous dispersion of $CaCO_3$ for adding $CaCO_3$ to the latex, the colloidal stabilities of unmodified- and surface-modified $CaCO_3$ particles in 0.5 % SDS aqueous solution were determined. The results shown in Figure 4.11 revealed that the modified-$CaCO_3$ shows greater colloidal stability in water than the unmodified-$CaCO_3$. Precipitation of unmodified-$CaCO_3$ began to occur only after one hour and completed in 24 hours. By contrast, the surface-modified $CaCO_3$ exhibited greater stability. It can be seen from Figure 4.11 that the surface-modified $CaCO_3$ remained suspended even after 2 hours.

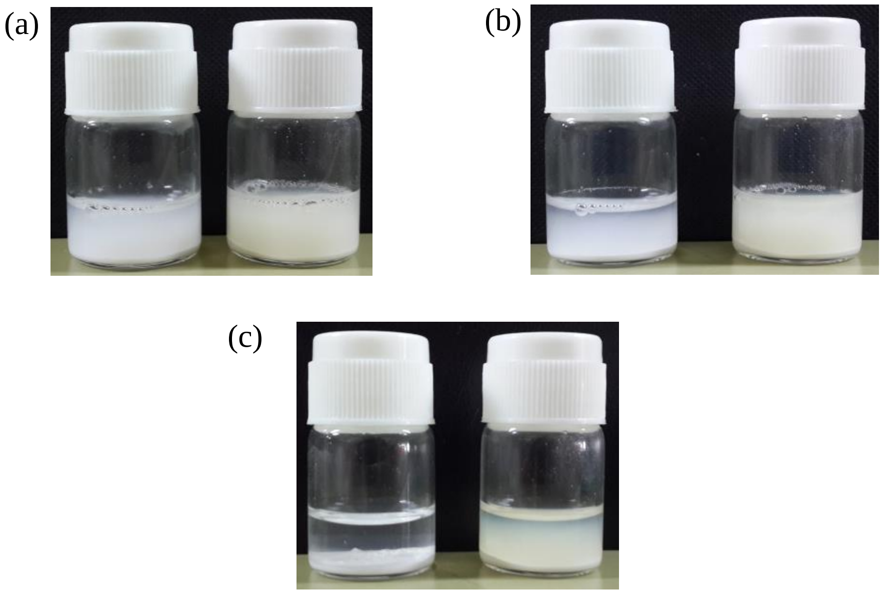


Figure 4.11 $CaCO_3$ dispersed in 0.5 %SDS aqueous solution at fixed 0.2 g of modified-$CaCO_3$ (left bottle) and modified-$CaCO_3$ (right bottle) (a) left for 1 h, (b) left for 2 h, and (c) left for 24 h.

4.10 Mechanical properties

The effects of unmodified- and modified-$CaCO_3$ on tensile properties of solid films from NR latex including tensile strength, % elongation, and 300% modulus were examined. The results are shown in Tables 4.8 and 4.9.

Table 4.8. Tensile properties of natural rubber filled with unmodified $CaCO_3$.

$CaCO_3$ (phr)	Tensile stress at break (MPa)	% Elongation	300% Modulus (MPa)
10	38.8	936	1.46
15	42.0	976	1.60

Table 4.9. Tensile properties of natural rubber filled with modified $CaCO_3$.

$CaCO_3$ (phr)	Tensile stress at break (MPa)	% Elongation	300% Modulus (MPa)
5	40.2	960	1.48
10	27.4	959	1.46
15	33.5	939	1.50

Figures 4.12-4.14 show plots of tensile strength, 300% modulus and %elongation of modified- and unmodified-$CaCO_3$ with various $CaCO_3$ content. For unmodified $CaCO_3$ samples, it can be observed that tensile stress at break, 300% modulus, and % elongation tend to increase with increasing $CaCO_3$ loading. For modified $CaCO_3$ samples, all tensile properties showed decreases when loaded with $CaCO_3$ greater than 5 phr. Beyond 5 phr, tensile strength, 300 %moduli and % elongations of modified $CaCO_3$-filled NR were lower than those of the unmodified $CaCO_3$-filled samples. This may be due to low dispersion of modified $CaCO_3$ in NR samples as evidenced by greater Payne effect shown by these samples (see Figure 4.15)

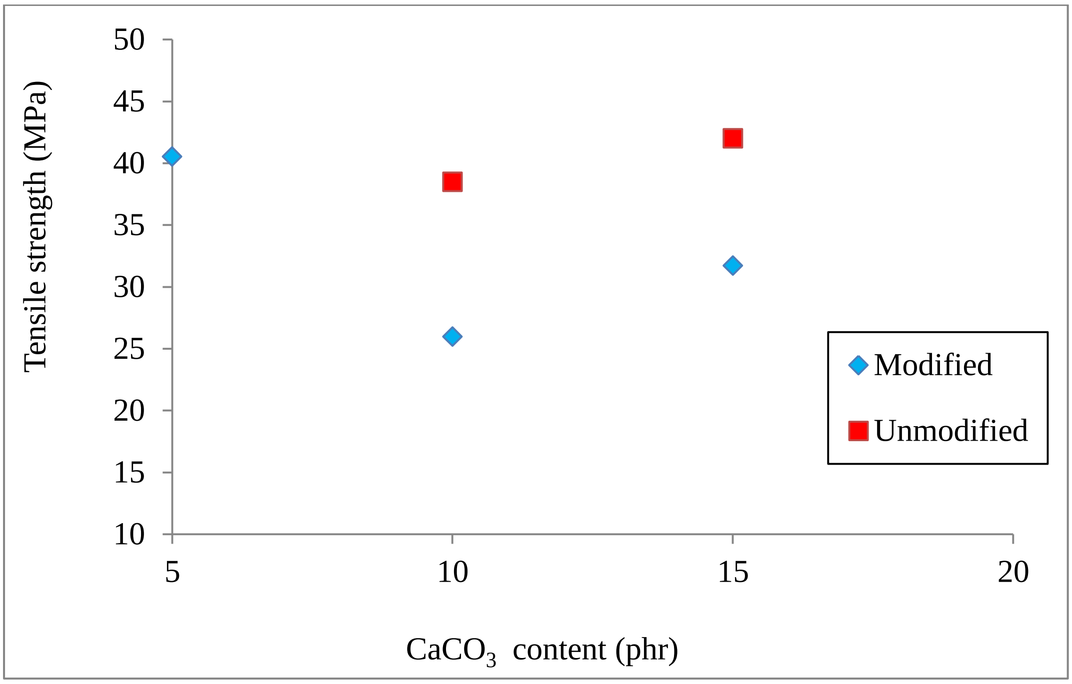


Figure 4.12 Tensile stress at break of unmodified- and modified-$CaCO_3$ filled natural rubber.

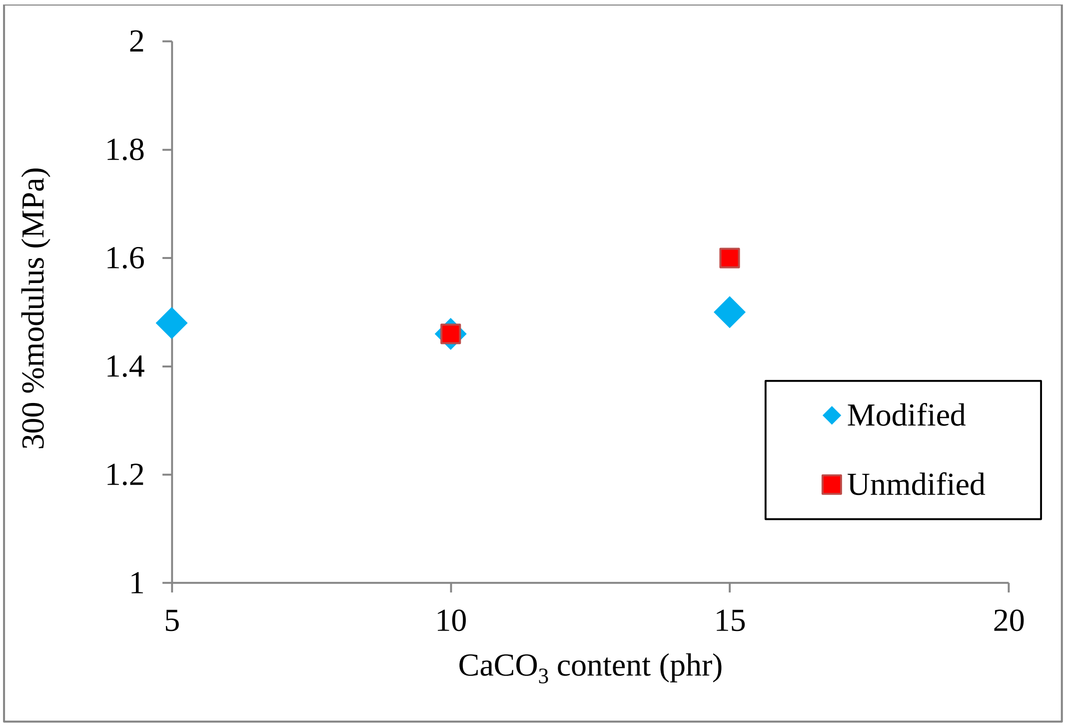


Figure 4.13 300% modulus of unmodified- and modified-$CaCO_3$ filled natural rubber.

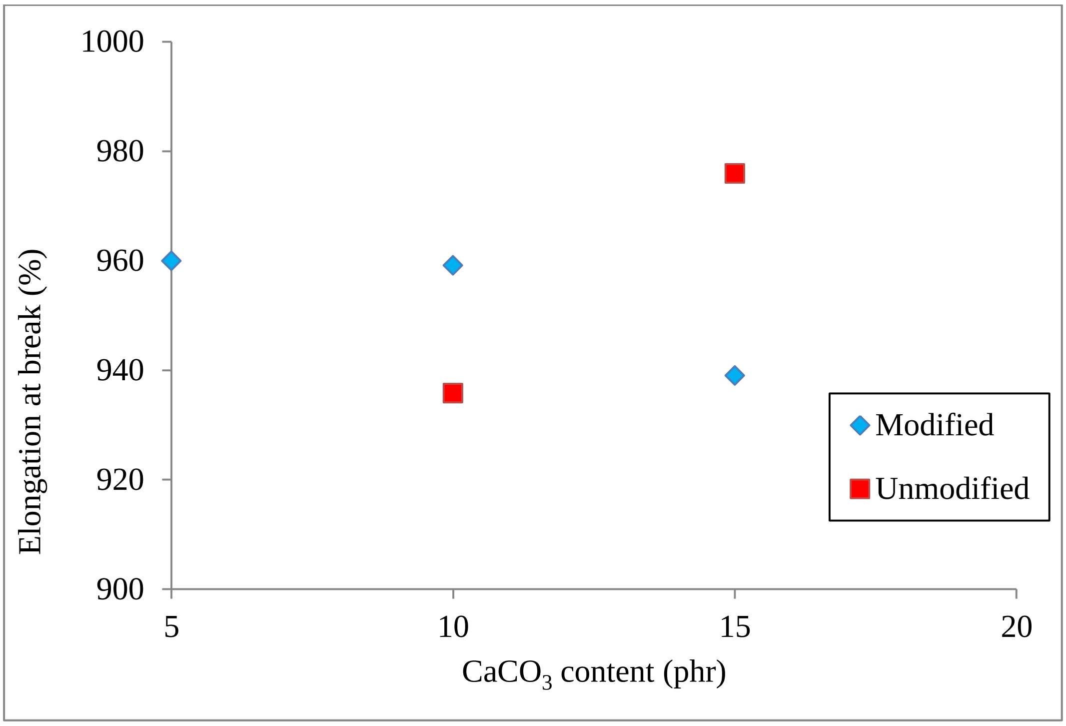


Figure 4.14 % elongation of unmodified- and modified-CaCO$_3$ filled natural rubber.

4.11 Dynamic Mechanical Properties

The dynamic mechanical properties have been used to study the viscoelastic properties of rubber. In this work, strain sweep test were selected to determine degree of dispersion, or Payne effect, of unmodified- and modified-$CaCO_3$ in natural rubber. Payne effect was determined by the difference between storage modulus (E’) after applying static strain. Good dispersion of filler is implied by small degree of Payne effect.

Figure 4.15 shows plots of storage modulus (E’) versus %strain. It can be observed that storage moduli of the unmodified-$CaCO_3$ samples at all $CaCO_3$ studied and that of the modified $CaCO_3$ (5 phr loading) did not significantly change with increasing strain for irrespective of $CaCO_3$ content. The results, thus, showed that there is no network formation of $CaCO_3$ in these rubber samples as a decrease in storage modulus with increasing strain would be expected if filler network is formed and broken upon being extended. By contrast, the modified $CaCO_3$-containing samples which contain 10 and 15 phr of $CaCO_3$ exhibited small decreases in storage moduli with increasing strain. The results indicate small extents of $CaCO_3$ network formation even at low filler loading of 10 and 15 phr. A possible explanation is that the polyisoprene formed on the $CaCO_3$ particle surface has low molecular weight as reported in Table 4.2, making the surface of $CaCO_3$ become sticky. Adhesion between modified $CaCO_3$ particles is, therefore, possible leading to some formation of filler network.

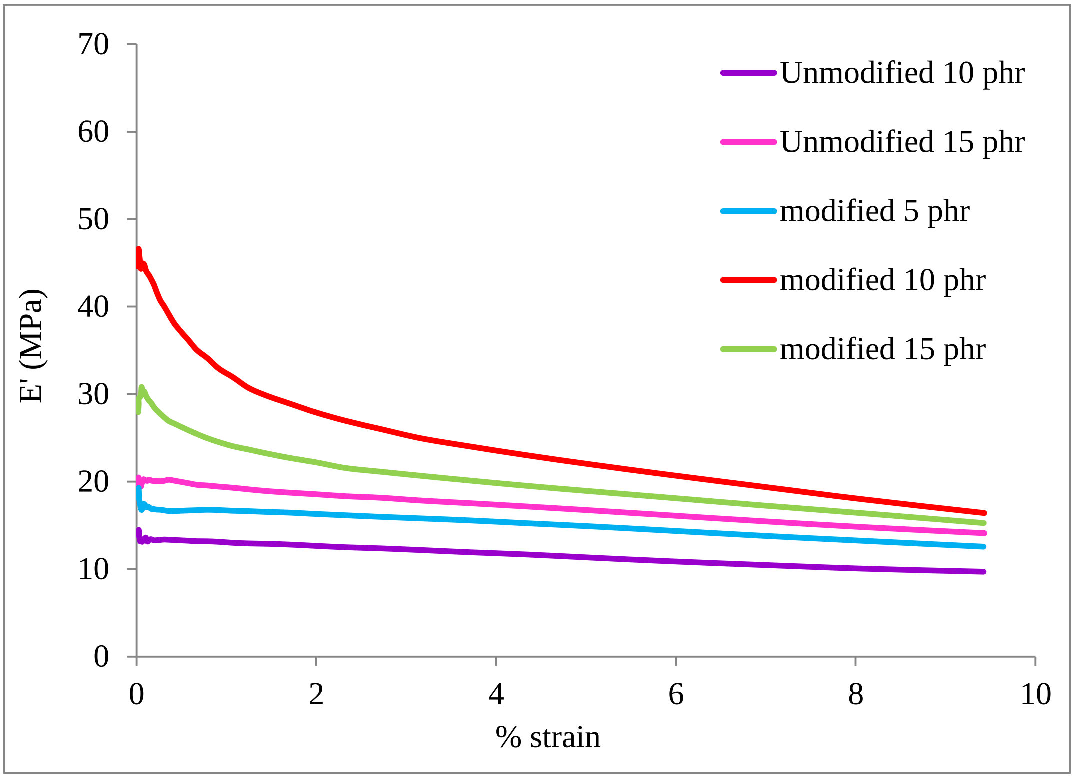


Figure 4.15 Strain-sweep test of unmodified- and modified-$CaCO_3$ with various contents filled natural rubber latex film.

CHAPTER V

CONCLUSIONS

1. Polyisoprene was successfully formed on $CaCO_3$ surface by admicellar polymerization. The molecular weights of polyisoprene were in the regions of 3,000 Daltons for M_n and 6,000 for Mw and the polydispesity index was about 2.2.

2. The amount of SDS adsorption on $CaCO_3$ surface was strongly influenced by pH value and NaCl concentration and not by ethanol.

3. The optimum mole ratio of SDS and isoprene monomer for the formation of polyisoprene on $CaCO_3$ surface was 1:8.

4. Polyisoprene-modified $CaCO_3$ gave improved tensile strength of NR film at lower $CaCO_3$ content than did the unmodified $CaCO_3$. In the case of modified $CaCO_3$, only 5 phr was required compared with 10 phr for unmodified $CaCO_3$.

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APPENDICES

APPENDIX A
SURFACE-CHARGED OF SOLID PARTICLE

A.1 Determination of surface-charged

Table A.1. Zeta potential of $CaCO_3$ dispersion in various pH after equilibrate the samples for 1 day.

pH 7.06	**(1)**	**(2)**	**(3)**	**Average**
Zeta (1)	18.10	17.10	18.40	17.87
Zeta (2)	11.44	11.99	12.40	11.93
Zeta (3)	14.2	15.20	15.10	14.83
pH 8.03	**(1)**	**(2)**	**(3)**	**Average**
Zeta (1)	30.40	32.10	32.50	31.67
Zeta (2)	21.90	22.60	23.40	22.63
Zeta (3)	27.20	27.20	29.90	28.10
pH 9.09	**(1)**	**(2)**	**(3)**	**Average**
Zeta (1)	22.60	23.60	23.70	23.30
Zeta (2)	23.40	23.30	22.30	23.00
Zeta (3)	19.70	22.80	22.00	21.50
pH 10.08	**(1)**	**(2)**	**(3)**	**Average**
Zeta (1)	10.30	10.80	9.66	10.25
Zeta (2)	10.6	10.6	10.2	10.47
Zeta (3)	9.18	9.27	11.00	9.82
pH 10.98	**(1)**	**(2)**	**(3)**	**Average**
Zeta (1)	-8.46	-7.63	-9.63	-8.57
Zeta (2)	-7.98	-6.16	-8.19	-7.44
Zeta (3)	-8.78	-10.80	-9.80	-9.79
pH 11.95	**(1)**	**(2)**	**(3)**	**Average**
Zeta (1)	-10.40	-11.00	-10.00	-10.47
Zeta (2)	-7.14	-10.70	-10.30	-9.38
Zeta (3)	-7.86	-9.43	-8.79	-8.69

APPENDIX B

CALIBRATION CURVE AND ADSORPTION RESULTS

B.1 Calibration curve of pure SDS

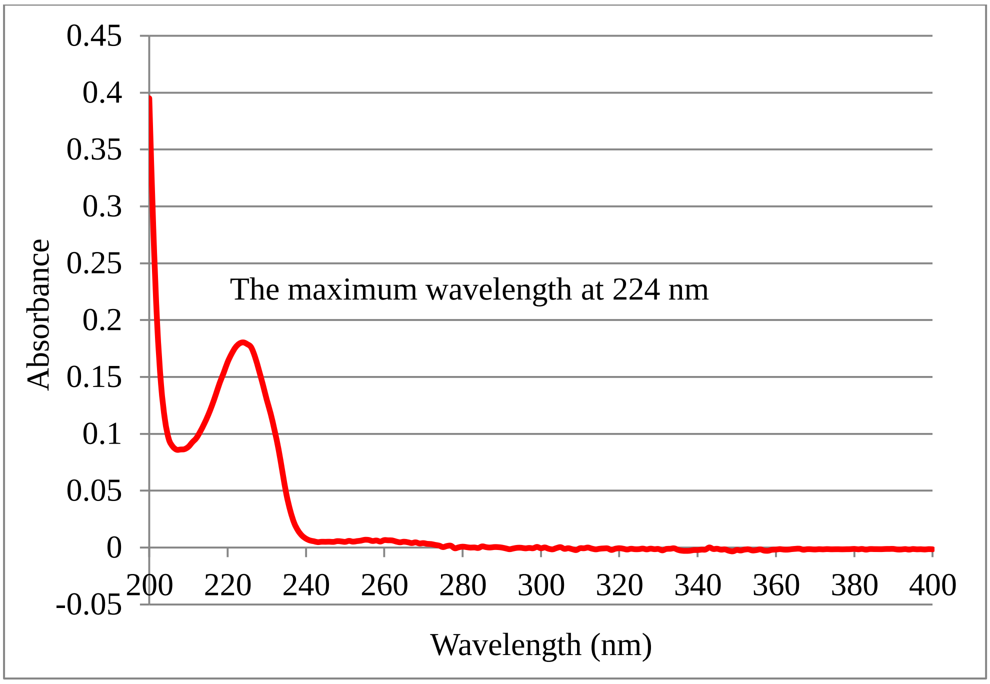

Figure B.1. UV-Vis spectra of pure SDS at 3 mM

The calibration curve of standard SDS determining at 224 nm was showed in Figure B.2.

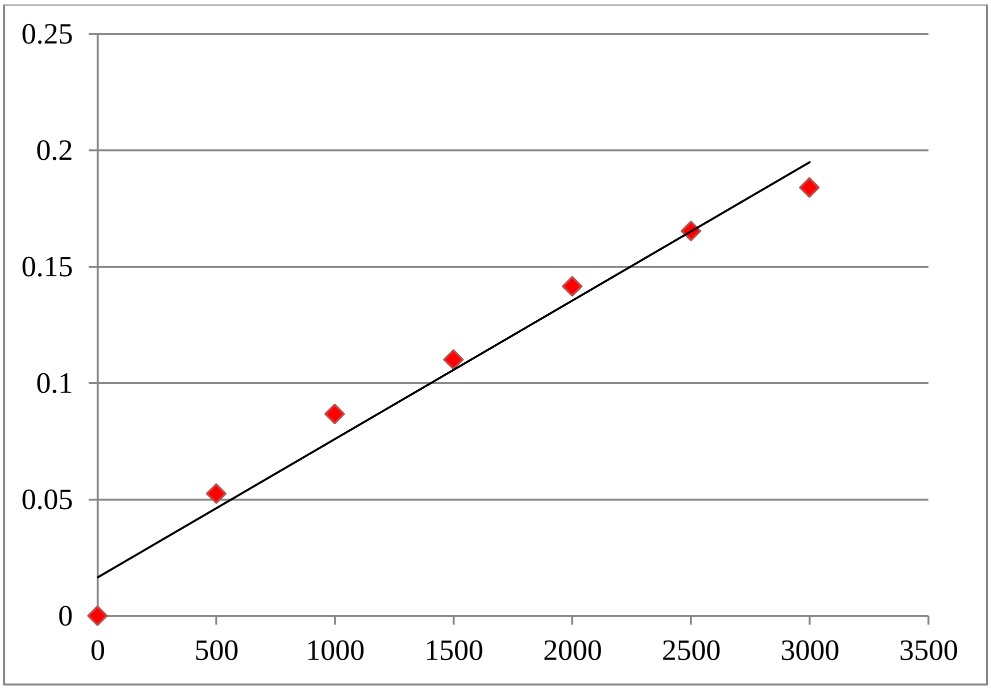

Figure B.2. Calibration curve of standard SDS for adsorption isotherm.

Calibration equation: $y = 6 \times 10^{-5}x + 0.0166$

R-squared value: 0.9763

B.2 UV-Vis spectrophotometry of varying pH

Table B.1 Absorbance at 224 nm of equilibrium SDS concentration with various pH values.

pH	**Absorbance (AU)**	**Absorbance (AU)**	**Absorbance (AU)**	**Average**	**Cf (μM)**	**Diluted**	**SDS adsorbed**
7.14	0.1324	0.1271	0.1312	0.130233	5681.667	2.5 in 5ml	1172.733
8.01	0.1325	0.1311	0.1287	0.130767	5708.333	2.5 in 5ml	1171.667
9.01	0.1231	0.1228	0.1242	0.123367	7117.778	2.5 in 5ml	1115.289
10.11	0.1257	0.1242	0.1261	0.125333	9061.111	2.5 in 5ml	1037.556
10.98	0.0832	0.0841	0.0824	0.083233	11105.56	1.25 in 5ml	955.7778
12.01	0.1011	0.0986	0.1008	0.100167	13927.78	1 in 5ml	842.8889

B.3 UV-Vis spectrophotometry of NaCl

The equilibrium SDS adsorption with varying NaCl concentration was determined by UV-Vis spectrophotometry at fixed pH of 8 and 35 mM initial SDS concentration.

Table B.2 Absorbance at 224 nm of equilibrium SDS concentration with various NaCl concentrations.

NaCl (M)	**Absorbance (AU)**	**Absorbance (AU)**	**Absorbance (AU)**	**Average**	**C_f (μM)**	**Diluted**	**SDS adsorbed**
0.10	0.1206	0.1196	0.1124	0.1175	6728.89	2.5 in 10 ml	1130.84
0.15	0.1450	0.1321	0.1336	0.1369	5012.50	2.0 in 5 ml	1199.50
0.20	0.1372	0.1345	0.1391	0.1369	5013.89	2.0 in 5 ml	1199.44
0.25	0.1253	0.1214	0.1235	0.1234	5933.33	3.0 in 10 ml	1162.67

NaCl (M)	**Absorbance (AU)**	**Absorbance (AU)**	**Absorbance (AU)**	**Average**	**Cf (μM)**	**Diluted**	**SDS adsorbed**
0.10	0.1110	0.1221	0.1012	0.1114	6322.22	2.5 in 10 ml	1147.11
0.15	0.1358	0.1365	0.1382	0.1368	5009.72	2.0 in 5 ml	1199.61
0.20	0.1317	0.1342	0.1331	0.1330	4850.00	2.0 in 5 ml	1206.00
0.25	0.1301	0.1298	0.1312	0.1304	6320.37	3.0 in 10 ml	1147.19

B.4 UV-Vis spectrophotometry of equilibrium SDS

The equilibrium SDS adsorption (C_f) with varying initial SDS concentration (C_i) was determined by UV-Vis spectrophotometry at fixed pH of 8 and 35 mM initial SDS concentration**.** The SDS adsorbed was calculated by the different of initial and final SDS concentration.

$$\mathrm{SDS_{adsorbed}} = \frac{\frac{(\mathrm{Ci}-\mathrm{Cf})}{1000}\times \mathrm{volume}}{\mathrm{g\ of\ solid\ particle}}$$

Table B.3 Absorbance at 224 nm of equilibrium SDS concentration with various initial SDS concentration. **(**Experiments were repeated 3 times)

Ci (μM)	**Absorbance (AU)**	**Absorbance (AU)**	**Absorbance (AU)**	**Average**	**Cf (μM)**	**Diluted**	**SDS adsorbed**
2000	0.0314	0.0379	0.0285	0.0326	266.67	-	69.33
4000	0.0402	0.0382	0.0373	0.0386	366.11	-	145.36
6000	0.0559	0.0493	0.0548	0.0533	612.22	-	215.51
8000	0.0761	0.0783	0.0748	0.0764	996.67	-	280.13
10000	0.0916	0.0892	0.0901	0.0903	1228.33	-	350.87
15000	0.1041	0.0979	0.1066	0.1029	1437.78	-	542.49
20000	0.1153	0.1194	0.1184	0.1177	1685.00	-	732.60
25000	0.0870	0.0966	0.0891	0.0909	2476.67	5 in 10 ml	900.93
30000	0.1303	0.1352	0.1401	0.1352	3953.33	5 in 10 ml	1041.87
35000	0.1464	0.1442	0.1431	0.1446	5331.94	2 in 5 ml	1186.72

Ci (μM)	**Absorbance (AU)**	**Absorbance (AU)**	**Absorbance (AU)**	**Average**	**Cf (μM)**	**Diluted**	**SDS adsorbed**
2000	0.031	0.0299	0.0286	0.0298	220.56	-	71.18
4000	0.0392	0.0411	0.0398	0.0400	390.56	-	144.38
6000	0.0488	0.0512	0.0452	0.0484	530.00	-	218.80
8000	0.0691	0.0711	0.0724	0.0709	904.444	-	283.82
10000	0.0798	0.0852	0.0876	0.0842	1126.67	-	354.93
15000	0.0988	0.1012	0.0927	0.0976	1349.44	-	546.02
20000	0.1122	0.1139	0.1141	0.1134	1613.33	-	735.47
25000	0.0775	0.0761	0.0777	0.0771	2016.67	5 in 10 ml	919.33
30000	0.1215	0.1193	0.1201	0.1203	3456.67	5 in 10 ml	1061.73
35000	0.1388	0.1394	0.1301	0.1361	4979.17	2 in 5 ml	1200.83

Ci (µM)	Absorbance (AU)	Absorbance (AU)	Absorbance (AU)	Average	Cf (µM)	Diluted	SDS adsorbed
2000	0.0323	0.0281	0.0226	0.0277	184.44	-	72.62
4000	0.0387	0.0378	0.0316	0.0360	323.89	-	147.04
6000	0.0471	0.0414	0.0374	0.0420	422.78	-	223.09
8000	0.0582	0.0645	0.0652	0.0626	767.22	-	289.31
10000	0.0858	0.0721	0.0749	0.0776	1016.67	-	359.33
15000	0.0796	0.0852	0.0867	0.0838	1120.56	-	555.18
20000	0.1112	0.1131	0.1098	0.1114	1579.44	-	736.82
25000	0.0879	0.0795	0.0957	0.0877	2370.00	5 in 10 ml	905.20
30000	0.1143	0.1154	0.1187	0.1161	3317.78	5 in 10 ml	1067.29
35000	0.1359	0.1349	0.1329	0.1346	4915.28	2 in 5 ml	1203.39

B.5 SDS adsorption isotherm with 0.5M ethanol

Table B.4 Absorbance at 224 nm of equilibrium SDS concentration with various initial SDS concentration containing 0.5M ethanol.

Ci (µM)	Absorbance (AU)	Absorbance (AU)	Absorbance (AU)	Average	Cf (µM)	SDS adsorbed
5000	0.0486	0.0421	0.0444	0.0450	473.89	181.04
10000	0.0521	0.0524	0.0516	0.0520	590.56	376.38
15000	0.061	0.0592	0.0588	0.0597	717.78	571.29
20000	0.0665	0.0632	0.0696	0.0664	830.56	766.78
25000	0.0849	0.0856	0.0817	0.0841	1124.44	955.02
30000	0.1104	0.1098	0.1039	0.1080	1523.89	1139.04
35000	0.1200	0.1197	0.1269	0.1222	1760.00	1329.60

APPENDIX C
CALCULATIONS

C.1 Calculation NaCl concentration

Example, 0.1M NaCl in 40 ml

solution 1000 ml $\longrightarrow$ NaCl solute 0.1 mol

If, solution 40 ml $\longrightarrow$ NaCl solute 4×10^{-3} mol

$$\text{mol} = \frac{g}{Molecular\ weight\ (MW)}$$

The molecular weight of NaCl = 58.443

So, $4 \times 10^{-3} = \frac{g}{58.443}$

$g = 2.3377 \times 10^{-1}$

Purity of NaCl = 99.5 %w/w

So, need weight (g) = $\frac{2.3377 \times 10^{-1}}{99.5} \times 100$

$= 2.3494 \times 10^{-1}$

C.2 Adsorption isotherm

C.2.1. SDS concentration

Example, 5000 µM in 50 ml volumetric flask

solution 1000 ml $\longrightarrow$ SDS solute 5000×10^{-6} mol

If, solution 50 ml $\longrightarrow$ SDS solute 2.500×10^{-4} mol

$$\text{mol} = \frac{g}{Molecular\ weight\ (MW)}$$

The molecular weight of SDS = 288.38

So, $2.500 \times 10^{-4} = \dfrac{g}{288.38}$

$g = 7.210 \times 10^{-2}$

Purity of SDS = 99.1 %w/w

So, need weight (g) $= \dfrac{7.210 \times 10^{-2}}{99.1} \times 100$

$= 7.275 \times 10^{-2}$ g

C.2.2. 0.5 M Ethanol

Example, 0.50 M of ethanol in 40 ml

solution 1000 ml $\longrightarrow$ ethanol solute 0.50 mol

If, solution 40 ml $\longrightarrow$ ethanol solute 0.02 mol

$$\text{mol} = \frac{g}{Molecular\ weight\ (MW)}$$

The molecular weight of ethanol = 46

So, $0.02 = \frac{g}{46}$

$g = 0.92$

$D = \frac{m}{v}$; m = mass (g), and v = volume (ml)

Density of ethanol = 0.789 g/cm^3

$0.789 = \frac{0.92}{v}$

$v = 1.2$ ml

C.3 Polyisoprene Formation

C.3.1 Mole ratio of ethanol to SDS

Example, 30:1 mole ratio of ethanol to SDS, Fixed SDS concentration at 23,000 μM

solution 1000 ml ⟶ SDS solute 23,000 x 10^{-6} mol

If, solution 40 ml ⟶ SDS solute 9.2000 x 10^{-4} mol

$$\text{mol} = \frac{g}{Molecular\ weight\ (MW)}$$

The molecular weight of SDS = 288.38

So, $9.2000 \times 10^{-4} = \frac{g}{288.38}$

$g = 2.6531 \times 10^{-1}$

Purity of SDS = 99.1 %w/w

So, need weight (g) = $\frac{2.6531 \times 10^{-1}}{99.1} \times 100$

$= 2.6772 \times 10^{-2}$ g

$= 9.2836 \times 10^{-4}$ mol

1:30 SDS to ethanol mole ratio

SDS 1 mol ⟶ ethanol 30 mol

SDS 9.2836×10^{-4} mol ⟶ ethanol 2.7851×10^{-2} mol

= 1.2811 g

Density of ethanol = 0.789 g/cm^3

$0.789 = \frac{1.2811}{v}$

v = 1.6 ml

C.3.2 Mole ratio of $K_2S_2O_8$ and isoprene monomer

Example, 0.15:1 mole ratio of $K_2S_2O_8$ and isoprene monomer , Fixed SDS concentration at 23,000 μM and 14:1 mole ratio of isoprene monomer and SDS

solution 1000 ml $\longrightarrow$ SDS solute 23,000 x 10^{-6} mol

If, solution 40 ml $\longrightarrow$ SDS solute 9.2000 x 10^{-4} mol

$$\text{mol} = \frac{g}{Molecular\ weight\ (MW)}$$

The molecular weight of SDS = 288.38

So, $9.2000 \times 10^{-4} = \frac{g}{288.38}$

$g = 2.6531 \times 10^{-1}$

Purity of SDS = 99.1 %w/w

So, needed weight (g) = $\frac{2.6531 \times 10^{-1}}{99.1} \times 100$

$= 2.6772 \times 10^{-1}$ g

$= 9.2836 \times 10^{-4}$ mol

<u>14:1 mole ratio of isoprene monomer and SDS</u>

SDS 1 mol $\longrightarrow$ Isoprene monomer 14 mol

SDS 9.2836×10^{-4} mol $\longrightarrow$ Isoprene monomer 1.2997×10^{-2} mol

The molecular weight of isoprene = 68.12

So, $1.2997 \times 10^{-2} = \frac{g}{68.12}$

$= 0.88536$ g

Purity of isoprene = 98.1%

So, needed weight (g) = $\frac{0.88536}{98.1} \times 100$

$= 0.90251$ g = 1.3249×10^{-2} mol

<u>0.15:1 mole ratio of $K_2S_2O_8$ and isoprene</u>

Isoprene monomer 1 mol $\longrightarrow$ $K_2S_2O_8$ 0.15 mol

Isoprene monomer 1.3249×10^{-2} mol $\longrightarrow$ $K_2S_2O_8$ 1.9874×10^{-3} mol

Molecular weight of $K_2S_2O_8$ = 270.31

So, $1.9874 \times 10^{-3} = \frac{g}{270.31}$

$= 0.53721$ g

C.3.3 Mole ratio of isoprene monomer to SDS

Example, 14:1 mole ratio of isoprene monomer and SDS, Fixed SDS concentration at 23,000 µM.

solution 1000 ml ⟶ SDS solute $23{,}000 \times 10^{-6}$ mol

If, solution 40 ml ⟶ SDS solute 9.2000×10^{-4} mol

$$\text{mol} = \frac{g}{Molecular\ weight\ (MW)}$$

The molecular weight of SDS = 288.38

So, $$9.2000 \times 10^{-4} = \frac{g}{288.38}$$

$$g = 2.6531 \times 10^{-1}$$

Purity of SDS = 99.1 %w/w

So, $$\text{needed weight (g)} = \frac{2.6531 \times 10^{-1}}{99.1} \times 100$$

$$= 2.6772 \times 10^{-1}\ \text{g}$$

$$= 9.2836 \times 10^{-4}\ \text{mol}$$

14:1 mole ratio of isoprene monomer and SDS

SDS 1 mol ⟶ Isoprene monomer 14 mol

SDS 9.2836×10^{-4} mol ⟶ Isoprene monomer 1.2997×10^{-2} mol

The molecular weight of isoprene = 68.12

So, $$1.2997 \times 10^{-2} = \frac{g}{68.12}$$

$$= 0.88536\ \text{g}$$

Purity of isoprene = 98.1%

So, needed weight (g) = $\frac{0.88536}{98.1} \times 100$

$= 0.90251$ g

Density of isoprene = 0.681 g/cm^3

$D = \frac{m}{v}$; $0.681 = \frac{0.90251}{v}$

$v = 1.33$ ml

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