จุฬาลงกรณ์มหาวิทยาลัย
ทุนวิจัย
กองทุนรัชดาภิเษกสมโภช

รายงานวิจัย

การปรับผิวซิลิกาโดยกระบวนการแอดไมเซลลาร์พอลิเมอไรเซชั่นด้วยเครื่องปฏิกรณ์แบบต่อเนื่องเพื่อปรับปรุงคุณสมบัติของยางธรรมชาติ

โดย

ปราโมช รังสรรค์วิจิตร

ธันวาคม 2549

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(Silica Surface Modification by Admicellar Polymerization with a Continuous Stirred Tank Reactor for Natural Rubber Property Improvement)

โดย
รองศาสตราจารย์ ดร. ปราโมช รังสรรค์วิจิตร
วิทยาลัยปิโตรเลียมและปิโตรเคมี

ธันวาคม 2549

ชื่อโครงการวิจัย	การปรับผิวซิลิกาโดยกระบวนการแอดไมเซลลาร์พอลิเมอไรเซชั่นด้วยเครื่องปฏิกรณ์แบบต่อเนื่องเพื่อปรับปรุงคุณสมบัติของยางธรรมชาติ
ชื่อผู้วิจัยหลัก	ปราโมช รังสรรค์วิจิตร
เดือนและปีที่ทำวิจัยสำเร็จ	ธันวาคม 2549

บทคัดย่อ

งานวิจัยนี้ศึกษาความเป็นไปได้ในการผสมสารลดแรงตึงผิวแบบมีขั้วบวก (เซททริวไตรเมททริวแอมโมเนี่ยมโบรไมด์, ซีแทบ) และแบบไม่มีขั้ว (ไทรทรอนเอ็กซ์ 100) แทนการใช้สารลดแรงตึงผิวแบบมีขั้วบวกอย่างเดียวในการปรับสภาพผิวของซิลิกา โดยกระบวนการแอดไมเซลลาร์พอลิเมอไรเซชั่นให้เหมาะต่อการผสมในยาง ในการทดลองนี้เป็นการเปรียบเทียบผลของอัตราส่วนโดยโมลซีแทบต่อไทรทรอนเอ็กซ์ 100 ต่อโครงสร้างในการดูดซับของสารลดแรงตึงผิวแบบชั้นเดียวและแบบสองชั้นต่อกระบวนการแอดไมเซลลาร์พอลิเมอไรเซชั่นรวมทั้งสมบัติทางกายภาพของยางผสมโมดิฟายด์ซิลิก้าที่ได้ โดยมีกระบวนการแอดไมเซลลาร์พอลิเมอไรเซชั่นที่ใช้ซีแทบเพียงอย่างเดียวเป็นฐานในการเปรียบเทียบด้วย ผลการทดลองพบว่ายางมีคุณสมบัติทางกลศาสตร์ดีขึ้น นอกจากนั้นยังพบว่าโครงสร้างการดูดซับแบบชั้นเดียวของการผสมสารลดแรงตึงผิวทั้งสองยังสามารถใช้ผสมในยางโดยที่คุณสมบัติของยางยังเหมาะสมอยู่ ส่งผลให้ค่าใช้จ่ายในการใช้สารลดแรงตึงผิวผสมลดลงประมาณสามเท่าเมื่อเปรียบเทียบกับการใช้สารลดแรงตึงผิวแบบมีขั้วบวกเพียงอย่างเดียว

Project Title	Silica Surface Modification by Admicellar Polymerization with a Continuous Stirred Tank Reactor for Natural Rubber Property Improvement
Principal Investigator	Pramoch Rangsunvigit
Year	December 2006

Abstract

Mixed surfactants of cationic and nonionic surfactants, cetyltrimethyl ammonium bromide (CTAB) and Triton X-100, were employed in the admicellar polymerization to replace the use of pure CTAB. Effect of the molar ratio of CTAB to Triton X-100 and the adsorption structure of surfactants, monolayer and bilayer, were investigated on the admicellar polymerization compared with the polymerization using only CTAB in terms of the compatibility between rubber and silica. Results indicated that the silica modification by the nonionic surfactant was successfully used to modify rubber compound. The properties of rubber compound modified by silica using the nonionic surfactant mixed with the cationic surfactant in the monolayer adsorption structure were acceptable compared to those of rubber compound modified by silica using pure cationic surfactant (bilayer adsorption structure). The use of nonionic surfactant can reduce the cost of the modified silica about 3 time less than the modified silica using the pure cationic surfactant.

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CHAPTER I
INTRODUCTION

Fillers or reinforcing materials are usually added to rubber to improve its tensile strength, abrasion, modulus and tear resistance. Carbon blacks are the most common and efficient fillers for the preparation of high quality rubber products such as tires because they offer excellent reinforcement at a relatively low cost. Carbon black is the most useful reinforcing materials that are usually added to rubber to improve its properties with low cost. But carbon black can only be used in products with black color, a search for alternative fillers, which permit the production of highly durable colored products, has led to silicas.

Silicas show a potential as an alternative filler because it provides natural color and compared to carbon black, lower hysteresis loss, which, for tire applications, leads to a lower rolling resistance and consequently fuel savings. However, silica surface requires some modification because unmodified silica cannot form chemical bonds with rubber due to low compatibility of hydrophilic silica with hydrophobic rubber. Several methods such as bifunctional organosilanes, grafting, and admicellar polymerization are available for the modification (Chinpan, 1996). Although the compatibility can be enhanced with bifunctional organosilanes, the organosilane agents are expensive (Thammathadanukul *et al.*, 1996).

Modification of the silica surface by admicellar polymerization beneficially reduces compound curing times and improves specific rubber compound performance in both chemical and physical properties (O'Haver *et al.*, 1996). Possibilities of using a continuous mode operation have been investigated and show a great potential to produce a large amount of modified silicas with consistent properties (Chaisirimahamorakot, 2001; Nontasorn *et al.*, 2005).

With the rationale described above, a research project entitled "Silica Surface Modification by Admicellar Polymerization with a Continuous Stirred Tank Reactor for Natural Rubber Properties Improvement" has been supported by the Ratchadapisak Somphot Endowment from July 2005 – June 2006. The main objective of this work was to study the effects of different surfactants and their mixtures in the admicellar polymerization process for the modification of silica surface properties and its use in the rubber compounding.

CHAPTER II
SURVEY OF RELATED LITERATURE

2.1 Natural Rubber

Natural rubber (NR) is a renewable polymer material exhibiting excellent physical and chemical properties. Natural rubber latex occurs in many plants, including the white sap of the common milkweed and dandelion. The most important source of natural rubber latex is the *Hevea brasiliensis* tree, which contains hundreds of proteins, including enzymes that are involved in the biosynthesis of the rubber molecules. NR is the strongest of all rubbers and also has excellent dynamic properties, such as resistance to fatigue, but it is less resistant to environmental damage such as by ozone in the atmosphere and by oils than some synthetic rubbers. Raw NR contains 93-95% *cis*-1,4-polyisoprene of about 5×10^5 g/mol, 2-3% proteins, 2% acetone-soluble resins (including fatty acids), small amounts of sugars, traces of minerals and water (Blow and Hepburn, 1982). The hydrocarbon component of NR, which consists of over 99.99% of linear *cis*-1,4-polyisoprene is shown in Figure 2.1.

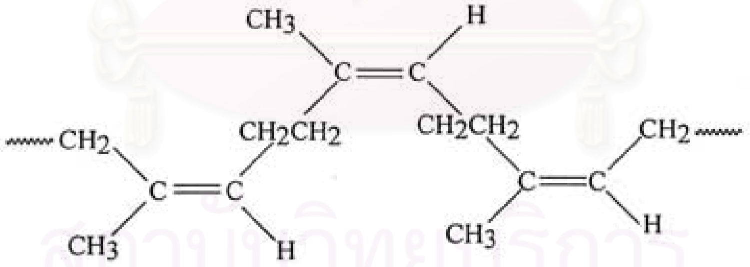


Figure 2.1 Chemical structure of NR (*cis*-1,4-polyisoprene).

Average molecular weight of the polyisoprene in NR ranges from 200,000 to 400,000 with a relatively broad molecular weight distribution, the cause of its excellent processing behavior. There is one double bond for each isoprene unit, which, along with the α-methylene groups contained in an NR molecular chain, are the reactive groups for vulcanization with sulfur. The glass transition temperature

(T_g) of uncured NR, the temperature or temperature range over which the polymer exhibits a remarkable change in several physical properties, is far below room temperature. Therefore, rubber is soft and can be melted by heat. Conversely, it is rigid and brittle at temperatures below the T_g. Hence, NR can be utilized in a narrow temperature range (Blow and Hepburn, 1982).

The thermal properties of NR can be enhanced by vulcanization with sulfur. Although vulcanized rubber has many advantages such as low T_g and high impact strength, it also has many undesirable properties such as low hardness, abrasion, stiffness and tear resistances. Consequently, fillers are utilized to improve the performance of these properties.

O'Haver *et al.* (1996) studied the modified silica surface by using copolymer prepared with a nonpolar and polar monomer to improve the performance of rubber compounds. The admicellar polymerization process serves to improve the rubber cure properties and the cured compound physical properties.

Kudisri (1997) produced polystyrene-isoprene copolymer on clay via admicellar polymerization. This study examined the effect of the amount of surfactant and monomer on the process. It was found that the increase in the compound cure rate decreases t_{90} cure time and improves tensile property, tear strength. hardness, flex cracking resistance and compression set.

2.2 Surfactant Structure

The word surfactant is a contraction of the term "surface active agent". Surfactants are among the most unique and versatile materials due to their chemical structure. Generally, water-soluble surface-active agents are comprised of a hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8-18 carbon atoms, attached to hydrophilic or water soluble functional groups. This dual-natured structure is referred to as *amphiphilic* and thus the molecules are called *amphiphiles*. Surfactants are said to have a "tail" and a "head" as shown in Figure 2.2. In aqueous systems, the tail is hydrophobic, which means water-hating, therefore oil-loving. It is typically depicted either as a straight line or a wavy line. The head is hydrophilic, which means water loving and is generally depicted as a circle.

Surfactants are classified according to the charge present in the hydrophilic portion of the molecule (after dissociation in aqueous solution). They can be categorized into 4 types (Rosen, 1989).

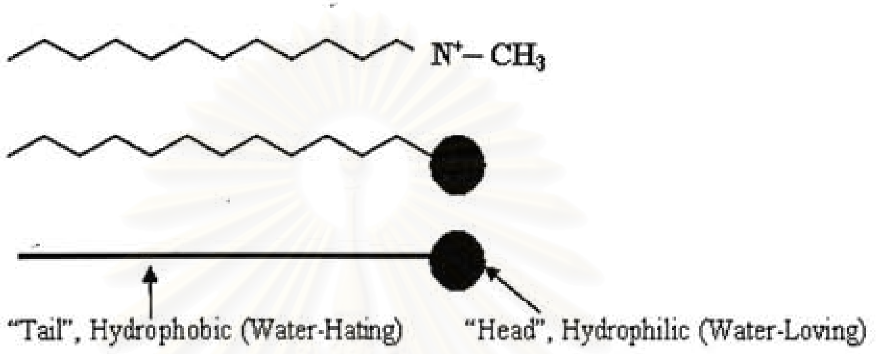


Figure 2.2 Surfactant structure.

Anionic surfactant: a surfactant molecule whose polar group is negatively charged. For example, alkylbenzene sulfonate, sodium dodecylsulfate.

Nonionic surfactant: no ion charge appears on the hydrophilic portion; for example, polyoxyethylenated alkylphenol.

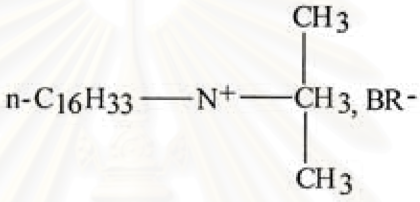
Cationic surfactant: the hydrophilic portion bears a positive charge, examples include quaternary ammonium chlorides and laurylamine hydrochloride.

Ampholytic or zwitterionic surfactant: a surfactant molecule which has both positive and negative charged portions. The presence of both charged hydrophilic groups in the same molecule leads to the head group hydrophilicity being an intermediate between the ionic and conventional nonionic classes (Laughlin, 1991). The charges present depend on solution pH. Examples include polyoxyethylenated alkylphenol and lauramidopropylbetaine.

2.3 Cationic Surfactant

The term "cationic surfactant" is used to denote an ionic compound in which the cation is amphiphatic and strongly surface active. Considering the effect of pH on molecular structure and physical chemistry, the cationic hydrophilic groups can be divided into two sub-groups; neutral and acidic.

Cetyltrimehylammoniumbromide (CTAB) is a familiar cationic surfactant in the neutral sub-group as shown in Figure 2.3.



$$\text{n-}C_{16}H_{33}\text{—}N^{+}\text{—}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}H_3,\ BR^{-}$$

Figure 2.3 Structure of CTAB.

Quaternary ammonium ions have four carbons bonded to a positive nitrogen atom. Quaternary ammonium surfactants have one or more of these substituent groups that are lypophillic (oil-loving). The cationic molecule exists paired with an anionic molecule in an electrically neutral salt. The quaternary ammonium nitrogen in CTAB displays *sp^3* bonding. This cationic molecule lacks both acidic protons and non-bonding electron pairs; therefore, it is neutral in water from an acid-base perspective. If the anionic partner in such a salt is also neither acidic nor basic, as is true of bromide, the molecular structure of this salt is independent of pH (Rubingh and Holland, 1990).

Ismail *et al.* (1997) studied the effects of a cationic surfactant (fatty diamine), termed a multifunctional additive (MFA), and a commercial silane coupling agent on the properties of a silica filled natural rubber compound. The results showed that the MFA (EN444) not only contributes to a better silica-elastomer adherence but also improves dispersion, resulting in a lower hysteresis and enhanced mechanical properties of the natural rubber compound.

2.4 Nonionic Surfactant

Nonionic surfactants are surface-active compounds, which have no net charge in the hydrophilic section. They are compatible with all other types of surfactants and generally available as 100% active material free of electrolyte. They are soluble in water and organic solvents, including hydrocarbons. Solubility in water decreases with increasing temperature. They can be made resistant to hard water, polyvalent metallic cations, and electrolytes at high concentration (Rosen, 1989). Commercial products are a mixture of structures with a wide distribution of polyoxyethylene chain lengths. Triton X-100 is a familiar nonionic surfactant, which is often used in biochemical applications to solubilize proteins. Triton X-100 has no antimicrobial properties. It is considered as a comparatively mild detergent, non-denaturing. It is a clear to slightly hazy, colorless to light yellow liquid. Triton X-100 structure is shown in Figure 2.5.

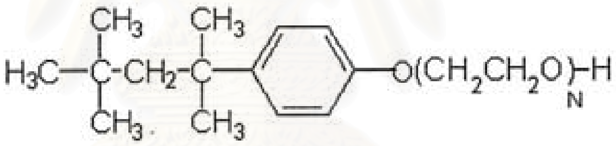


Figure 2.4 Octyl phenol ethoxylates (Triton X-100).

2.5 Surfactant Adsorption

The adsorption of an ionic surfactant on oppositely charged surfaces involves many mechanisms. However, only a few parameters affect the adsorption including 1) the nature of the structural groups on solid surface 2) the molecular structure of the adsorbate (the surfactant being adsorbed) and 3) the environment of the aqueous phase such as pH (Rosen, 1989).

Data from adsorption experiments are normally expressed in an adsorption isotherm, which shows the relationship between the amount of the adsorbed surfactant and the equilibrium concentration of the surfactant in liquid phase. The adsorption isotherm for an ionic surfactant onto an oppositely charged substrate is typically "S-shaped" when plotting the log of the adsorbed surfactant density versus the log of the equilibrium concentration of surfactant. It can be divided into four regions (Rosen, 1989) as shown in Figure 2.5.

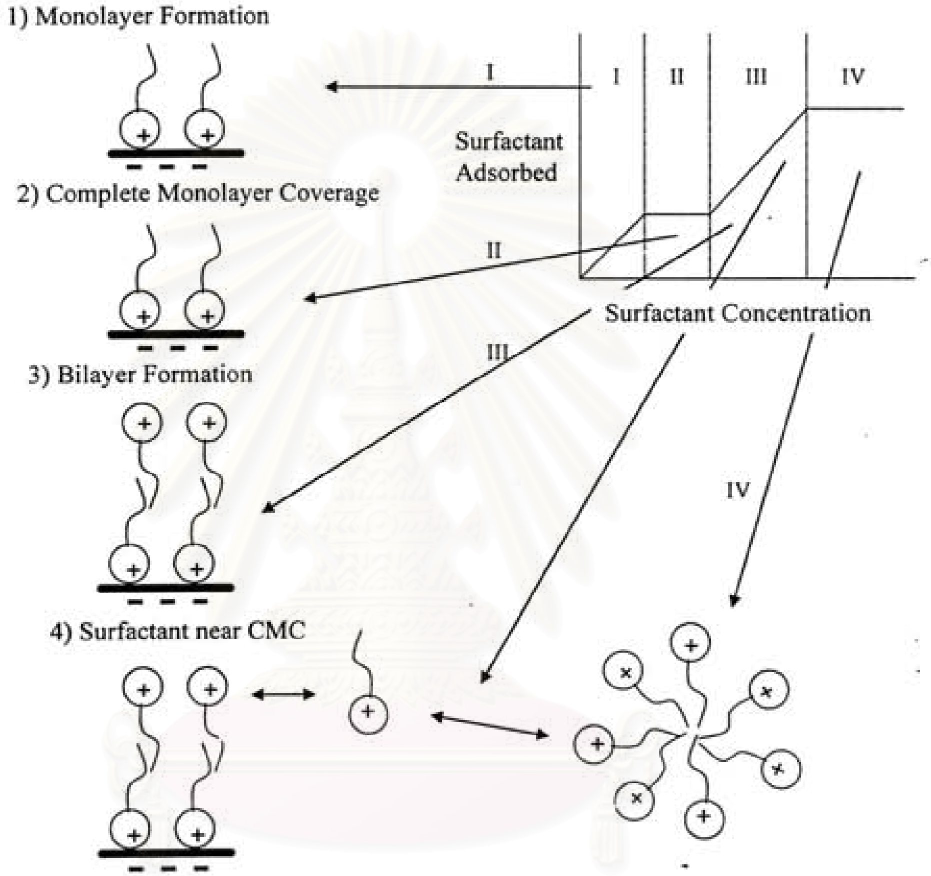


Figure 2.5 Adsorption isotherm of an ionic surfactant on an oppositely charged substrate.

Region I of the adsorption isotherm, corresponding to both very low bulk concentration of surfactant and low adsorption of the surfactant, is commonly referred to as the Henry's law region. The adsorption driving force is largely due to electrostatic attraction between the surfactant head groups and the oppositely charged surface. Because the interaction between molecules of the surfactants is negligible, the adsorbed surfactants in this region are viewed as being adsorbed alone and aggregates are not thought to be present.

Region II, distinguished by a sharply increased isotherm slope relative to the slope in the Henry's Law region, indicates the beginning of lateral interaction between the surfactant molecules, which results from the formation of surfactant aggregates on the most energetic surface patches. The aggregation of adsorbed surfactants are called admicelles (Harwell *et al.,* 1985) or hemimicelles (Somasundaran and Fuerstenau, 1966), depending upon whether the aggregates are viewed as monolayers or bilayers. The admicelle is a local bilayer structure with a lower layer of head group adsorbed on the substrate surface and an upper layer of head groups exposed to the solution. The hemimicelle is a monolayer structure having the head groups adsorbed on the surface while tail groups expose to the solution. The transition point from region I to region II, representing the equilibrium concentration at which the first formation of adsorbed surfactant aggregates, is called the critical admicelle concentration (CAC) (Harwell *et al.*, 1985) or hemimicelle concentration (HMC) (Somasundaran and Fuerstenau, 1966). During aggregate formation, the original charge on the solid may be neutralized and eventually reversed. Thus, by the end of this region, the solid surface usually has the same sign on its overall charge as the surfactant ions.

A sharp decrease in the slope of the isotherm indicates the beginning of region III. This decrease in slope is thought to be caused by the repulsion between the like-charged head groups on the surface, the beginning of adsorption on lower energy surface patches, or the charge neutralization of the surface. Thus, additional adsorption becomes more difficult.

Region IV is referred as the plateau adsorption region. The position of this plateau usually corresponds to a maximum adsorption, having almost constant surfactant adsorption with further increases in surfactant concentration. Normally, the equilibrium surfactant concentration at the transition point from region III to IV is roughly at the critical micelle concentration (CMC), the concentration at which micelles first form (Rosen, 1989).

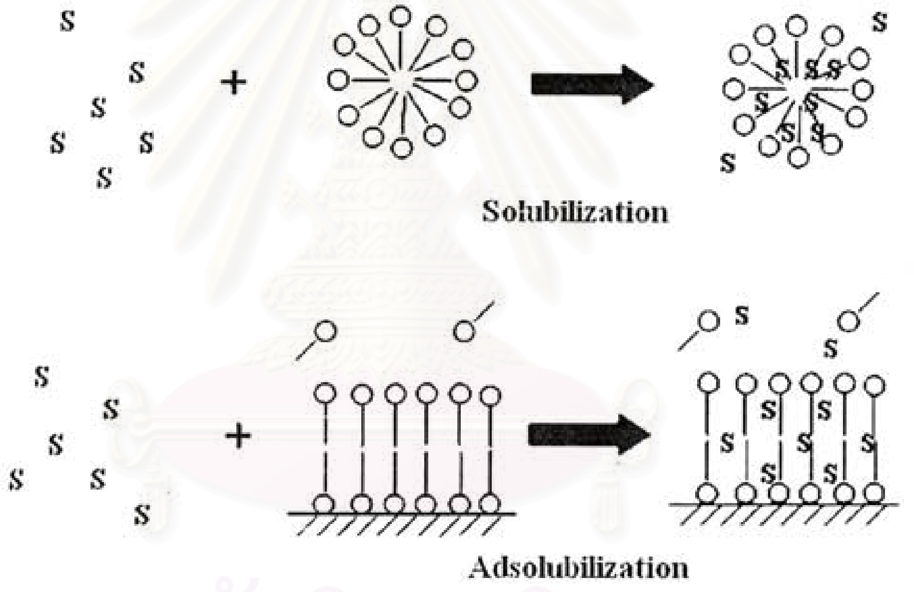
Yeskie and Harwell (1988) found that there are conditions under which a second layer of surfactant always forms simultaneously with the first layer of surfactant. Accordingly, there are wide ranges of condition under which only a single layer forms. This was shown to be the result of the electrostatic contributions of the free energy of transfer for a surfactant monomer from a hemimicelle to an admicelle, which are potentially much larger in magnitude than the largest possible hydrophobic contributions. In addition, admicelles do form little if there is any interpenetrating of the hydrocarbon tails of second layer between the hydrocarbon tails of the first layer because the electrostatic repulsion between the two layers of head groups is larger than the largest possible gain in hydrophobic bonding that could result from the interpenetrating.

2.6 Solubilization

Solubilization is an important property of surfactants that is directly related to the presence of aggregates in solution called micelles. Surfactant solutions above their CMCs can dissolve considerably larger quantities of organic materials than pure water or surfactant solutions with concentrations below their CMCs. The additional capacity is obtained by solubilizing the solute in the micelles. Solubilization can be defined as "the spontaneous dissolving of substance (solid, liquid or gas) by reversible thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material" (Rosen, 1989). Consequently, a water-insoluble material in a dilute surfactant solution could appreciably increase its solubility when the surfactant concentration surpasses the CMC. Solubility increases approximately linearly with the concentration of surfactant above the CMC. There are a number of different sites in a micelle: 1) on the surface of the micelle 2) between the hydrophilic head group 3) in the palisade layer of the micelle located between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups and 4) in the inner core of the micelle. Depending on the nature of the material solubilized (the solubilizate), the exact location in the micelle at which solubilization occurs can vary (Rosen, 1989).

2.7 Adsolubilization

Similar to the solubilization of organics into micelles, organic molecules are integrated into surfactant aggregates at the solid-liquid interface (Figure 2.6). Adsolubilization is defined as *"the excess concentration of a species at an interface in the presence of an admicelle that would not exist in the absence of the admicelle"* (Wu *et al.,* 1987). This definition conveys the idea that the particular solute of interest does not adsorb onto the adsorbent surface by itself. The removal of solute from bulk solution occurs because of the presence of adsorbed surfactant aggregates and the incorporation of the solute into that aggregates.



"S"s represent solute molecules, monomers

Figure 2.6 Phenomenon of solubilization and adsolubilization.

The adsolubilization of styrene, isoprene, and mixtures of these into CTAB bilayers on precipitated silica was investigated by Kitiyanan *et al.* (1996). The adsolubilization equilibrium constant is defined as $K_i=X_i/C_{ib}$, where K_i is the adsolubilization equilibrium constant of the assolubilizate (*i*), X_i is mole fraction of adsolubilizate (*i*) in the admicelle, and C_{ib} is the concentration of solute (*i*) in the bulk aqueous phase (M). The styrene adsolubilization constant is nearly unchanged with increasing styrene equilibrium concentration in aqueous phase while the isoprene adsolubilization constant increases with increasing isoprene partial pressure. This suggests that styrene adsolubilizes into both the palisade layer and the core of the admicelle while isoprene adsolubilizes into only the palisade layer.

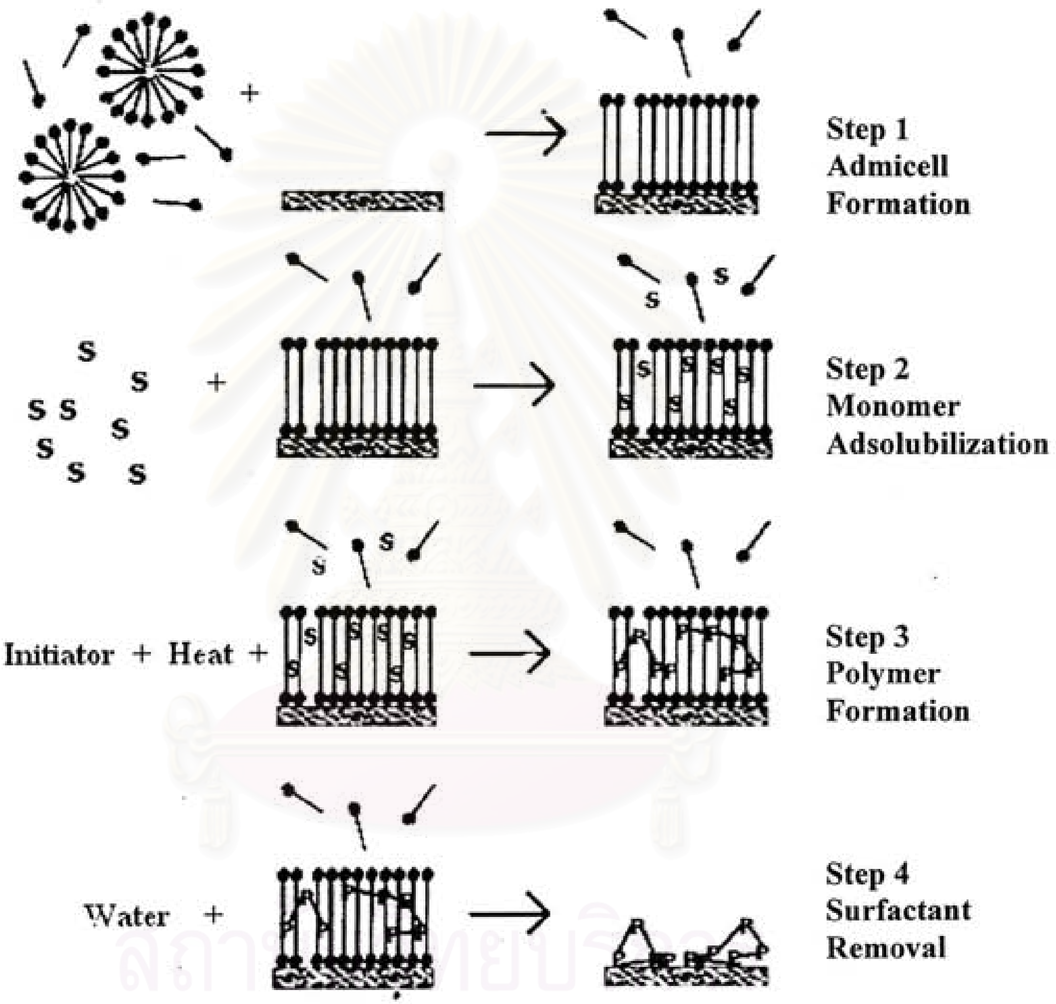
2.8 Ultra-Thin Film Formation

Formation of ultra-thin films on solid surfaces has been the object of powerful study in recent years because of a wide variety of possible applications of these films. The method used for the modification of inorganic powders by the formation of ultra-thin polymer films in adsorbed surfactant bilayers, called admicellar polymerization, was first developed by Wu *et al.* (1987). Admicellar polymerization can be considered to occur in four basic steps as show in Figure 2.7.

Step 1 is admicelle formation by the aggregation of surfactants at solid/liquid interfaces to form admicelles/aggregates through adsorption from an aqueous solution. For this step to be successful, the most critical parameter to be manipulated is the solution pH, relative to which the surface exhibits a net surface charge of zero (referred to the point of zero charge or PZC). The surface becomes protonated and positively charged at pH values below the PZC and surface is negatively charged above the PZC.

Step 2 consists of hydrophobic monomer molecules concentrating in the admicelle, adsolubilization, under conditions favorable for the formation of admicelles on a solid surface and unfavorable for the presence of micelles in an aqueous supernatant (Wu *et al.*, 1987). The hydrophobic monomers (e.g., styrene and isoprene in this study) adsolubilize or partition into the adsorbed surfactant aggregates of step 1. This step can occur after the formation of admicelle or concurrently with surfactant adsorption.

Step 3 is the *in-situ* polymerization of adsolubilized monomer. Further than the purpose of concentrating monomer at the surface of the substrate, the admicelles function as reaction loci or a two-dimensional reaction solvent for polymerization. Initiators begin the formation of polymer, possibly by mechanisms similar to those occurring in conventional emulsion techniques (Sakhalkar and Hirt, 1995). Once the reaction has started, additional monomer from the bulk solution diffuses into the admicelle (Wu *et al.*, 1987). If the reaction is continuous for a sufficient length of time, virtually all monomers can be converted to polymer.



"S"s represent solute molecules, monomers
"P"s connected by lines represent polymer chain formed during reaction

Figure 2.7 Admicellar polymerization process for the formation of a thin polymer film.

Step 4 is the removal of accessible surfactant by washing in order to expose the polymer-modified surface. To increase the rate of surfactant removal, Waddell *et* *al.* (1995) suggested that the continuous, counter-current washing would be preferred. The powder is then dried in an oven at a suitable temperature to vaporize unreacted monomer and excess solvent, but not affect the properties of the polymer.

2.9 Silica

Silica fillers can be classified as either natural or synthetic, which comprise the crystalline and amorphous forms, respectively. Among the synthetic silicas, precipitated silica is manufactured with a wide range of particle sizes and specific surface areas for different applications. Reinforcing fillers account for 90% of the total annual silica usage in rubber (Hewitt, 2000). Two fundamental properties of silica that influence their uses in rubber compounds reinforcement are particle size and the extent of hydration (Mark *et al.*, 1994). The specific surface area of silica has shown to be a good indicator of silica performance as filler (Waddell *et al.*, 1995). In addition, dispersibility and freedom from dusting are important practical characteristics, which are related to silica manufacturing process. Suppression of gel during precipitation prevents formation of large particles, visible in mixed compounds, which contain un-milled silica.

The small size of silica particles provides the desired high tensile strength, tear strength, and abrasion resistance in rubber compounds. The actual size of the reinforcing unit, however, is not that of the individual particle, but that of an agglomerate (Mark *et al.*, 1994). Small particles produce small agglomerates while large particles produce large agglomerates. Although particle size is the influential property, which governs its performance in rubber, a more usual and convenient means of classification is surface area, expressed in square meters per gram (Mark *et al.*, 1994).

Precipitated silica is often used in the production of translucent and colored products. Admicellar polymerization modified silica in rubber compounding significantly reduces cure time, increases tensile strength, and lowers the compression set and heat buildup as compared to compounds made from unmodified silica (Waddell *et al.*, 1995). Precipitated silica is used in both tires and shoe soles applications. In combination with reinforcing carbon black, they improve tear resistance and adhesion to fabrics. Hydrated silica retards the cure time and requires the use of accelerator of addition of materials such as glycols or amines to promote curing (Katz and Milewski, 1987).

Silica is considered a polymer of silicic acid, in which the bulk structure is produced by interlinking SiO_4 tetrahedral. At the surface, the structure consists of siloxane groups (-Si-O-Si-) and one of the several forms of silanol groups (-Si-OH). The silanol groups make precipitated silica hydrophilic. Unmodified silica does not interact well with most polymers, requiring high amount of shear and energy to incorporate them evenly (Wagner, 1976).

Silane coupling agents are considered a unique and greatly effective method to increase silica-polymer interactions. The coupling agent is able to form new chemical bonds between the silica surface and the polymer. This process increases the production cost because of the high price of the reagents and synthesis process (Barlow, 1993). An alternative to replace silane coupling agent is the admicellar polymerization process (Waddell *et al.*, 1995; Thammathadanukul *et al.*, 1996; and Chinpan, 1996).

O'Haver *et al.* (1993) studied the ultra-thin polystyrene film on silica. Polystyrene was successfully polymerized into cetyltrimethylammoniumbromide (CTAB) as a cationic surfactant and using 2,2'-azobis-2-methylpropionitrile (AIBN) as water-insoluble initiator. Extraction and characterization of polymer formed were measured by using techniques including PA-FTIR and GPC. The molecular weight of polymer formed was investigated with respect to polymerization time. Polymeric films on porous silica tend to slightly increase particle size and decrease surface area of silica. The presence of polystyrene on the silica was shown by PA-FTIR spectra and the distribution of molecular weight of extracted polymer was studied by GPC.

Thammathadanukul *et al.* (1996) studied the comparison of rubber reinforcement using various surface modifications. All copolymer-treated silicas offered greater improvements in rubber performance than silica modified by a silane coupling agent. Moreover, the improvement of filler-elastomer interaction by in situ polymerization process depends on amount and type of polymer developed on the silica surface.

Chinpan (1996) studied the admicellar polymerization modified silica with butadiene and isoprene as co-polymer with styrene. The polymer can form bonds with the rubber compound during the curing process. Significant improvements in the rubber properties were achieved, and it was also found that using the lower loadings of monomer and surfactant provided the greater improvement.

Chaisirimahamorakot (2001) studied the modification of silica surface by admicellar polymerization process using cetyltrimethylammoniumbromide (CTAB) adsorbed on the surface, comonomers styrene and isoprene dissolving into the admicelle aggregates and 2,2'-azobis-2-methylpropionitrile (AIBN) as the water-insoluble initiator. The polymeric films can be produced successfully on the surface by polymerization in a continuous stirred tank reactor. The highest amount of polymer occurred with a loading of 5 g comonomers at 60 min residence time. The effect of comononer loading and polymerization time on the mechanical property improvements of modified-silica filled natural rubber was further studied by Nontasorn *et al.* (2005). It was found that 5 g of co-monomer loading at 30 min residence time provided the highest overall improvements. Kaitdamneon-ngam (2003) studied the effect of initiator and surfactant loading of the similar system. The result showed that 1.65 grams of AIBN initiator and 1.46 g of CTAB provided the highest of overall improvement as indicated by surface characterization results and rubber physical properties.

CHAPTER III
EXPERIMENTAL

3.1 Materials

Hexadecyltrimethylammonium bromide (CTAB) (98%), Triton X-100 (100%), styrene (99+%) and isoprene (98+%) were obtained from Fluka. Azobisisobutyronitrile (AIBN), water-insoluble initiator, was purchased from Aldrich Chemicals Company with 98% purity. Sodium hydroxide pellets with 99% purity were obtained from BDH Laboratory Supplies. Tetrahydrofuran (THF) was obtained from Lab-Scan Analytical Sciences. Anhydrous ethyl alcohol was purchased from ITALMAR Co., Ltd. Amorphous precipitated silica, Hi-Sil®255, was obtained from PPG-Siam Silica Co., Ltd.

3.2 Experimental Set-up

The continuous system mainly consisted of a stirred feed tank, a polymerization reactor and a product tank. The feed tank made of stainless steel was approximately 17 liters with a lid and baffles. The reactor vessel was a one-liter-borosilicate glass bottle with a screw cap. The product tank was a stainless steel bucket. Mixtures in the reactor and feed tanks were well mixed with a magnetic bar and mechanical stirrer, respectively. Reactor temperatures were maintained using a circulative heater, water bath, with 70±2 °C. Fluid flow rates were controlled using a Masterflex Digital console drive peristaltic pump with easy-load model 7518-60 head. The reactor system is shown in Figure 3.1.

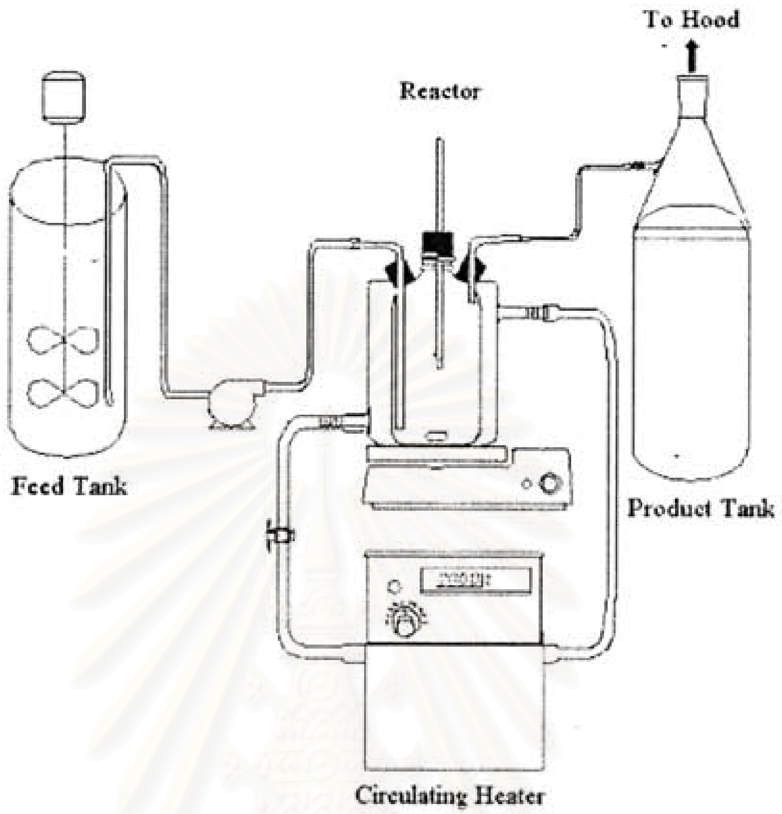


Figure 3.1 Continuous admicellar polymerization system.

3.3 Experimental Procedures

3.3.1 Adsorption Isotherm of surfactants onto Silica Hi-Sil®255

Adsorption experiments were conducted in 24-ml capped vials. Two -gram samples of silica were mixed with 20 ml of pH 8 CTAB solution at different concentrations. The samples were allowed to equilibrate at 30°C for 24 hr and then centrifuged at 2000 rpm for 10 min. The supernatant was taken and the CTAB concentration analyzed. The CTAB adsorption was calculated by the concentration difference method and the adsorption isotherm was plotted. Also the complete monolayer can be analyzed by a Zeta meter.

The same procedure was used for Triton X-100 and mixed surfactants experiments. The mixed surfactants consist of CTAB and Tritron X-100 at different molar ratios, 1:3, 1:1, 3:1.

From the adsorption isotherm, the critical micelle concentration (CMC) of each surfactant on Hi-Sil®255 can be determined as well as the feed concentration that would result in the system equilibrating just below the CMC. That is critical in preventing micelle formation and emulsion polymerization.

3.3.2 Surface Modification Procedure

The amorphous precipitated silica was modified using combinations of styrene and isoprene co-monomers at a 1:3 molar ratio, which was reported to be the suitable condition (????). The amount of the co-monomers fed into the feed tank was 5 g per kg of silica and the polymerization time was 30 min. The surface modification procedure was performed as follows: (1) Weighing one kg of silica, (2) CTAB was weighed, added to 12.5 liter of deionized water and stirred until the surfactant completely dissolved, (3) Adjusting the pH of the surfactant solution to 8 by adding sodium hydroxide solution, (4) Adding the silica to the surfactant solution in the feed tank, (5) Dissolving AIBN and 1:3 molar ratio of styrene and isoprene co-monomer into 99.7% ethanol at the ratio of 30 ml per 0.5 g of AIBN and then slowly adding this mixture to the feed tank, and (6) Allowing the system to equilibrate with constant stirring for 24 h, forming the feed stock.

The reactor was heated to 70°C in a water bath heated by a circulating heater to initiate the polymerization. Using the constant pump flow rate and the polymerization reaction was allowed to proceed at 30 min resident times. The reaction effluent, collected in the product tank, was allowed to settle and the supernatant was decanted. The modified silica was washed by counter current washing for five days with daily stirring or until the wash water no longer foamed on agitation. The silica was then dried at 110°C for 24 h and reground into a powder through a 120-mesh sieve.

The same procedure was applied for the modification with Tritron X-100 and the mixed surfactants.

3.3.3 Testing Procedure

The amount of adsorbed surfactants on Hi-Sil®255 was calculated by the concentration difference method using a mass balance of the concentration of surfactant in the aqueous feed solution and the equilibrium supernatant. The CTAB concentration was estimated by using a Total Organic Carbon analyzer (TOC-500A, Shimadzu), the Triton X-100 concentration was estimated by using a UV-VIS spectrometer (UV/VIS spectrometer Lamda 10 PERKIN ELMER) and the complete monolayer coverage was analyzed by a Zeta meter (ZETA-METER 3+).

The properties listed in Table 3.1 were determined for all modified silicas. Polymer extraction was performed by boiling 7 g of the modified silicas in refluxing tetrahydrofuran (THF) for 4 h. The slurry was cooled to room temperature, filtered and rinsed with hot THF. The polymer was precipitated by adding the filtrate to water. Extracted polymer was analyzed by a Fourier Transform Infrared spectrophotometer (FTIR). The silica aggregates observation was performed by Scanning Electron Microscope (SEM). Thermogravimetric Analyzer (TGA) was used to demonstrate the amount of copolymer developed on the modified silica. Moreover, nitrogen BET surface area and mean agglomerate particle size were also investigated.

Table 3.1 Properties tested and equipment used for silica analysis

PARAMETER	TECHNIQUE/INSTRUMENT
Specific surface area	BET N_2 surface area Autosorb-1 Quantachrome
Particle size	MALVERN Mastersizer X Ver. 2.15
Surface morphology	Scanning Electron Microscope (SEM) JEOL JSM-5200
Functional groups	Fourier Transform Infrared Spectroscopy (FTIR) BRUKER EQUINOX55/S
Amount of polymer formed	Thermogravimetric Analysis (TGA) Du Pont Instrument TGA 2950

The rubber compound formula is given in Table 3.2. The compound is a primary rubber formulation modified by eliminating poly(ethylene glycol), which is used to complex with the silanol groups on the surface of the silica to prevent them from reacting with the activator, and designed specifically for physical properties testing (Thammathadanukul *et al.*, 1996).

A two-stage mixing procedure was employed to prepare all compounds. In the first stage, the rubber, filler and other ingredients (except vulcanizing agent) were mixed in a Dispersion Kneader Machine. The vulcanizing agent was added to the master batch in the second mixing step using a two-roll mill. All compounds were cured at 150°C to a time corresponding to T_{90} as determined on the moving die rheometer.

Table 3.2 Rubber compound formula

INGREDIENT	PARTS PER HUNDRED RUBBER (PHR)
Natural Rubber (STR 5L)	100
Silica	40
Zinc Oxide	5
Stearic Acid	2
Paraffinic Oil	5
Antioxidant (6PPD)	1
Benzothiazyl Disulfide (MBTS)	1.8
Diphenyl Guanidine (DPG)	0.25
Sulphur	2

Standard test procedures as prescribed by ISO or ASTM were used for the determination of compound and vulcanized properties. The procedures are listed in Table 3.3.

Table 3.3 Rubber compound test methods

PROPERTY	METHOD	INSTRUMENT
Cure Time (Maximum Torque, dNm; T90, min)	ASTM D 2084-93	RheoTech/TechPRO
Tensile (Maximum Stress, MPa; Elongation to Break %; Modulus, MPa)	ASTM D 412-92	Instron Model 1011
Tear Strength, (N/mm)	ASTM D 2262-83	Lloyd Instruments LS 500
Abrasion Loss, (ml/kilocycles)	ISO 4649	Akron Abrasion Tester
Compression Set, %	ASTM D 395-89	Compression Set Tester MILANO/ITALIA
Resilience, %	ISO 4662	Wallace Dunlop Tripsometer
Hardness, Shore A	ASTM D 2240	Lever Loader Model 716

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Adsorption of Surfactants

4.1.1 Adsorption Isotherm of Surfactants on Silica Hi-Sil®255

Adsorption isotherms with various CTAB to Triton X-100 molar ratios, 0:1, 1:3, 1:1, 3:1 and 1:0, were obtained to determine the maximum adsorption concentration. The maximum surfactant adsorbed is determined when the surfactant is completely adsorbed on the silica surface in the bilayer structure. With a further increase in surfactant concentration beyond its CMC, the excess surfactants will form multilayer or even micellar structure. From the adsorption isotherm results, in our previous works relating to the bilayer adsorption structure the surfactant concentration, slightly lower than the maximum surfactant concentration was used to investigate the improvement of the properties of modified silicas for rubber compounds.

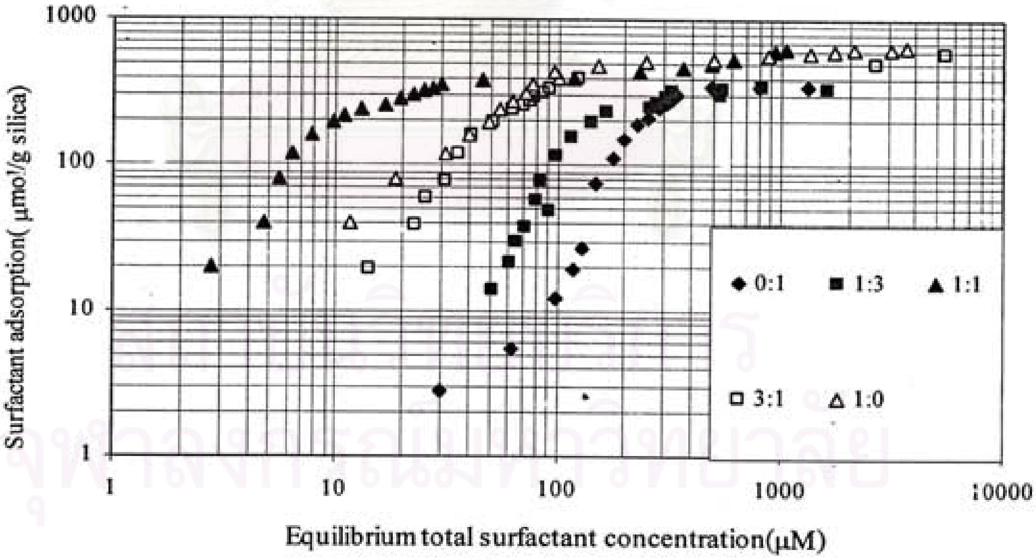


Figure 4.1 Adsorption isotherm of surfactants on silica Hi-Sil® 255 at pH 8 and 30 °C at various CTAB : Triton X-100 molar ratios.

Figure 4.1 shows surfactant adsorption at the feed pH of 8 and 30°C on Hi-Sil®255. Pure CTAB (1:0 molar ratio of CTAB:Triton X-100) shows the maximum adsorption, 600 μmol of CTAB per g of silica. The maximum total surfactant adsorption was found to decrease with decreasing the molar ratio of CTAB to Triton X-100. The minimum adsorption concentration at 300 μmol of Triton X-100 per g of silica was obtained with pure Triton X-100. Interestingly, at a molar ratio of CTAB to Triton X-100 of 1:1, the maximum adsorption of total surfactant on the silica surface is almost as high as that of the pure CTAB system and it also gives the lowest equilibrium concentration of total surfactant shown in Figure 4.1. The results imply that the 1:1 molar ratio of CTAB : Triton X-100 provides both the best packed admicelles and micelles. The selected surfactant concentrations used to prepare the modified silica was 290, 320, 390, 510 and 600 μmols per gram of silica for ratios of CTAB to Triton X-100, 0:1, 1:3, 1:1, 3:1 and 1:0, respectively.

4.1.2 Molar Ratios of Surfactant Adsorbed on Silica Hi-Sil®255

The total surfactant concentrations before and after adsorption were measured using a Total Organic Carbon (TOC) analyzer. The total concentration of Triton X-100 was determined by a UV VIS spectrometer. Then, the molar ratio of CTAB to Triton X-100 could be calculated. It was found that the molar ratio of CTAB to Triton X-100 adsorbed on the silica surface is very much the same as that of the initial ratio of mixed surfactants in the solution (Figure 4.2.).

4.1.3 Adsorption Concentration in Monolayer Region

Since it is very difficult to identify any monolayer coverage accurately from the adsorption isotherm, the amount of total surfactants adsorbed in the monolayer structure on the silica surface (μmol per g of silica) was verified by a Zeta meter. Due to the negatively charged silica surface, the adsorption of the positive head group of CTAB on the silica surface results in the depression of the negative charges. Therefore, the neutral surface is obtained theoretically when CTAB completely covers the surface of silica in the monolayer structure. Figure 4.3 shows Zeta potential of the silica surface as a function of amount of total surfactants adsorbed at different molar ratios of CTAB to Triton X-100. For pure CTAB, the adsorption of surfactant of 200 μmol/g silica was obtained for the monolayer coverage. A decrease in the molar ratio of CTAB to Triton X-100 resulted in decreasing the total surfactants adsorbed for the monolayer coverage structures. For the monolayer structures at 1:3, 1:1, 3:1 and 1:0 molar ratios of CTAB to Triton X-100, the total surfactants adsorbed on the surface of silica are 240, 200, 160 and 200 μmol per g of silica, respectively. However, in the case of pure Triton X-100 as shown in Figure 4.3, the monolayer structure cannot be verified by the ZETA potential measurement because the negative surface of silica cannot be neutralized by Triton X-100, which is known as nonionic surfactant.

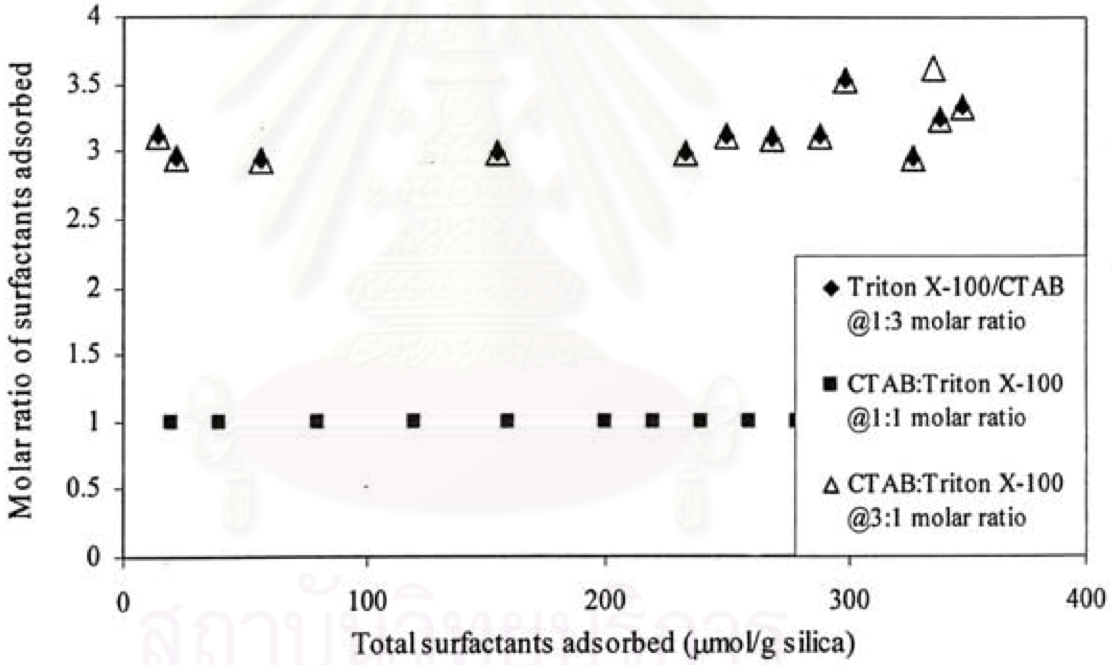


Figure 4.2 Molar ratios of surfactant adsorbed on silica Hi-Sil®255 at various CTAB : Triton X-100 molar ratios and different total surfactants adsorbed.

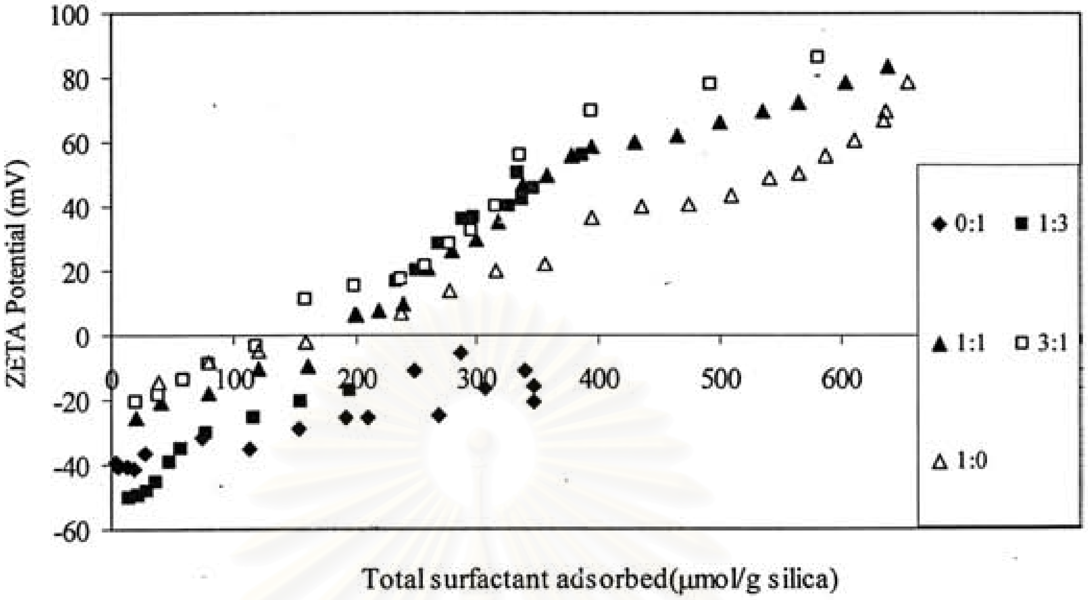


Figure 4.3 Charge on silica surface on different total surfactants adsorbed at various CTAB : Triton X-100 molar ratios.

4.2 Surface Characterization of Modified Silicas

For the polymerization experiments, both monolayers and bilayers of surfactants adsorbed were selected to investigate their effects on the properties of the polystyrene-isoprene films formed on the silica surface at different molar ratios of CTAB to Triton X-100. For the case of the monolayer structure with any given molar ratio of CTAB to Triton X-100, the amount of total surfactants adsorbed at Zeta potential of zero obtained from Figure 4.3 was used to determine the equilibrium surfactants concentration from the adsorption isotherm plot shown in Figure 4.3. A total amount of surfactants required is the summation of these two values to be used to prepare the feed solution. For the bilayer structure, the CMC as the equilibrium surfactants concentration and the maximum adsorption were used to calculate the total amount of surfactants, instead.

4.2.1 Morphology of Modified Silicas

The scanning electron micrographs (SEM) of the modified and unmodified silicas with both monolayer and bilayer structures at various molar ratios of CTAB to Triton X-100 are shown in Figures 4.4. All modified silica micrographs show obviously increases in the particle size compared with that of the unmodified one because of the formation of the poly-styrene-isoprene film on the silica particles as well as the agglomeration during the polymerization. Interestingly, the particle surface becomes much smoother after the modification process and the modified silicas with the bilayer structures appear much more spherical and smoother compared to those with monolayer structures.

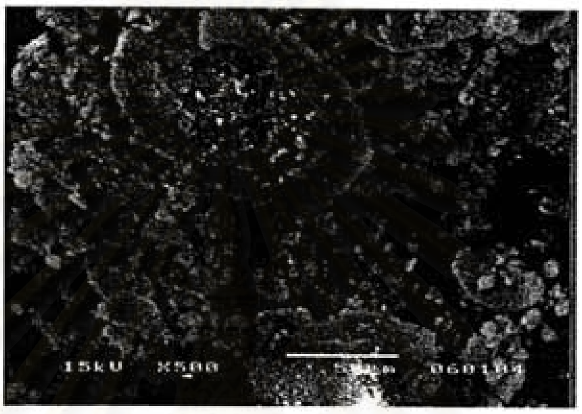


Figure 4.4 Scanning electron micrograph of unmodified silica, Hi-Sil®255.

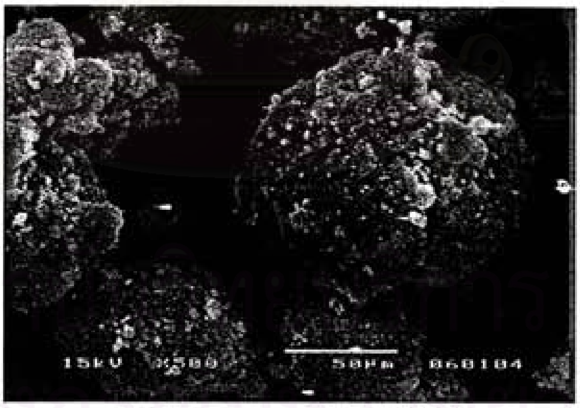


Figure 4.5 Scanning electron micrograph of the modified silica surface in monolayer with 1:3 CTAB: Triton X-100 molar ratio.

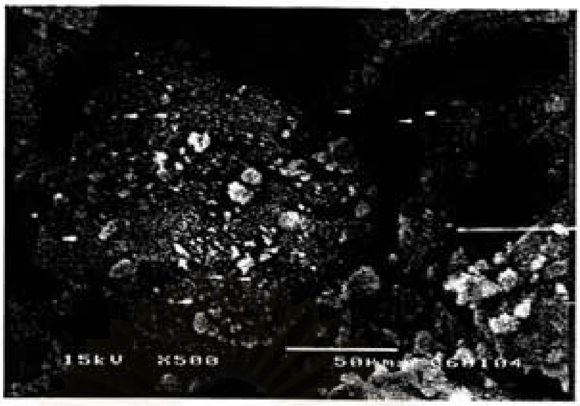


Figure 4.6 Scanning electron micrograph of the modified silica surface in monolayer with 1:1 CTAB : Triton X-100 molar ratio.

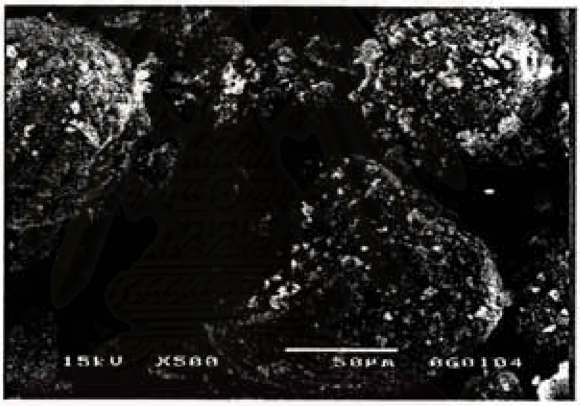


Figure 4.7 Scanning electron micrograph of the modified silica surface in monolayer with 3:1 CTAB : Triton X-100 molar ratio.

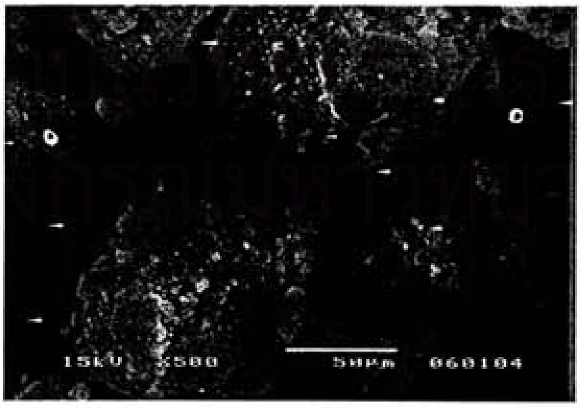


Figure 4.8 Scanning electron micrograph of the modified silica surface in monolayer with 1:0 CTAB : Triton X-100 molar ratio.

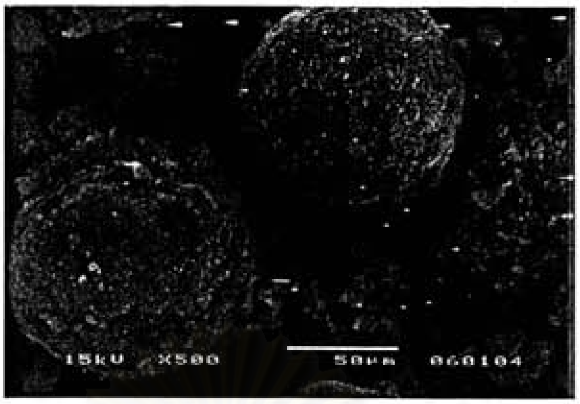


Figure 4.9 Scanning electron micrograph of the modified silica surface in bilayer with 0:1 CTAB : Triton X-100 molar ratio.

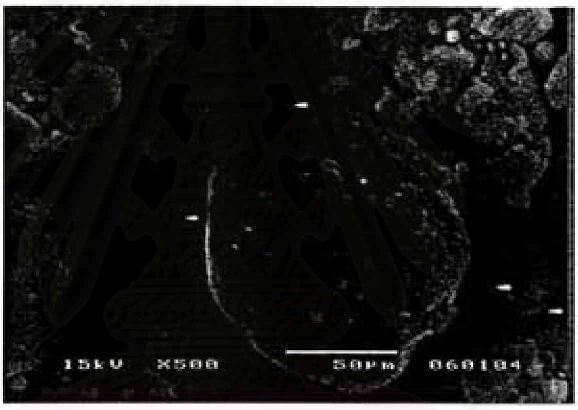


Figure 4.10 Scanning electron micrograph of the modified silica surface in bilayer with 1:3 CTAB : Triton X-100 molar ratio.

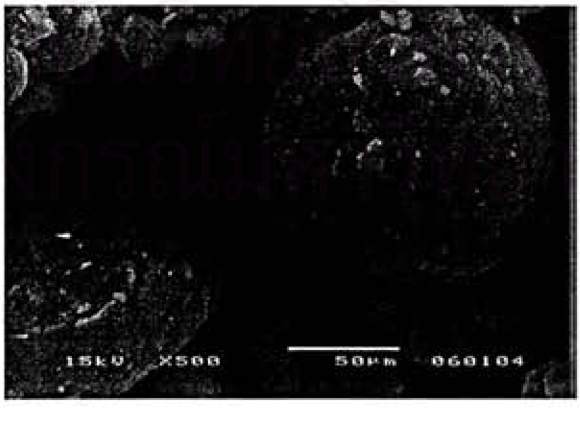


Figure 4.11 Scanning electron micrograph of the modified silica surface in bilayer with 1:1 CTAB : Triton X-100 molar ratio.

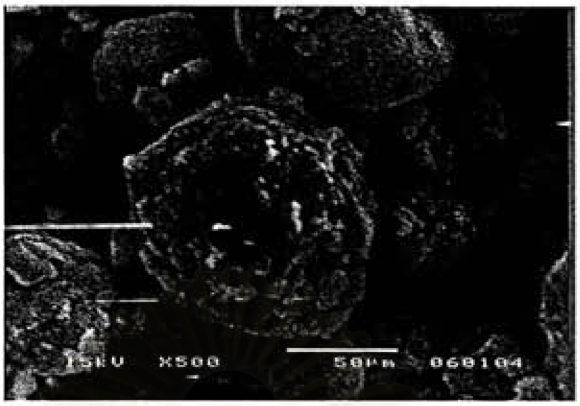


Figure 4.12 Scanning electron micrograph of the modified silica surface in bilayer with 3:1 CTAB : Triton X-100 molar ratio.

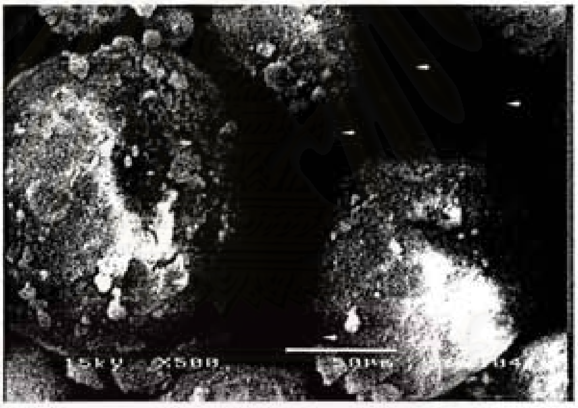


Figure 4.13 Scanning electron micrograph of the modified silica surface in bilayer with 1:0 CTAB : Triton X-100 molar ratio.

4.2.2 BET Surface Area

The surface areas of modified and unmodified silicas were determined by a BET surface area analyzer. The silica surface area is reduced significantly after the modification as shown in Figure 4.14. The modified silica surface with the bilayer structure has slightly lower surface area than that with the monolayer structure. For either monolayer or bilayer structure for the modification, the surface area of the modified silica is independent on the molar ratio of CTAB to Triton X-100 indicating the amount of poly(styrene-isoprene) may be the same.

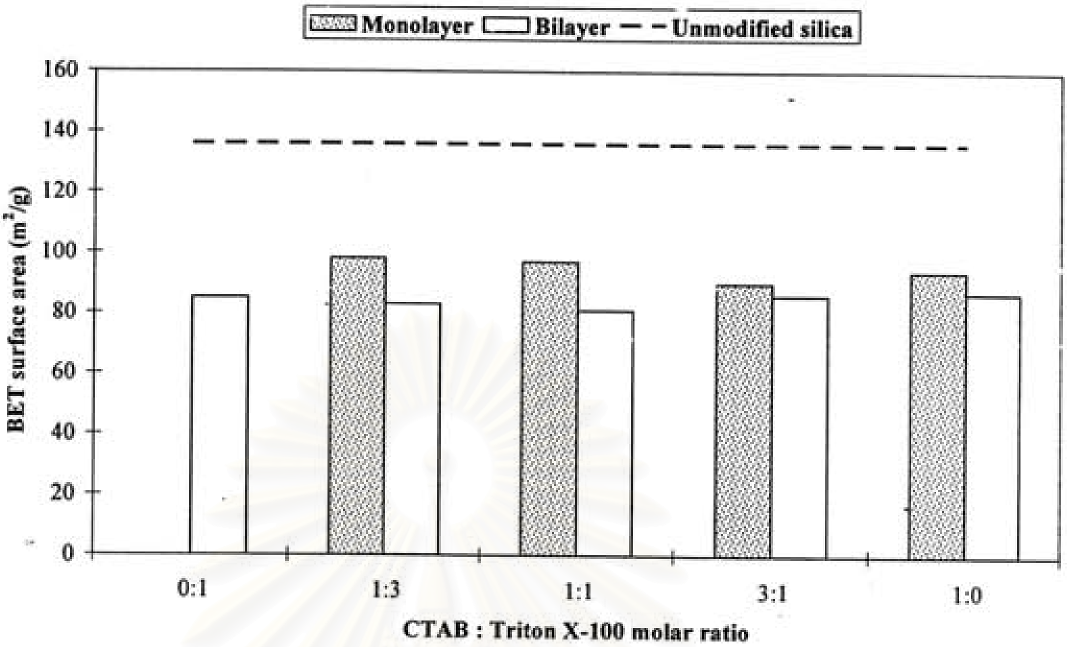


Figure 4.14 BET surface areas of modified and unmodified silicas.

4.2.3 Mean Agglomerate Particle Size

An increase in the mean agglomerate particle size of the modified silicas may simply be attributed to the subsequent polymerization step to form the organic polymer-layer on the silica surface. Figure 4.15 shows the effect of the molar ratio of CTAB to Triton X-100 on the mean agglomerate particle size after the modification. An increase in the mean agglomerate particle size of all modified silicas may be due to the development of polymer bridges between silica particles (Chaisirimahamorakot, 2001). For any given molar ratio of CTAB to Triton X-100, the mean agglomerate particle size of the modified silica with the bilayer structure is larger than that with the monolayer structure.

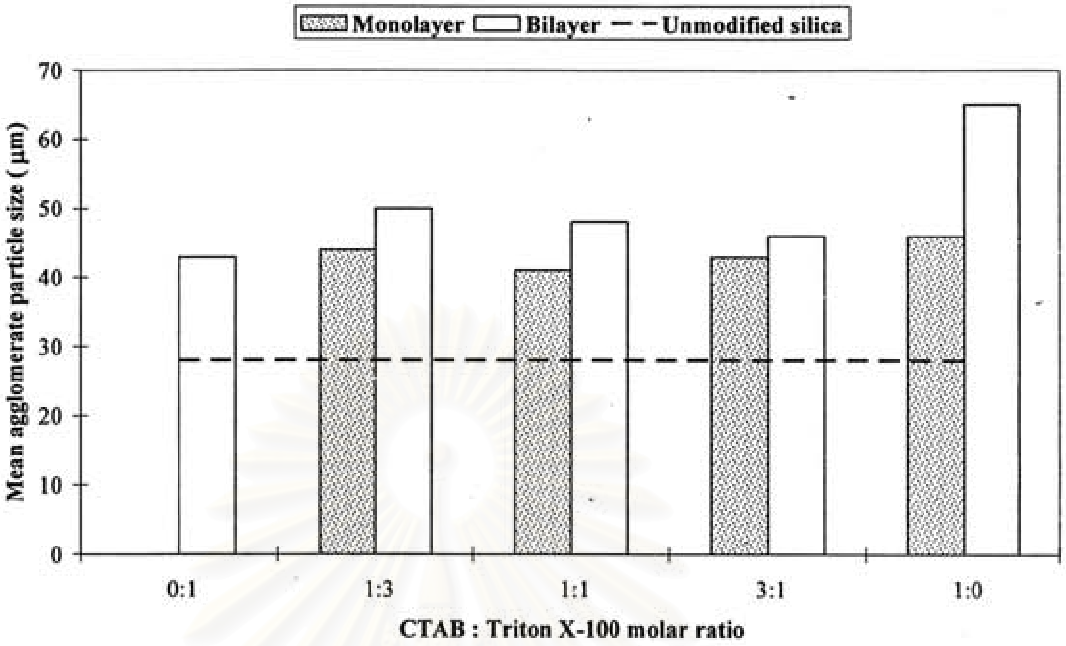


Figure 4.15 Mean agglomerate particle size of modified and unmodified silicas at different molar ratios of CTAB : Triton X-100.

4.2.4 Verification of the Existence of Poly(styrene-isoprene)

All samples were examined by TGA in order to verify the existence of poly(styrene-isoprene) forming on the silica surfaces. The water loss from the unmodified silica below 150°C is shown in Figure 4.16. Figure 4.17 shows the decomposition of pure CTAB between 200 to 300°C. Figure 4.18 shows the decomposition of Triton X-100 between 400 to 450°C. Interestingly, the decomposition of CTAB adsorbed onto the silica occurs in two steps; the first step from 170 to 300°C and the second step is 300 to 450 °C (Figure 4.19.). The second peak of the weight loss may result from the stronger bonding between silica and CTAB molecules.

Samples of modified silicas were dissolved with THF to extract the poly(styrene-isoprene) onto silica for TGA analysis. The decomposition of the poly(styrene-isoprene) sample appears in the temperature range from 350 to 480°C as shown in Figure 4.20. Poly(styrene-isoprene) was decomposed from the admicellar polymerization modified silica as shown in Figure 4.21. Figure 4.19 evidently shows the decomposition of CTAB taking place between 200 to 280°C and 300 to 450°C while the polymer starts from 280 to 400°C. The TGA results of all modified silicas with both monolayer and bilayer structured at different molar ratios of CTAB to Triton X-100 are shown in Figures 4.22. – 4.30.

All modified silicas have two dominant peaks at two temperature ranges of 200°-280°C and 350°-450°C. The first peak corresponds to the decomposition of CTAB while the second peak exhibits the decomposition of CTAB, poly(styrene-isoprene) and Triton X-100.

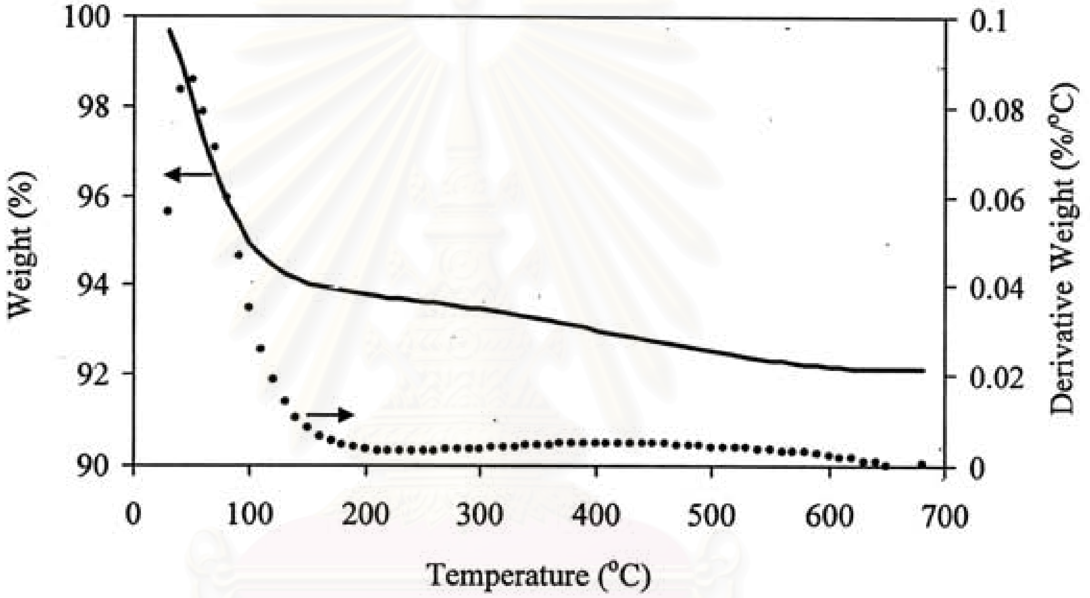


Figure 4.16 TGA results of unmodified silica Hi-Sil®255.

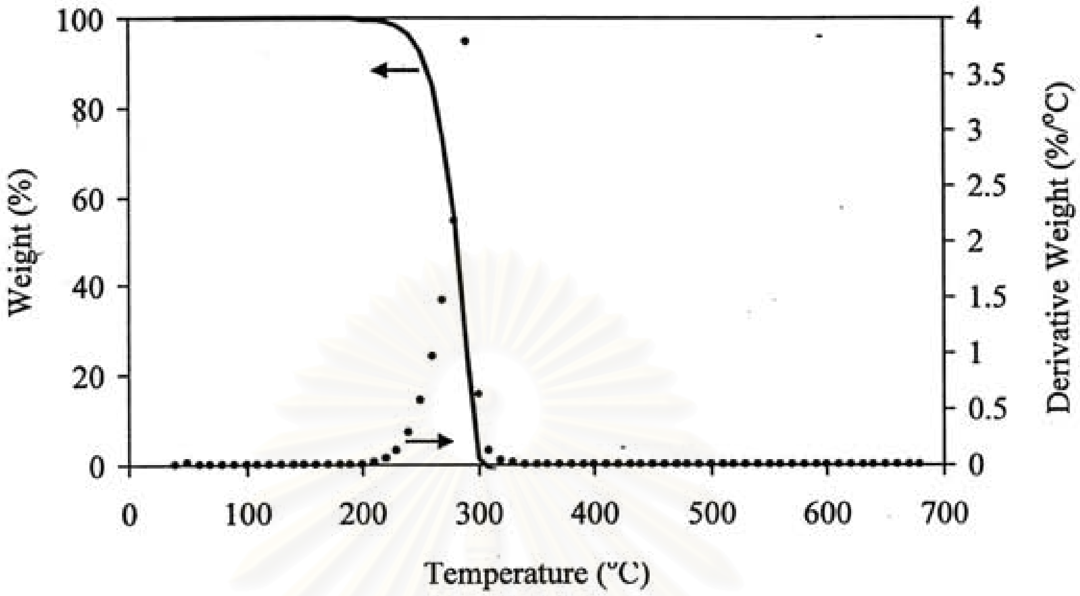


Figure 4.17 TGA results of CTAB.

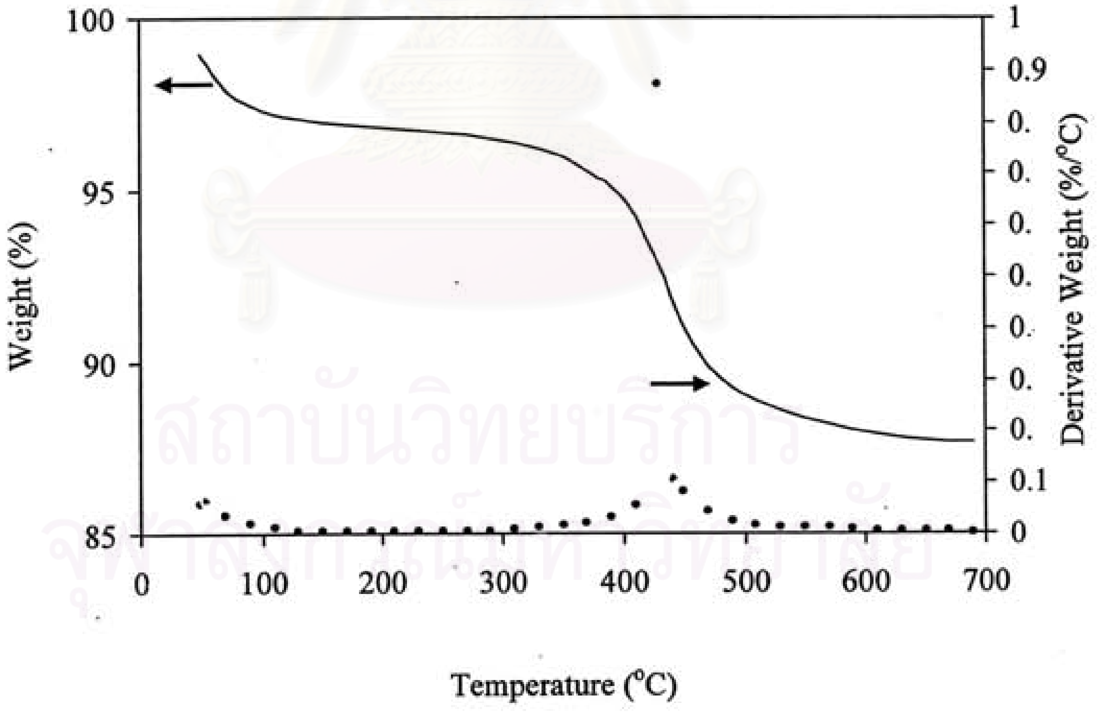


Figure 4.18 TGA results of Triton X-100.

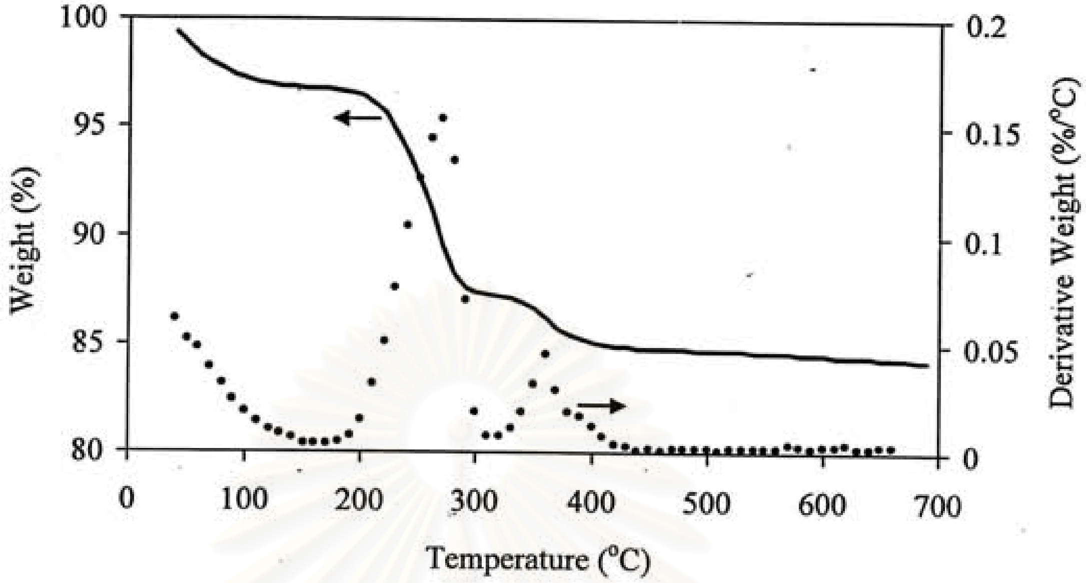


Figure 4.19 TGA results of silica Hi-Sil®255 adsorbed with CTAB (Chaisirimahamorakot, 2001).

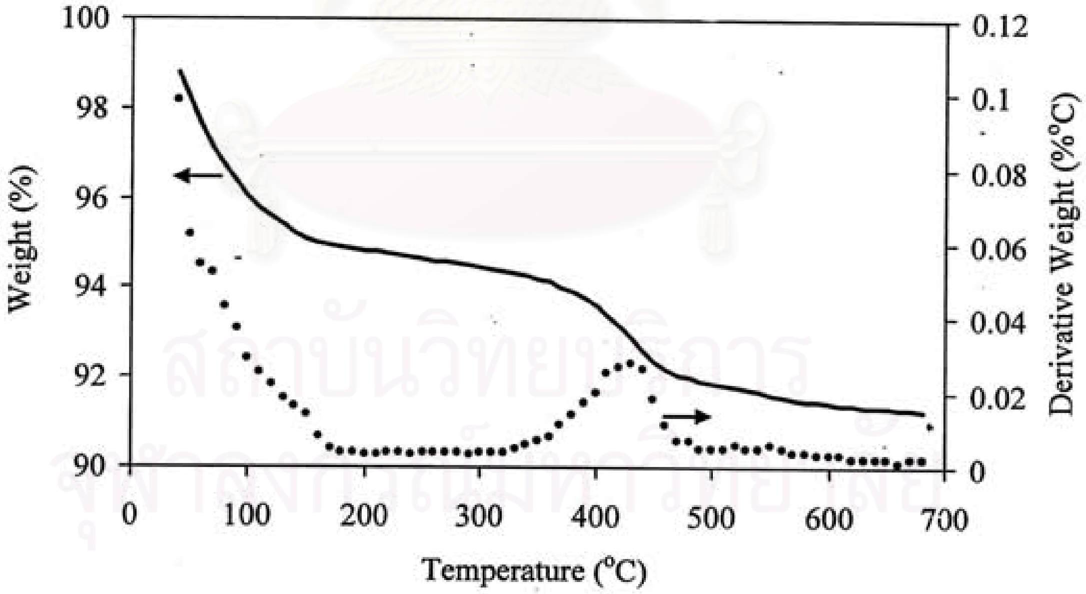


Figure 4.20 TGA results of silica Hi-Sil®255 adsorbed with poly(styrene-isoprene) extracted from the modified silica (Chaisirimahamorakot, 2001).

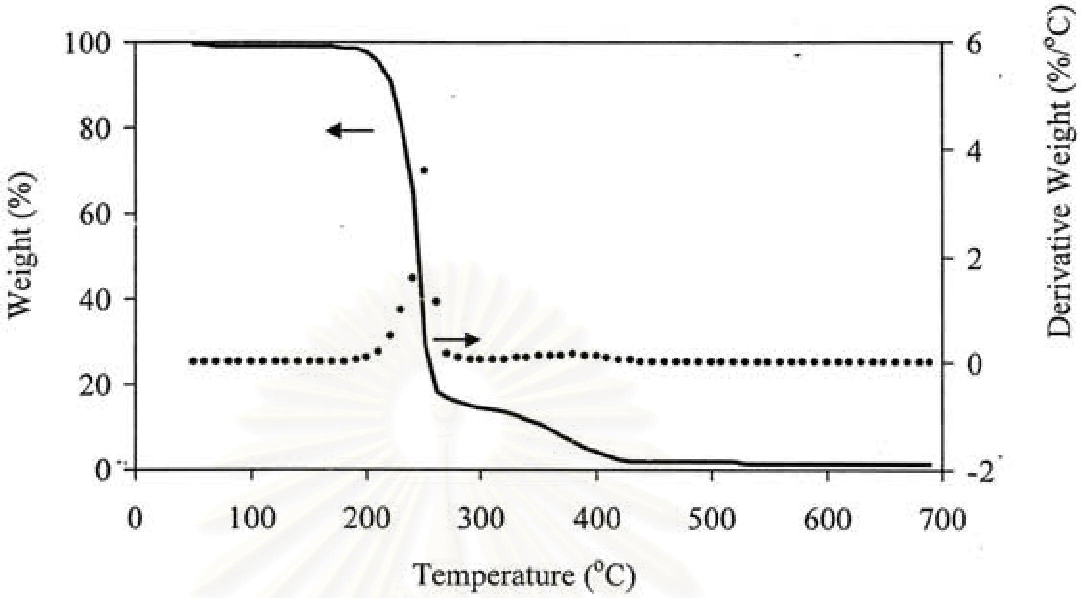


Figure 4.21 TGA results of poly(styrene-isoprene) polymerized in CTAB (Chaisirimahamorakot, 2001).

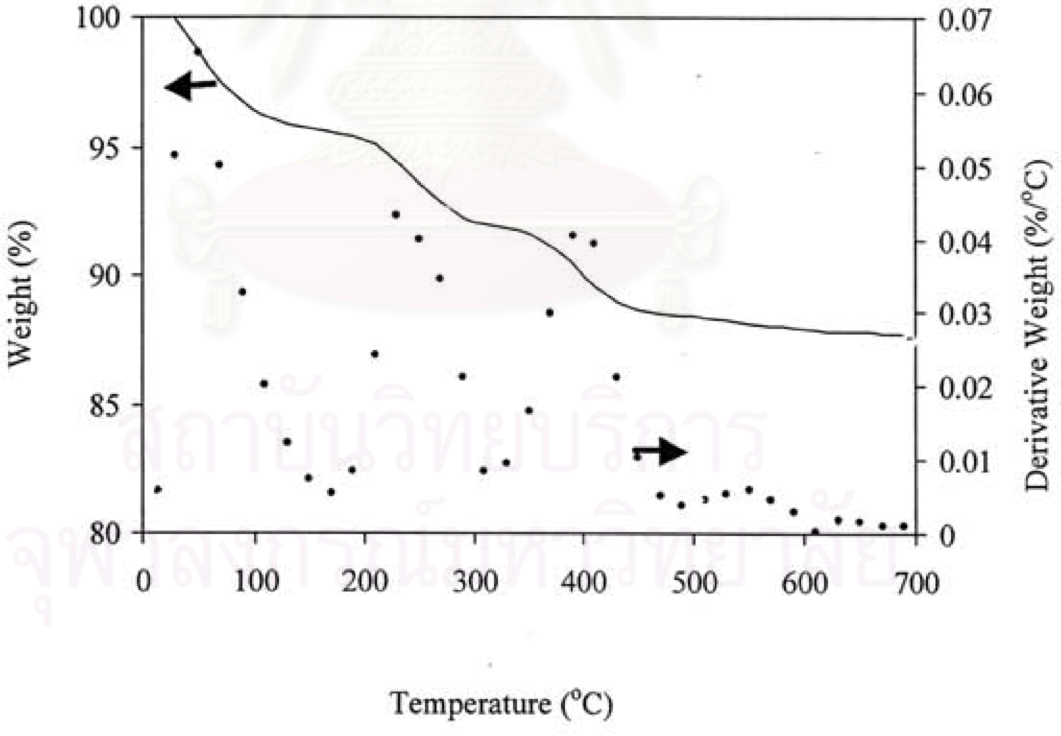


Figure 4.22 TGA results of the modified silica surface in monolayer with 1:0 CTAB: Triton X-100 molar ratio.

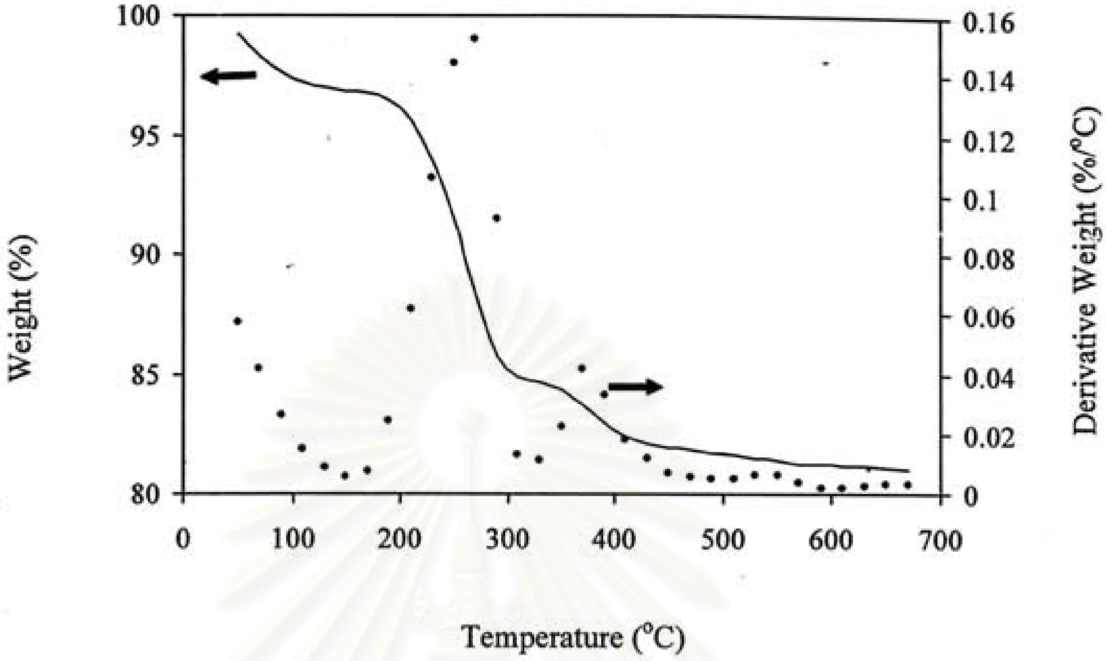


Figure 4.23 TGA results of the modified silica surface in bilayer with 1:0 CTAB: Triton X-100 molar ratio.

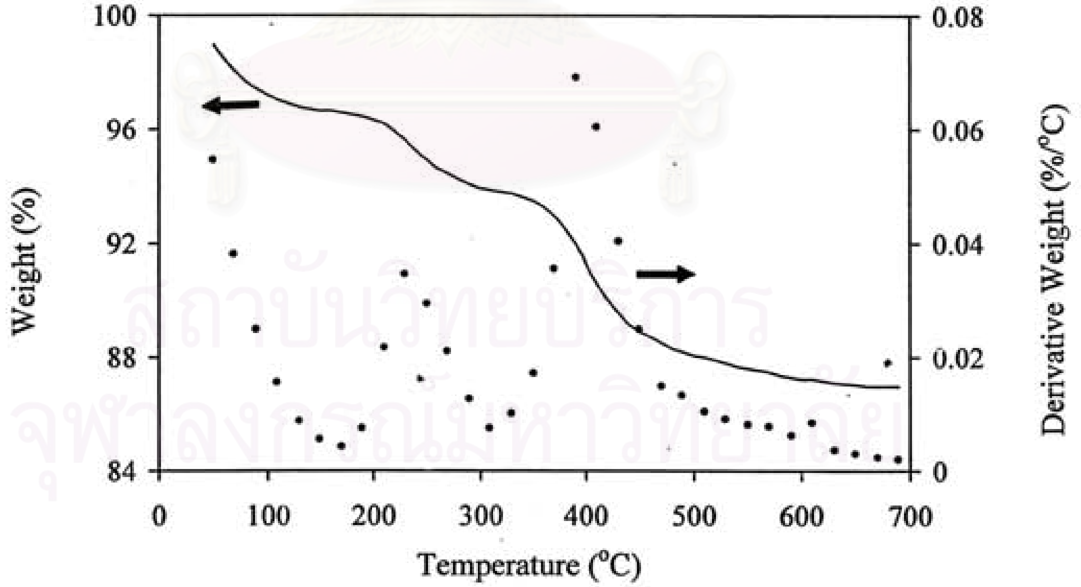


Figure 4.24 TGA results of the modified silica surface in monolayer with 1:3 CTAB: Triton X-100 molar ratio.

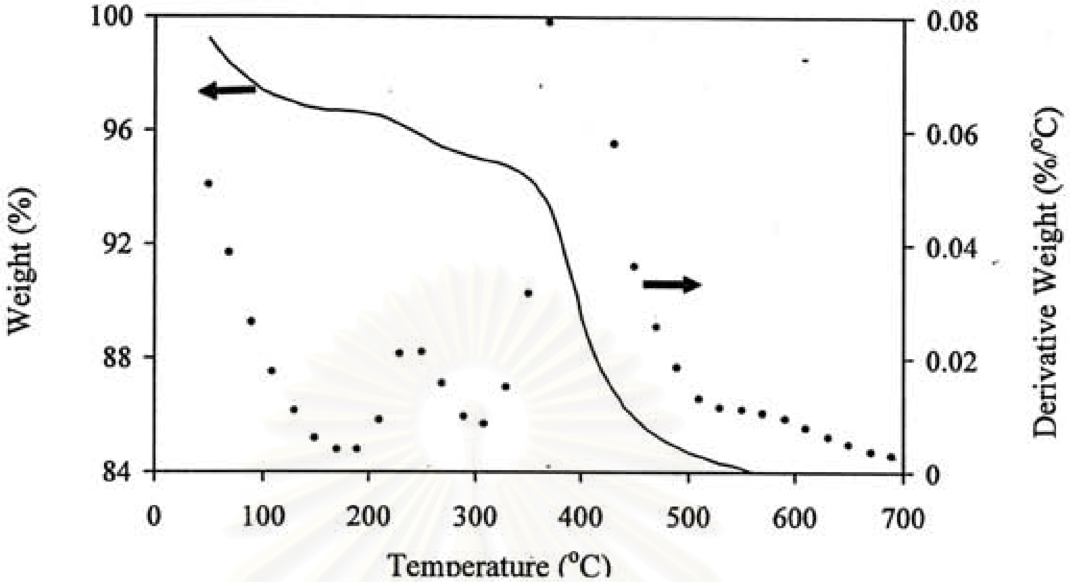


Figure 4.25 TGA results of the modified silica surface in bilayer with 1:3 CTAB: Triton X-100 molar ratio.

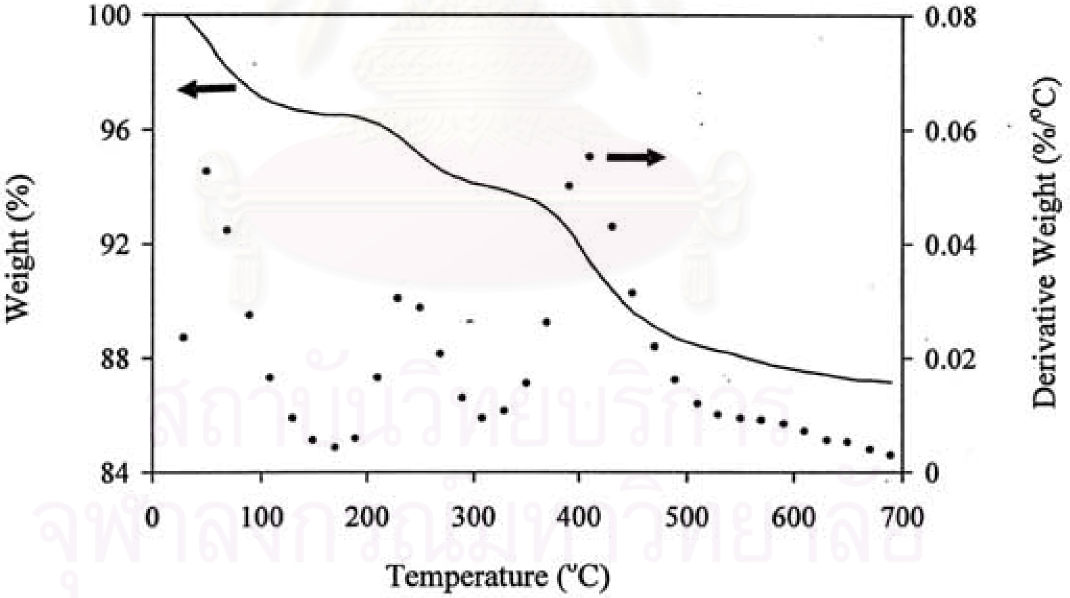


Figure 4.26 TGA results of the modified silica surface in monolayer with 1:1 CTAB: Triton X-100 molar ratio.

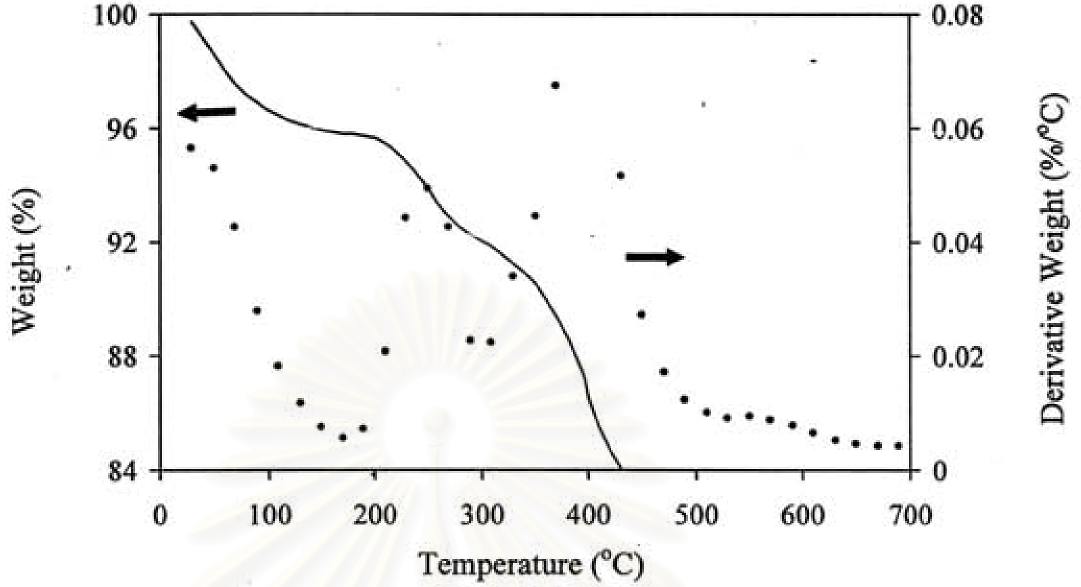


Figure 4.27 TGA results of the modified silica surface in bilayer with 1:1 CTAB: Triton X-100 molar ratio.

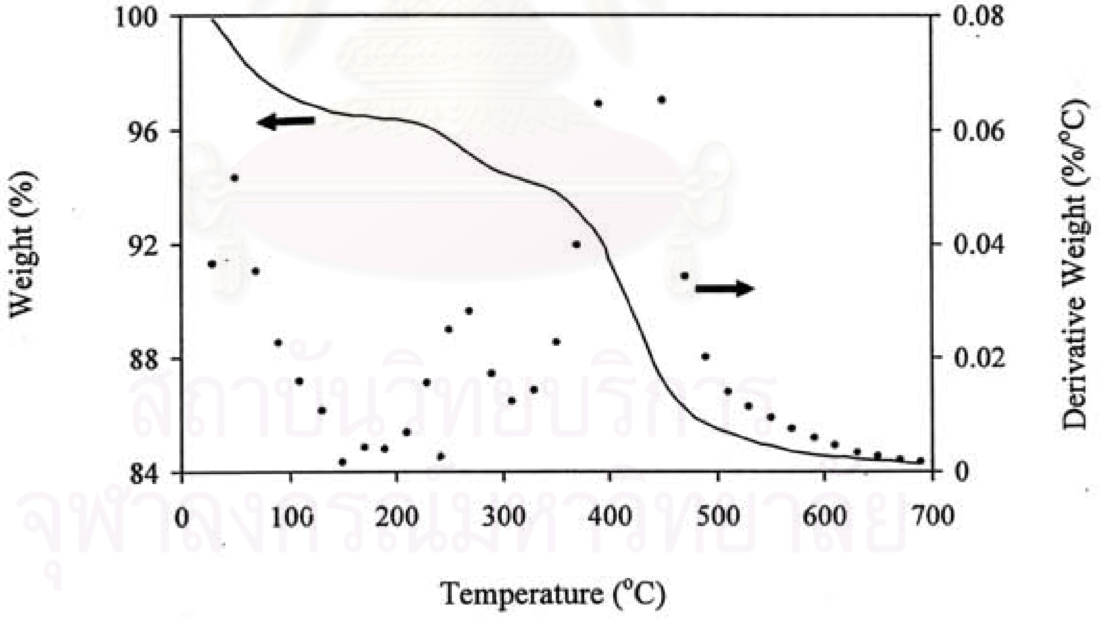


Figure 4.28 TGA results of the modified silica surface in monolayer with 3:1 CTAB: Triton X-100 molar ratio.

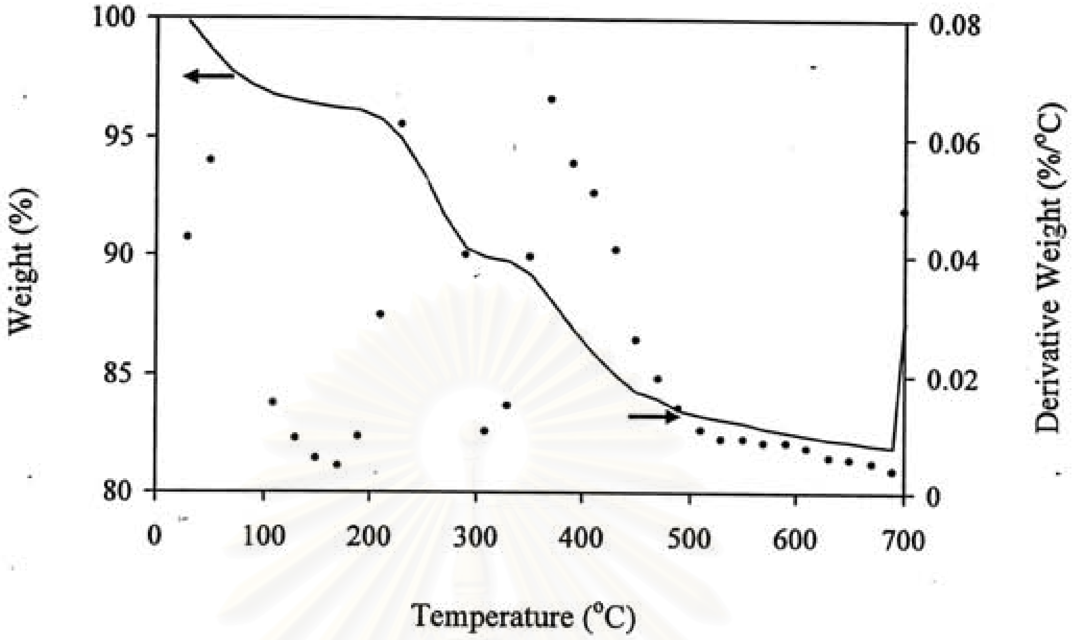


Figure 4.29 TGA results of the modified silica surface in bilayer with 3:1 CTAB: Triton X-100 molar ratio.

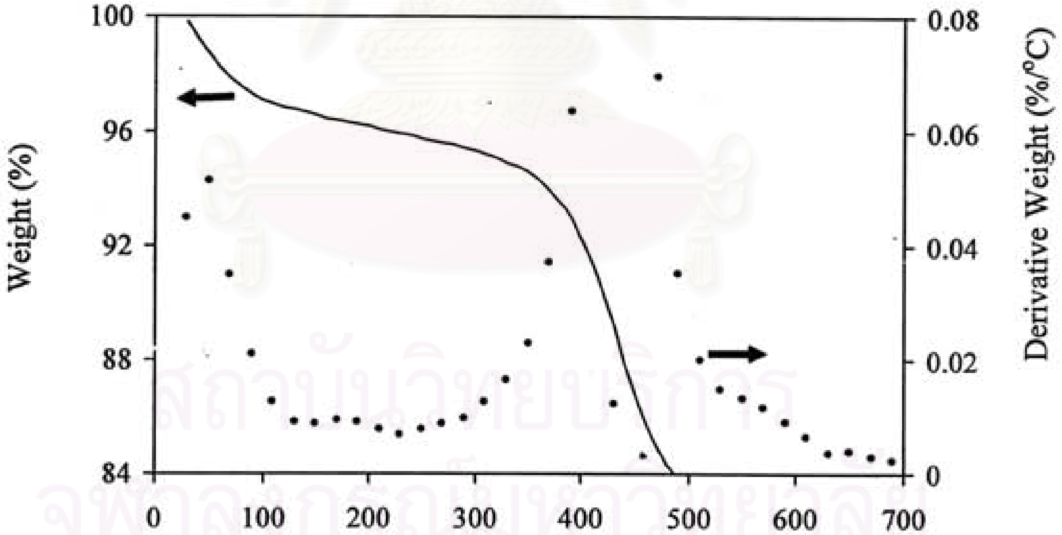


Figure 4.30 TGA results of the modified silica surface in bilayer with 0:1 CTAB: Triton X-100 molar ratio.

4.3 Rubber Compound Physical Properties

The effects of the molar ratio of CTAB to Triton X-100 as well as the surfactant adsorption structures on rubber compound physical properties were investigated systematically. As seen from Figure 4.31, the adsorption structures of mixed surfactants exhibit an insignificant effect on the cure time. Both monolayer and bilayer structures of various molar ratios of CTAB to Triton X-100 from 1:3 to 3:1 give the cure time of about 5.3 min, which is in the same range as the previous result with the bilayer structure (Thammathadanukul *et al.*, 1996).

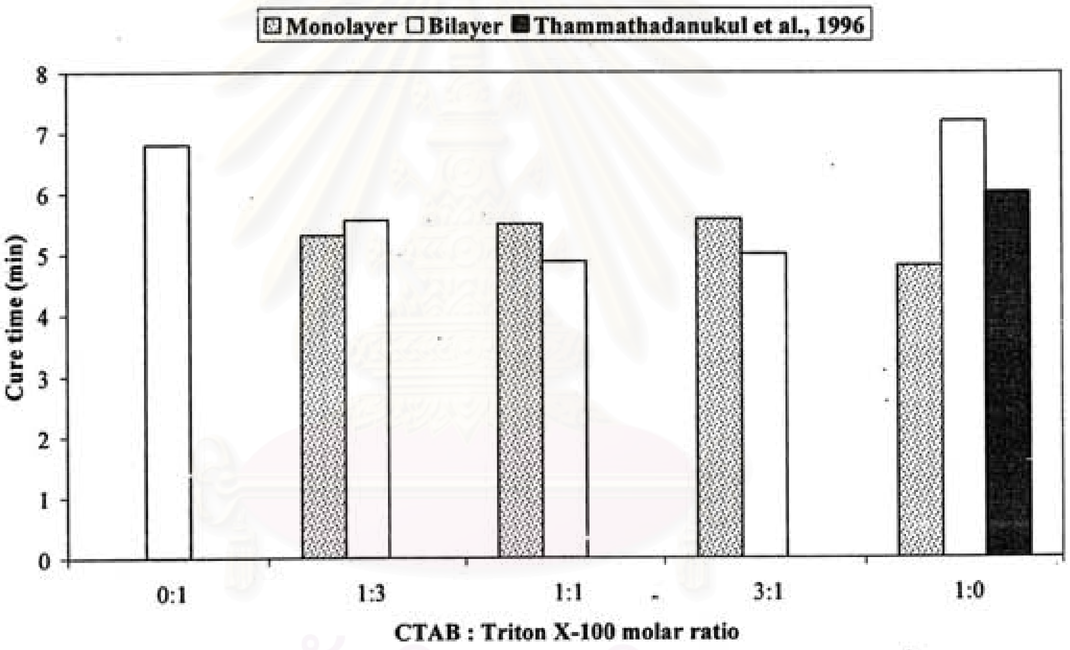


Figure 4.31 Cure time of modified silicas prepared with different CTAB to Triton X-100 molar ratios and different adsorption structures.

Several physical properties of rubber compounding with the modified silicas such as compression set, resilience, tear, hardness and abrasion, are shown in Figures 4.32 - 4.40. The results show that various molar ratios of CTAB to Triton X-100 affect most physical properties. Type of surfactant adsorption structures on the silica surface also affects the physical properties of the rubber compound. For example, the bilayer structure yields better compression set and abrasion than those derived from the monolayer structure. On the other hand, the hardness of composite rubber modified by the monolayer structure is better than that of the bilayer structure silica, as shown in Figures 4.32 - 4.34. Results from previous work using batch type reactor in the modification (Thammathadanukul *et al.*, 1996) are also included in most physical properties.

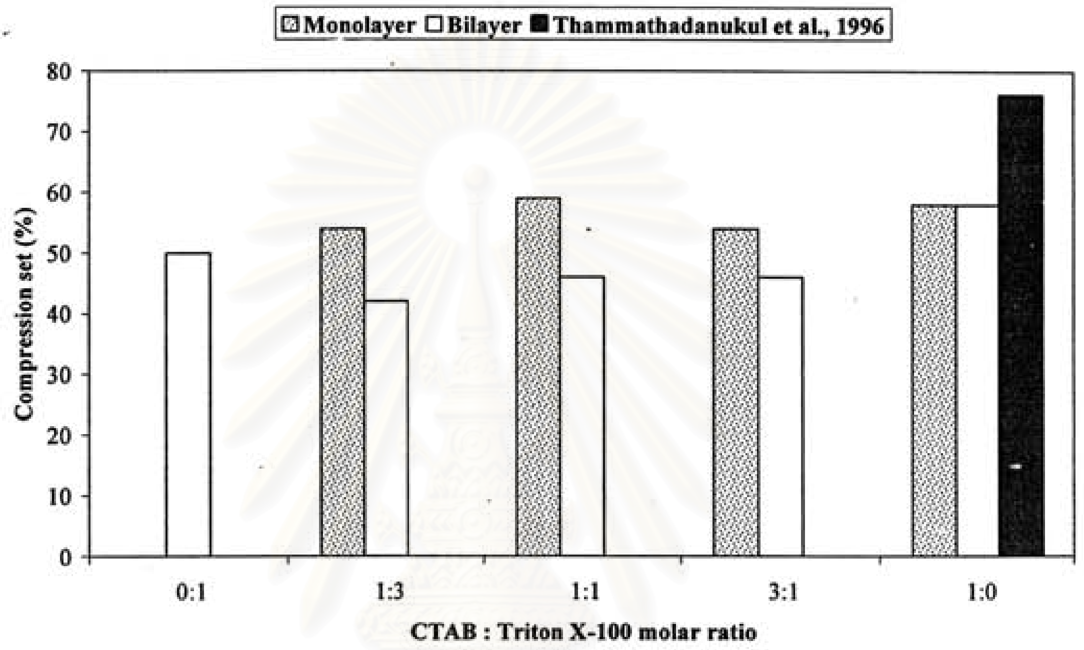


Figure 4.32 Compression set of rubber compounds with different modified silicas.

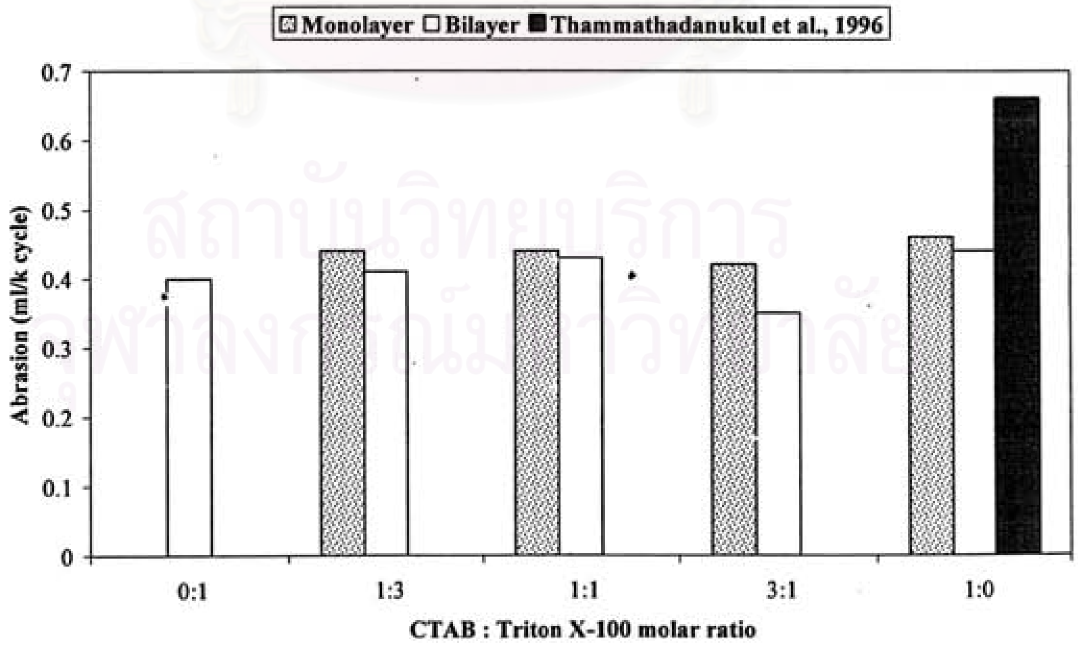


Figure 4.33 Abrasion set of rubber compounds with different modified silicas.

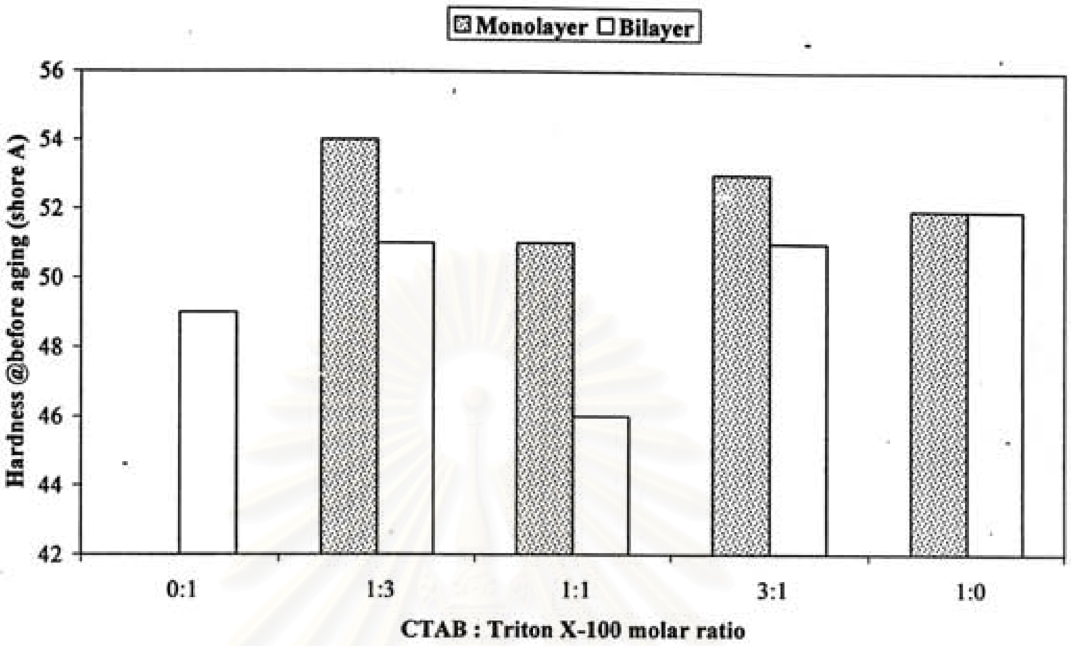


Figure 4.34 Hardness@before aging of rubber compounds with different modified silicas.

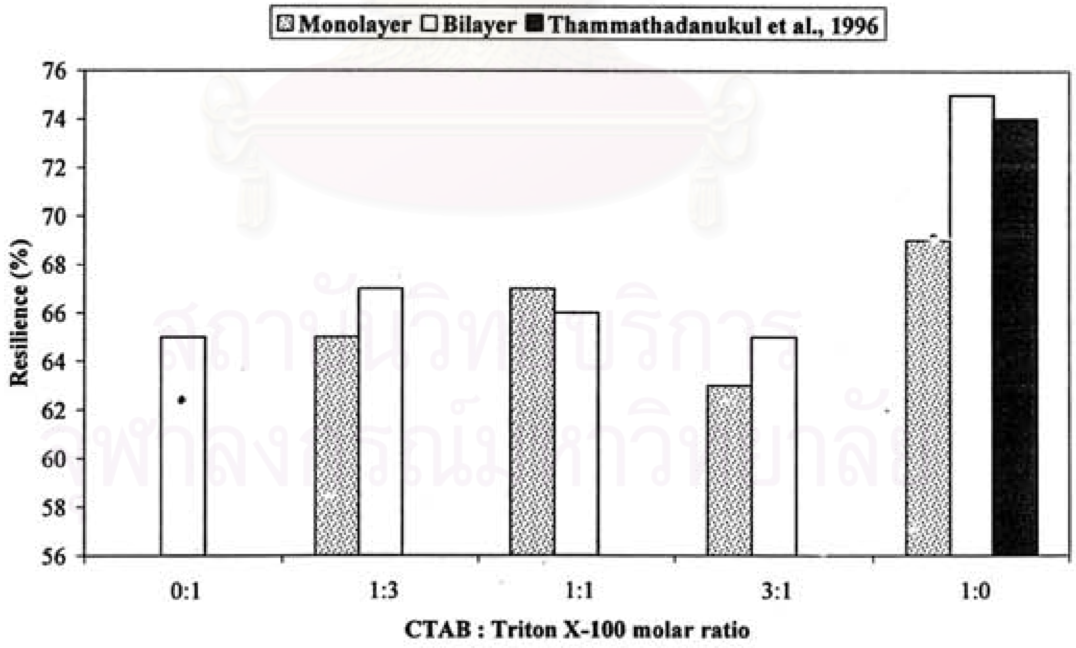


Figure 4.35 Resilience of rubber compounds with different modified silicas.

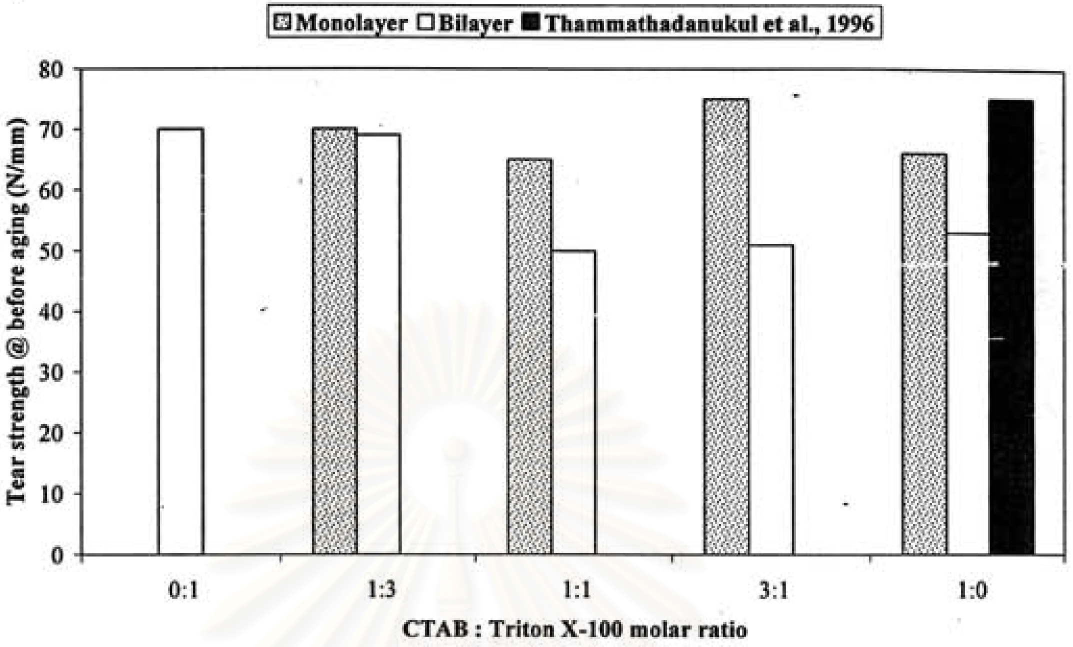


Figure 4.36 Tear strength@before aging of rubber compounds with different modified silicas.

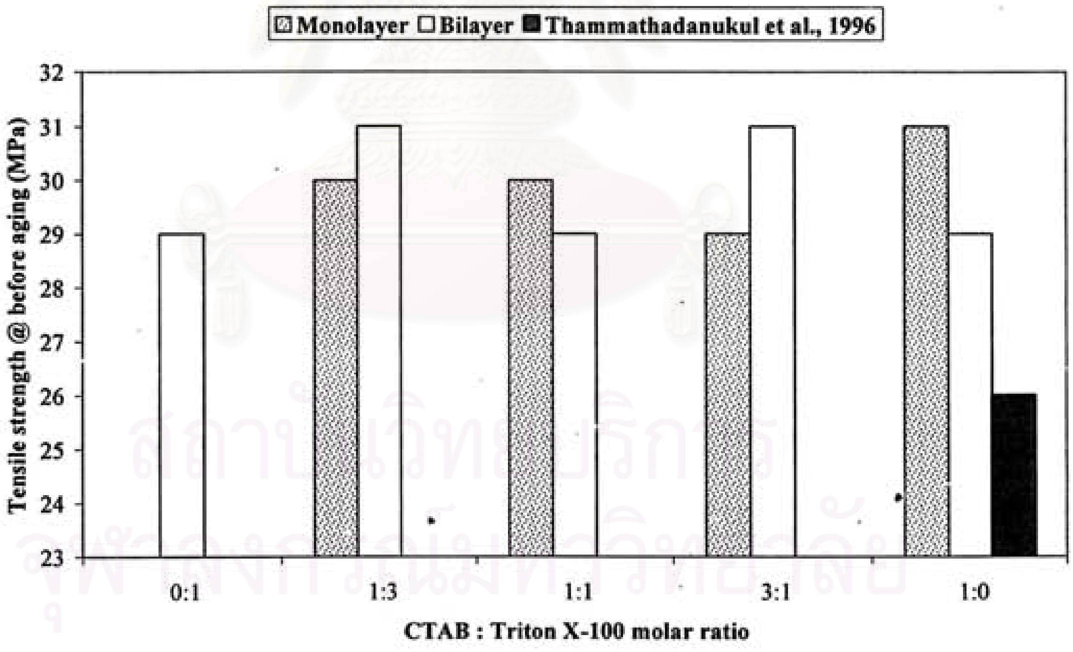


Figure 4.37 Tensile strength@before aging of rubber compounds with different modified silicas.

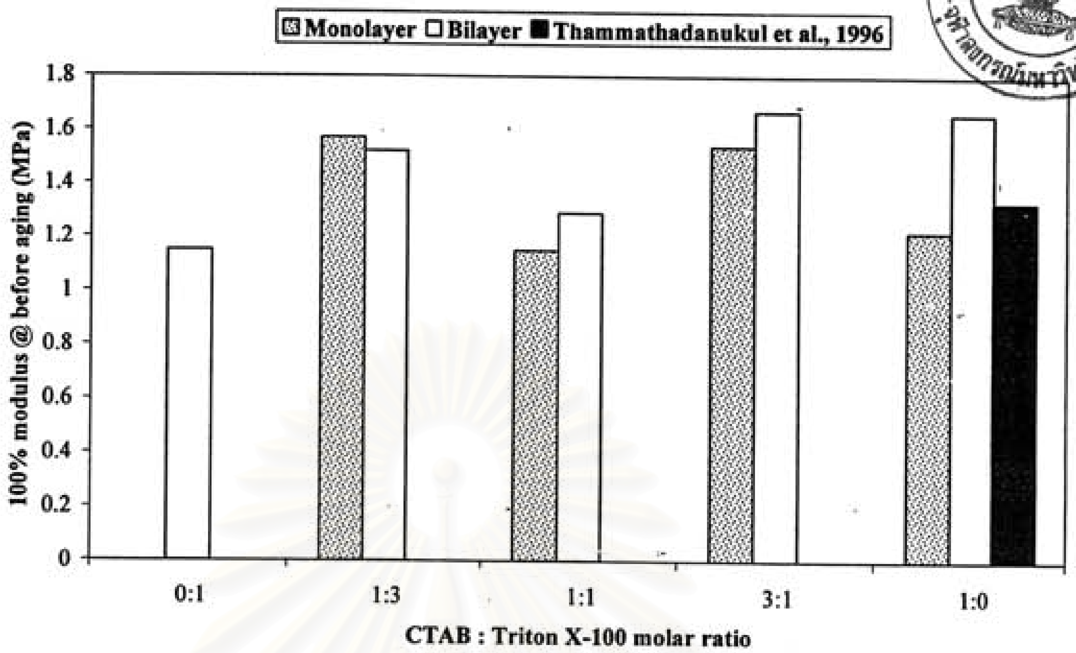


Figure 4.38 100% modulus@before aging of rubber compounds with different modified silicas.

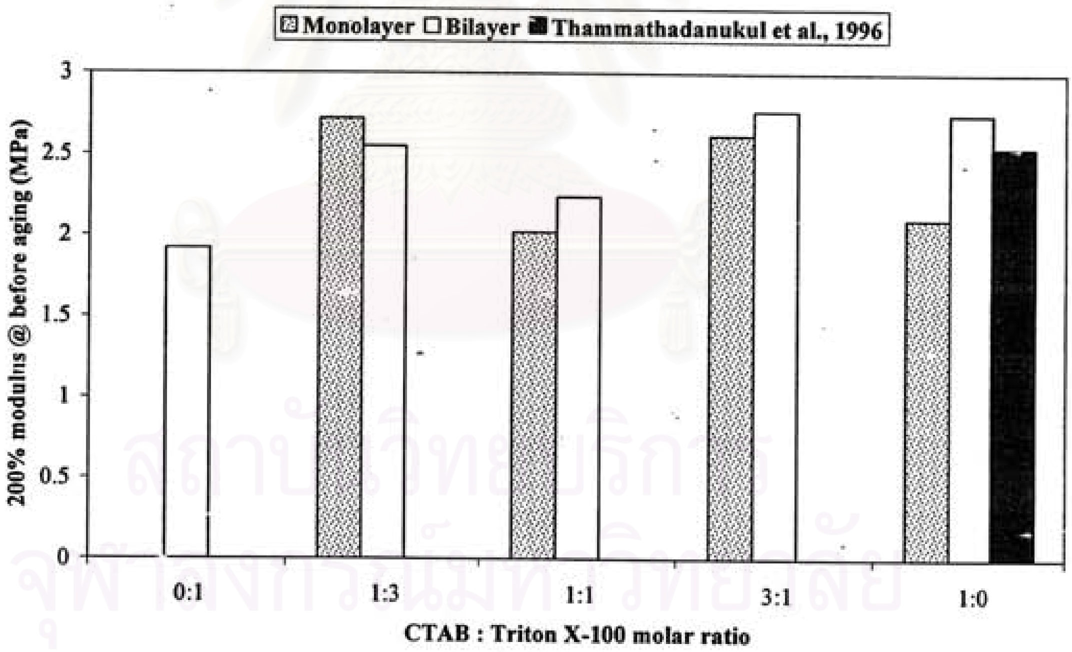


Figure 4.39 200% modulus@before aging of rubber compounds with different modified silicas.

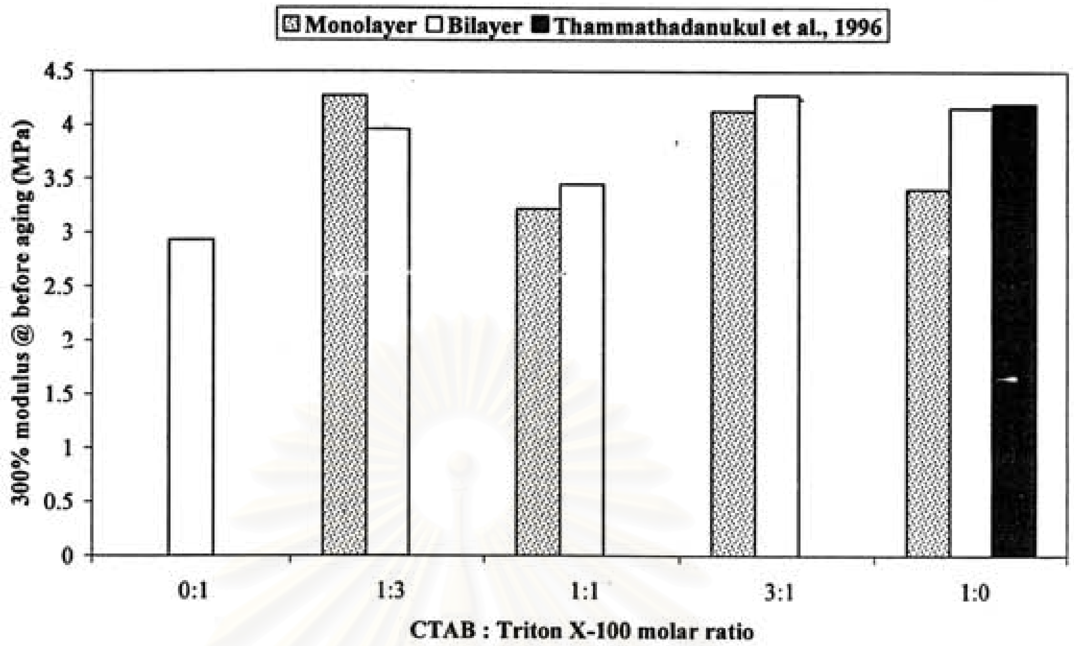


Figure 4.40 300% modulus@before aging of rubber compounds with different modified silicas.

All tested physical properties of rubber compounds using different modified silica are summarized in Table 4.1. The present results of all testing physical properties of rubber compounds are also compared to the previous result as shown in Table 4.2.

Table 4.1 Rubber compound physical properties using different modified silicas

Property	B01	M13	B13	M11	B11	M31	B31	M10	B10
100%Modulus @before aging (MPa)	1.15	1.57	1.52	1.15	1.29	1.54	1.67	1.22	1.66
100%Modulus @after aging (MPa)	2.17	2.15	2.01	1.92	1.98	2.12	2.01	1.91	1.85
200%Modulus @before aging (MPa)	1.92	2.72	2.55	2.02	2.24	2.62	2.77	2.10	2.75
200%Modulus @after aging (MPa)	3.76	3.96	3.56	3.35	3.60	3.85	3.41	3.48	3.17
300%Modulus @before aging (MPa)	2.93	4.27	3.96	3.22	3.45	4.13	4.28	3.40	4.16
300%Modulus @after aging (MPa)	5.84	6.27	5.39	5.63	5.78	6.07	5.29	5.45	4.80
Tensile Strength @before aging (MPa)	29.12	29.88	30.59	29.91	29.27	29.35	30.63	30.69	29.49
Tensile Strength @after aging (MPa)	27.90	28.00	25.70	26.90	27.30	26.20	25.60	25.60	27.70
Tear Strength @before aging (N/mm)	69.85	69.82	68.80	64.74	49.81	75.38	50.62	65.60	52.80
Tear Strength @after aging (N/mm)	48.56	57.60	49.20	54.61	51.81	54.98	46.09	55.26	51.26
Abrasion (ml/kcycle)	0.40	0.44	0.41	0.44	0.43	0.42	0.35	0.46	0.44
Resilience (%)	65.00	65.37	66.50	67.03	65.53	63.43	64.53	69.20	75.30
Compression set (%)	49.63	54.48	42.67	58.80	46.30	53.98	46.17	57.59	58.13
Hardness @before aging (shore A)	49.30	53.73	51.07	50.50	46.23	53.37	51.10	51.73	51.73
Hardness @after aging (shore A)	57.83	59.57	57.40	57.93	52.90	59.87	57.43	57.90	57.03

01, 13, 11, 31, 10 : ratio of surfactants, CTAB:Triton X-100 molar ratio

M, B : type of adsorption structure, monolayer, bi-layer, respectively

Table 4.2 Rubber compound physical properties using different modified silicas obtained from the present study compared to the modified silicas of the previous batch system with bilayer structure (Thammathadanukul *et al.*, 1996)

Property	**Batch***	**B01**	**M13**	**B13**	**M11**	**B11**	**M31**	**B31**	**M10**	**B10**
Cure time (min)	**5.98**	6.81	5.28	5.55	5.49	4.87	5.58	5.00	4.82	7.19
100%Modulus @before aging (MPa)	**1.33**	1.15	1.57	1.52	1.15	1.29	1.54	1.67	1.22	1.66
200%Modulus @before aging (MPa)	**2.54**	1.92	2.72	2.55	2.02	2.24	2.62	2.77	2.10	2.75
300%Modulus @before aging (MPa)	**4.19**	2.93	4.27	3.96	3.22	3.45	4.13	4.28	3.40	4.16
Tensile Strength @before aging (MPa)	**26.43**	29.12	29.88	30.59	29.91	29.27	29.35	30.63	30.69	29.49
Tear Strength @before aging (N/mm)	**75.37**	69.85	69.82	68.8	64.74	49.81	75.38	50.62	65.6	52.8
Abrasion (ml/kcycle)	**0.66**	0.40	0.44	0.41	0.44	0.43	0.42	0.35	0.46	0.44
Resilience (%)	**73.6**	65.00	65.37	66.5	67.03	65.53	63.43	64.53	69.2	75.30
Compression set (%)	**76.02**	49.63	54.48	42.67	58.8	46.3	53.98	46.17	57.59	58.13

01, 13, 11, 31, 10 : ratio of surfactants, CTAB:Triton X-100 molar ratio

M, B: type of adsorption structures, monolayer, bilayer, respectively

*Thammathadanukul *et al.* (1996)

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There are many properties, which has an important effect on the overall performance of modified rubber. For example, the tensile modulus, which represents how rigidity of rubber are, the higher the modulus, the better rigidity. The tear strength is the maximum force required to rip a rubber product. The tensile strength shows how rubber resists undergoing determination. Thus, to determine the overall properties of modified rubber appropriately, the scoring technique was applied. Each physical properties of modified rubber, such as tensile strength value are weighted to 9. The higher the value means the better properties. For example, the rubber, which has highest modulus or tensile strength values, are weighted to 9 while the worse properties are represented by value 1. After that, all scores from each property are summarized, and the final value is used to represent overall performance of the modified rubber as show in Table 4.3. It seems that the overall performance of rubber obtained from the monolayer structure is better than those bilayer structure.

The effects of type of surfactants adsorption structures and the molar ratio of mixed surfactants of the modified silica on various physical properties of the rubber compound are shown qualitatively in Table 4.4, in which a "+" indicates greater than 10% improvement in the property over unmodified silica, a "-" indicates a greater than 10% negative impact on the property, and an "=" indicates no significant difference. A "+" is given a value of 1; a "-" is given a value of -1; and an "=" is given a 0 values for qualitative calculation of overall improvement relative to the respective unmodified silicas.

The best properties of rubber compound is obtained with 1:3 molar ratio of CTAB:Triton X-100, which resulted in the monolayer structure. In the case of silica modification using the bilayer structre, the 3:1 molar ratio is the optimum condition.

CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the experimental results, it demonstrated that both surfactant adsorption structures and the molar ratio of CTAB to Triton X-100 are important controlling variables to control and optimize the admicellar polymerization process for industrial applications. Modification of the silica surface increased the mean agglomerate particle size and lowered BET surface areas as compared to that of the unmodified ones. Scanning electron microscope (SEM) showed that the particle size of the modified silica was increased after the modification. The TGA results confirmed the polymer formed on the silica surface.

The silica modification by the nonionic surfactant was successfully used to modify rubber compound. The properties of rubber compound modified by silica using the nonionic surfactant mixed with the cationic surfactant in monolayer adsorption structure are acceptable compared to those of rubber compound modified by silica using pure cationic surfactant (bilayer adsorption structure). The use of nonionic surfactant can reduce the cost of the modified silica about 3 time less than the modified silica using the pure cationic surfactant.

5.2 Recommendations

- A kneader internal mixer was used for mixing in this study. Even, the mixer is a laboratory scale mixer with a volume of 5 liters, the modified silica obtained from the laboratory scale is not enough to fill the optimum volume of mixer. Thus, low dispersion of modified silica in natural rubber may result in the low cut growth resistance of the rubber compound.

REFERENCES

Barlow, F.W. (1993). Rubber Compounding: Principles, Material and Techniques, 2nd Edition. New York: Marcel Dekker.

Blow, C.V. and Hepburn, C. (1982). Rubber Technology and Manufacture, 2nd Edition. London: Butterworths, 77-80.

Chaisirimahamorakot, S. (2001). Modification of silica surface for rubber reinforcement using a continuous admicellar polymerization system. M.S. Thesis in Petrochemical Technology, The Petroleum and Petrochemical College, Chulalongkorn University.

Chinpan, N. (1996). Comparison of rubber reinforcement using various surface modified silicas. M.S.Thesis in Petrochemical Technology, The Petroleum and Petrochemical College, Chulalongkorn University.

Kaitdamneon-ngam, T. (2003) Admicellar Polymerization in a Continuous Stirred Tank Reactor: Effects of Surfactant and Initiator Loadings. M.S. Thesis in Petrochemical Technology, The Petroleum and Petrochemical College, Chulalongkorn University.

Harwell, J.H., Hoskins, J.C., Schechter, R.S. and Wade, W.H., (1985), Pseudophase Separation Model of Surfactant Adsorption: Isomerically Pure Surfactant, Langmuir, 1, 251-262.

Herwitt, N.L. (2000, August) An introduction to silica fillers. Paper presented at The Petroleum and Petrochemical College, Chulalongkorn University.

Ismail, H., Ishiaku, U.S., Ishak, Z.A.M., and Freakley, P.K. (1997). The effects of a cationic surfactant (fatty diamine) and a commercial silane coupling agent on the properties of a silica filled natural rubber compound. European Polymer Journal, 33(1), 1-6.

Katz, H.S. and Milewski, J.V. (1987). Synthetic Silica. Handbook of Fillers for Plastics, New York: Van Notrand Reinhold, 165 – 201.

Kittiyanan, B., O'Haver, J.H., Harwell, J.H., and Osuwan, S. (1996). Absolubilization of styrene and isoprene in cetyltrimethylammonium bromide admicelle on precipitated silica. Langmuir, 12(9), 2162-2168.

Kudisri, R. (1997). Comparison of surface modified fillers to clay for natural rubber composites. M.S. Thesis in Polymer Scicence, The Petroleum and Petrochemical College, Chulalongkorn University.

Laughlin, R.G. (1991) Fundamentals of the zwitterionic hydrophilic group. Langmuir, 7, 842-847.

Mark, J.E., Eramm, B., and Erich, F.R. (1994) Science and Technology of Rubber, 2nd Edition. New York: Academic Press.

Nontasorn, P., Chavadej, S., Rangsunvigit, P., O'Haver, J.H., Chaisirimahamorakot, S., Na-Ranong, N. (2005). Admicellar polymerization modified silica via a continuous stirred-tank reactor system: Comparative properties of rubber compounding. Chemical Engineering Journal, 108, 213-218.

O'Haver, J.H., Harwell, J.H., Evans, L.R., and Weddell, W.H. (1996). Polar copolymer-modified precipitated silica. Journal of Applied Polymer Science, 59, 1427-1435.

O'Haver, J.H., Harwell, J.H., O'Rear, E.A., Waddell, W.H., Snodgrass, L.J., and Parker, J.R. (1993). Formation of ultrathin polystyrene films in adsorbed surfactant bilayers on silica. Materials Research Society, 304, 161-166.

Rosen, M.J. (1989). Surfactants and Interfacial Phenomena, 2nd Edition. New York: John Willey and Sons.

Rubingh, D.N. and Holland, P.M. (1990) Cationic surfactant: physical chemistry. Surfactant Science Series, 37. New York: Marcel Dekker.

Sakhalkar, S.S. and Hirt, D.E. (1995) Admicellar Polymerization of Polymerization of Polystyrene no Glass Fibers, Langmuir, 11, 3369-3373.

Somasundarun, P. and Fuerstenau, D.W., (1966), Mechanism of Alkyl Sulfonate at the Alumina-Water Interface, The Journal of Physical Chemistry, 79, 90-96.

Thammathadanukul, V., O'Haver, J.H., Harwell, J.H., Osuwan, S., Na-Ranong, N., and Weddell, W.H. (1995). Comparison of rubber reinforcement using various surface-modified precipitated silicas. Journal of Applied Polymer Science, 59, 1741-1750.

Waddell, W.H., O'Haver, J.H., Evans, L.R., and Harwell, J.H. (1995). Organic polymer-surface modified precipitated silica. Journal of Applied Polymer Science, 55, 1627-1641.

Wagner, M.P. (1976). Reinforcing silicas and silicates. Rubber Chemistry and Technology, 49(3), 703-774.

Wu, J., Harwell, J.H., and O'Rear, E.A. (1987). Two-dimentional reaction solvents: surfactant bilayers in the formation of ultrathin films. Langmuir, 3(4), 531-537.

Yeskie, M.A., and Harwell, J.H. (1988). On the structure of aggregates of adsorbed surfactants: the surface charge density at the humimicelles / admicelle transition. The Journal of Physical Chemistry, 92(8), 2346-2352.